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## Formation of metallofullerenes from laser ablation of lanthanum- and yttrium-containing C<sub>60</sub> materials

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### Abstract

Photofragmentation of composite materials composed of M<sub>2</sub>O<sub>3</sub> (M = La, Y) and ozonized C<sub>60</sub> precipitate as well as metal fullerides C<sub>60</sub>M<sub>x</sub> (M = La, Y) has been studied by XeCl excimer laser ablation-TOF mass spectrometry. Evidence of the encapsulation of La and Y atoms in fullerene cages forming endohedral fullerenes has been observed in both kinds of materials. Under similar experimental conditions but with pristine C<sub>60</sub> replacing the ozonized C<sub>60</sub>, no endo-metallofullerenes have been observed. Odd-numbered ‘fullerene’ clusters have been detected in the negative ion mass spectra of these samples. Formation of endohedral metallofullerenes is supposed to be related to the odd-numbered ‘fullerene’ intermediates. © 2001 Published by Elsevier Science B.V.

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### 1. Introduction

The hollow structure of fullerenes has attracted scientists to explore the endohedral chemistry soon after the discovery [1] and macroscopic production [2] of fullerenes. Insertion of heteroatoms in the fullerene cage will change the chemical and physical properties of fullerenes to fulfill specific applications [3]. The discovery of the metallofullerenes with metal atoms trapped inside the hollow vacancy of the fullerene cage was nearly concurrent with that of C<sub>60</sub> and is equally exciting. The mostly used methods to produce endohedral fullerenes are laser vapor-

ization and arc discharge of graphite–metal composite rod at high temperatures [4,5] and evidence was provided for the successful production of various types of metallofullerenes by these methods. For example, group III elements (La, Y, and Sc) and group II elements (Ca, Sr, and Ba) are preferentially trapped into fullerene cages. The drawback of these methods is the low efficiency of the metallofullerene production. In these methods fullerene molecules are formed in the presence of metal atoms or ions which can thus be encapsulated inside the fullerene cage during cage formation. In order to synthesize endohedral fullerenes directly from the hollow fullerene cage already formed, ion implantation has been used in ion beams with high kinetic energy [6]. An alternative route [7] for the production of endohedral fullerenes directly from

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fullerene cages is by heating  $C_{60}$  under atmospheres of the gas atoms to be trapped. Theoretical studies of Murry et al. [8] indicated that large holes (about 2.48 Å) could be formed by opening one C–C bond on the fullerene surface in the triplet excited state with a relatively mild conditions (only about 3.5 eV), whereas the direct insertion of helium atoms through a six-membered carbon ring needs very high energy (about 8.7 eV). So the insertion of atoms and molecules into the fullerene cage through the large hole is much easier than direct penetration through the center of a pentagon or hexagon. Shihe Yang et al. [9] has reported the successful formation of  $La@C_{2n}$  by direct laser ablation of  $C_{60}/La_2O_3$ . They attributed the formation of these endohedral metallofullerenes to the ‘window’ mechanism. It is very probable that the enhancement of the window formation might lead to the increase of production efficiency of endohedral fullerenes.

In our laser ablation studies of fullerenes [10,11], odd-numbered ‘fullerene’ fragments were observed in the mass spectra of many fullerene derivatives, such as  $C_{60}O_n$  ( $n=1-6$ ),  $C_{60}CH_2$  and others. The odd-numbered carbon clusters observed in the fullerene regime could not take the usual closed cage forms of fullerenes. Our theoretical calculation [11] indicates that the odd-numbered carbon clusters in the fullerene regime can be regarded as pseudo-open-cage ‘fullerenes’. It is probable that when a metal-containing fullerene sample is subjected to laser ablation, the metal atom evaporated from the sample will have a chance to collide with the odd-numbered ‘fullerene’ intermediates and to go into the interior of the cage through the window just formed by laser ablation. The enhancement of odd-numbered high carbon cluster formation through the derivatization of fullerene may provide a new preparation route of endo-metallofullerenes.

In this Letter, we report the observation of metallofullerene clusters of the type  $M@C_{2n}$  ( $M = La, Y$ ) in our laser ablation studies on composite materials composed of  $M_2O_3$  ( $M = La, Y$ ) and ozonized  $C_{60}$  precipitate (designated as  $C_{60} + O_3$  below) as well as metal fullerides

$C_{60}M_x$  ( $M = La, Y$ ) prepared by chemical synthesis. The probable endohedral nature and the formation mechanism of the metallofullerenes are discussed.

## 2. Experimental

The metal fullerides  $C_{60}M_x$  ( $M = La, Y, x \approx 1$ ) were synthesized by the reactions of  $C_{60}^{3-}$  generated chemically in THF solution phase with anhydrous metal trichlorides  $LaCl_3$  and  $YCl_3$ , respectively.

The composite samples are pellets pressed from a 1:1 (weight ratio) mixture of  $La_2O_3$  (or  $Y_2O_3$ ) and ozonolysis product of  $C_{60}$  fullerene. The ozonized  $C_{60}$  precipitate was obtained by the reaction of  $C_{60}$  in toluene solution with  $O_3$  gas generated from a discharge generator. The ozonized  $C_{60}$  product was characterized as polyoxyderivatives of  $C_{60}$  by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and elemental analysis.

The reflectron time-of-flight (RTOF) mass spectrometer has been described in detail in another paper [11] and only a brief discussion will be given here. Fig. 1 is the schematic diagram of the apparatus. The sample was placed in a position about 5 cm from the acceleration region, a 308 nm XeCl excimer laser beam ( $\sim 20$  ns) was used to perform the laser ablation. For the detection of negative ions, a pulsed voltage of  $-1200$  V was applied on the double stage ion source. An Einzel lens was used to focus the ions into the reflector, which allows a second-order space focusing of the ions. In the reflection region the ions were decelerated and reflected by a constant voltage of  $-1300$  V applied on the reflector, and then drifted at an angle of  $2.8^\circ$  from the incidence direction. The total field-free flight path was 1800 mm. The ions are detected by a triple-microchannel plate detector followed by a transient digitizer controlled with a computer. For the detection of positive ions, positive voltages were applied on the ion source and the reflector. All spectra reported in this Letter have been averaged over 30 laser shots. The resolution of the reflectron TOF is  $M/\Delta M \sim 1000$ .

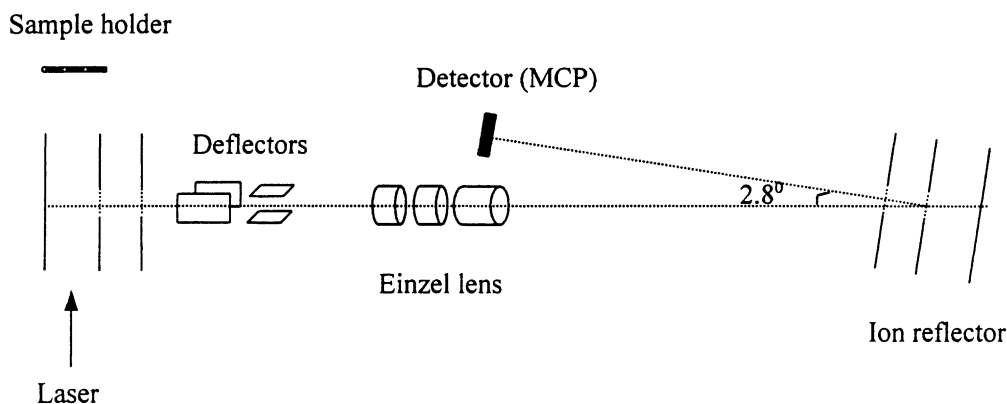


Fig. 1. Schematic diagram of the reflectron time-of-flight mass spectrometer (RTOF).

### 3. Results and discussion

#### 3.1. Laser ablation mass spectra – formation of metal-containing heterofullerenes

Fig. 2 shows the typical positive ion mass spectra of composite material pellets  $C_{60}/La_2O_3$ ,  $(C_{60} + O_3)/La_2O_3$  and  $(C_{60} + O_3)/Y_2O_3$  (from top to bottom) with a laser fluence of about  $700 \text{ mJ/cm}^2$ .  $C_{60}$  and its photofragments as well as some mass peaks in the higher mass range due to  $C_2$  addition are the dominant clusters detected. The interesting feature of the mass spectra is the appearance of a sequence of mass peaks  $C_{2n}M^+$  ( $M = La, Y$ ) in the neighborhood of the pure fullerene sequence. The mass range of the metal-containing fullerene clusters is different for different precursor materials. For the composite materials  $(C_{60} + O_3)/La_2O_3$  and  $(C_{60} + O_3)/Y_2O_3$ ,  $2n = 44\text{--}52$  and  $2n = 44\text{--}50$  are obtained, respectively. For composite sample with pristine  $C_{60}$ , no metal containing fullerene clusters are observed under our experimental conditions, as shown in Fig. 2a. This result is different from that of Shihe Yang et al. [9], in which endohedral fullerenes were observed in the laser ablation of  $C_{60}/La_2O_3$  composite.

Fig. 3 shows the mass spectra of metal fullerides  $C_{60}La_x$  and  $C_{60}Y_x$  under the same laser ablation conditions. Similar to Fig. 2, in addition to the fullerene sequence the metallofullerene sequence appears. Moreover, it is interesting to notice that in comparison with the case of composite material

samples, the mass range of the metal-containing sequence  $C_{2n}M^+$  ( $M = La, Y$ ) from metal fullerenes is much broadened with  $2n$  extending to 64, whereas the termination in the low mass side remains nearly the same, i.e., at  $2n = 42$ . Due to the low ionization potentials of lanthanum and yttrium, mass peaks  $La^+$  and  $Y^+$  were observed in the low mass region.

The common feature of the metal containing fullerene sequence is the termination around  $C_{44}M$ , or  $C_{42}M$  in the low mass side, which is coincident with the 'shrink wrap' behavior reported previously [12]. At the same time, the fragmentation behavior of this sequence clearly shows the general feature of the fragmentation of fullerene cages, that is, the removal of carbon dimers from the cage skeleton without losing the metal atoms. These results are reasonable for inside-cage-doped metallofullerenes. Theoretical calculations predict that the encaged La in  $C_{60}$  possesses a formal charge of +3 [13] and  $La^{3+}$  has an ionic radius of  $1.06 \text{ \AA}$  [14], so it can form metallofullerenes of small sizes. Exohedrally-doped metallofullerenes will behave in a distinctly different way in photofragmentation. We believe that the metal atoms in the composite materials or in the metal fullerides (exohedrally doped) had entered the interior of the fullerene cage during the laser ablation process. Shihe Yang et al. demonstrated the endohedral nature of the metallofullerenes formed in the laser ablation of the  $C_{60}/La_2O_3$  composite. The formation of endohedral metallofullerenes in our case is similar to

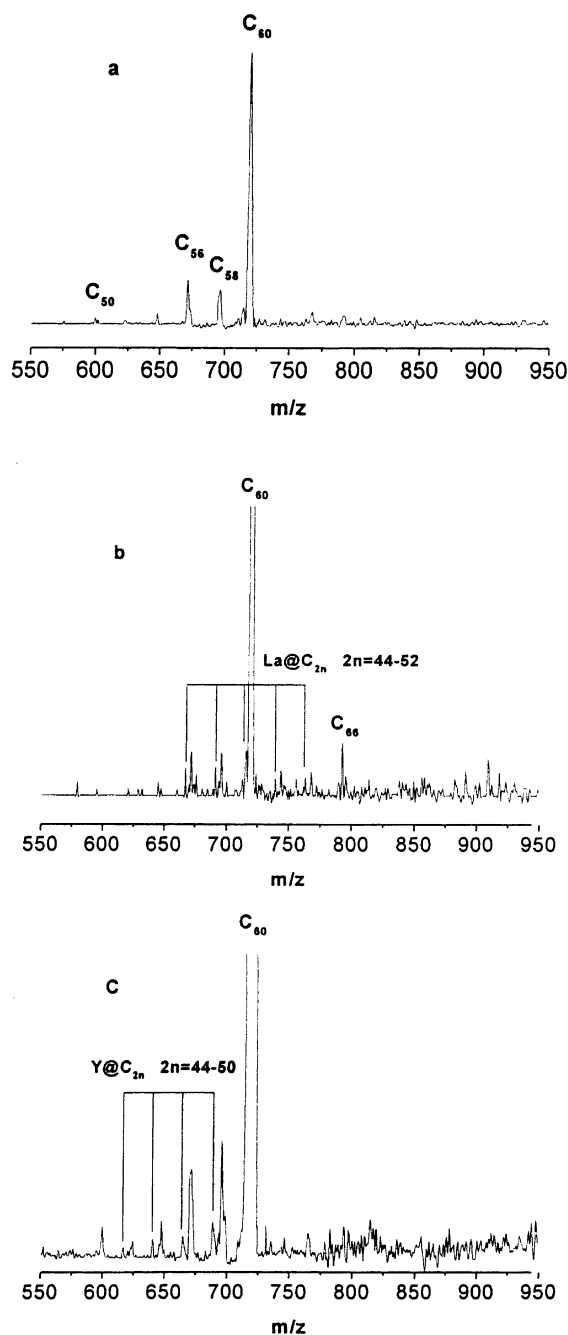


Fig. 2. Typical positive ion TOF mass spectra of (a)  $C_{60}/La_2O_3$ , (b)  $(C_{60} + O_n)/La_2O_3$ , and (c)  $(C_{60} + O_n)/Y_2O_3$  with a laser fluence of about  $700 \text{ mJ/cm}^2$ .

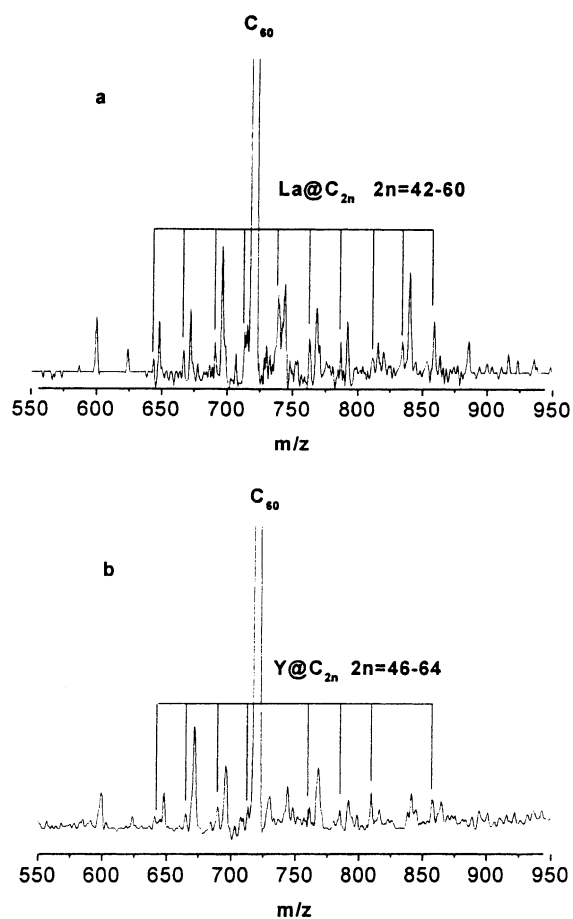


Fig. 3. Typical positive ion TOF mass spectra of metal fullerenes (a)  $C_{60}La_x$  and (b)  $C_{60}Y_x$  with a laser fluence of about  $700 \text{ mJ/cm}^2$ .

theirs in the encapsulation through ‘window’ mechanism. The result that no endo-metallofullerene was obtained from the composite sample with pristine  $C_{60}$  in our case might be due to our milder experimental conditions. The significance of our experiments is that the efficiency of formation has been enhanced through fullerene derivatization, the mechanism of which will be discussed in later sections.

Fig. 4 shows the negative ion TOF mass spectra of  $C_{60}/La_2O_3$ ,  $(C_{60} + O_3)/Y_2O_3$  and metal fullerenes  $C_{60}Y_x$  (from top to bottom) with a laser fluence of about  $650 \text{ mJ/cm}^2$ . Unlike in the positive ion mass spectra, the only metal-containing fullerene clusters observed in the negative ion mass

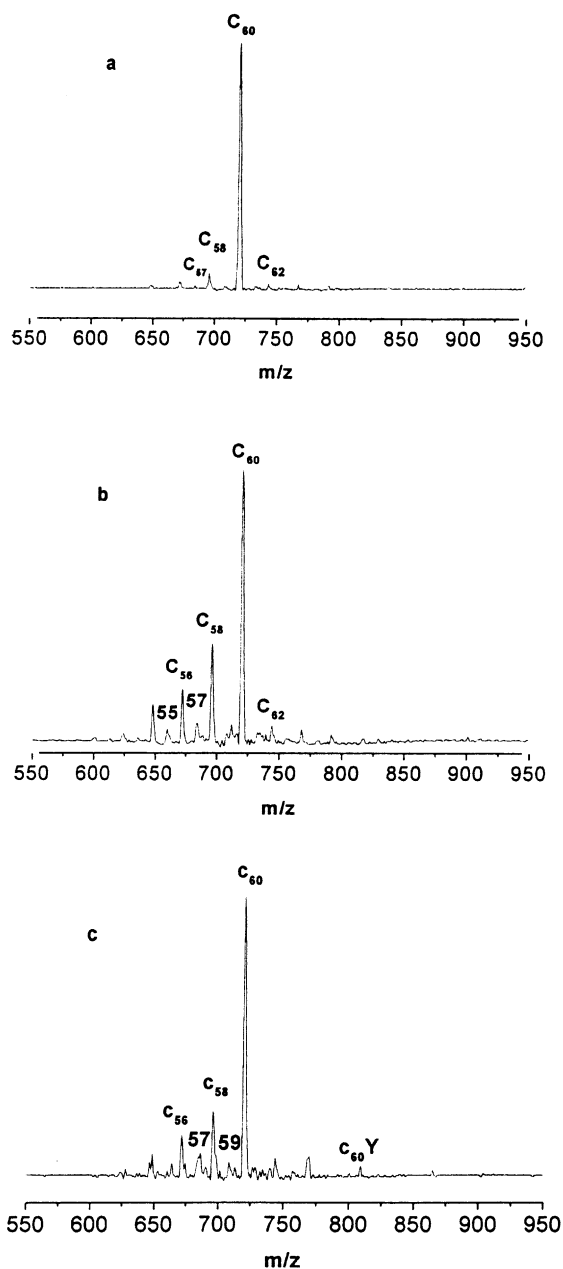


Fig. 4. Typical negative ion TOF mass spectra of (a)  $C_{60}/La_2O_3$ , (b)  $(C_{60} + O_3)/Y_2O_3$  and (c)  $C_{60}Y_x$  with a laser fluence of about  $650 \text{ mJ/cm}^2$ .

spectra are  $C_{60}La^-$  (not shown) and  $C_{60}Y^-$  from the fullerides. Careful inspection of the positive spectra of the metal fullerides indicates that the mass peaks corresponding to  $C_{60}La^+$  and  $C_{60}Y^+$

are particularly intense, even stronger than the neighboring mass peaks of fullerene ions. One possibility is that these two mass peaks are composed of two parts, one endo-originating from laser ablation and one exo-originating from fulleride sample after evaporating part of the metal atoms. Another possibility is that 60 is a magic number. We found that  $C_{50}La^+$  is relatively stronger than other metallofullerenes, in agreement with the magic nature of  $C_{50}$ . It is probable that the exo-metallofullerenes appear in both ionic modes, but the endo-ones appear only in the positive ion channel. The reason is not clear. One possible interpretation is that the formation of the endo-metallofullerenes is a quite slow process so that the  $M@C_{2n}$  formed in the laser ablation has no chance to catch electron to form anions [15]. All these results are in consistency with the endohedral nature of the metallofullerenes  $M@C_{2n}$  ( $M = La, Y$ ).

### 3.2. Formation of odd-numbered carbon anion clusters in the fullerene regime

Fig. 4 shows that a feature to be noticed in the negative ion mass spectra of  $C_{60}/La_2O_3$ ,  $(C_{60} + O_3)/Y_2O_3$  and  $C_{60}Y_x$  (from top to bottom) is that for the fullerene-containing samples – the composite and metal fullerides, in the fullerene mass regime in addition to the usual even-numbered fullerenes, odd-numbered carbon anion clusters  $C_{55}^-$ ,  $C_{57}^-$ ,  $C_{59}^-$  and sometimes also  $C_{61}^-$  were observed. The corresponding La samples give similar results. For  $C_{60}/La_2O_3$  studied under the same experimental conditions, only very weak odd-numbered fragments were detected in the mass spectrum as shown in Fig. 4a.

The enhancement of the formation of odd-numbered carbon clusters through the oxidation of fullerenes has been discussed in detail in our previous report [10], the enhanced formation of odd-numbered ‘fullerene’ clusters from the composite material  $(C_{60} + O_3)/M_2O_3$  is thus not surprising. The experimental result shown in this Letter indicates that the formation of odd-numbered ‘fullerene’ clusters can also be enhanced through the formation of exohedral fullerenes with metal atoms located outside the cage. The origin of

the enhancement is not clear, as the nature of the interaction between the metal atoms and the carbon cages in the samples is still unknown. As has been discussed in another paper [11], the split of the MC from  $C_{60}M$  may be responsible for the  $C_{59}$  formation, although no MC has been observed in our mass spectra (the MC split off may be in neutral state). The subsequent loss of  $C_2$  might be a possible way of the formation of the smaller odd-numbered clusters  $C_{57}^-$ ,  $C_{55}^-$ . From our experimental studies up to now [10,11], we found that the formation of odd-numbered ‘fullerenes’ can be realized through the use of various fullerene-containing materials, if they fulfill certain compositional and/or structural requirements.

In our laser ablation experiments, odd-numbered ‘fullerene’ fragments have never been detected in the cationic mode. Figs. 2 and 3 are typical examples. The absence of odd-numbered ‘fullerenes’ in the positive ion mass spectra is an open question. The previous laser ablation studies of other authors [16,17] gave results similar to ours, no odd-numbered fullerene ions had ever been observed in the positive ion channel. Van Cleempoel and coworkers [18] reported their observation of the formation of odd-numbered carbon clusters in fullerene regime in both the negative and the positive ion modes, but was through collision-induced dissociation of  $C_{60}$  and  $C_{70}$  oxides. In recent years, very little new information about formation of odd-numbered ‘fullerenes’ is reported. A study on the structures and the energetics of the odd-numbered ‘fullerenes’ might shed some light on this question.

### 3.3. Structures and formation mechanism of metallofullerenes $C_{2n}M$

In recent years, research progress on heterofullerenes has stimulated structure investigations of these systems both experimentally and theoretically. Jarrold et al. [19] has made successful experimental measurements on the structure of metallofullerene clusters using the gas phase ion mobility technique providing conclusive evidence that  $C_{2n}La$  with an even number of carbon atoms at the mass regime of  $C_{36}$  or larger are closed-cage structures with lanthanum atom trapped inside the

cage. Early theoretical studies indicated that the trapped metal atoms have a large ionic contribution to the stability of endohedral metallofullerenes [13]. Lanthanum has three valence electrons and relatively low ionization energies that favor the charge transfer from the metal to the carbon cage stabilizing the formation of the endohedral geometry. Calculation studies by other group [20] gave similar results. From studies up to now, the accumulated evidence leaves little doubt that lanthanum-containing metallofullerenes with even number of carbon atoms in the mass range larger than  $C_{36}$  have structures with the metal atom trapped inside the fullerene cage forming endohedral metallofullerenes. Yttrium is a similar case.

In our laser ablation studies of other metal fullerides  $C_{60}M_x$  ( $M = Sm, Pt, Ni$  and  $Rh$ ) under almost the same experimental conditions, metal-doped fullerene clusters containing an odd number of carbon atoms have been detected. As has been discussed in another paper [21], the metallofullerenes with odd number of carbon atoms have similar heterofullerene structures with the metal atom substituting one of the carbon atoms of the fullerene cages forming heterocages with even total number of atoms. The different behavior between  $C_{60}M_x$  ( $M = La, Y$ ) and the above mentioned other metal fullerides are consistent with the previous studies that metal atoms of  $La, Y$  and  $Sc$  are preferentially trapped into fullerene cages, while the other metal atoms such as  $Rh, Ni$  and  $Nb$  readily form localized covalent bonds at the defect site of odd-numbered fullerenes to produce a stable networked geometry [13]. Such networked heterocage structures have not been observed in the laser ablation spectra of  $La$ - and  $Y$ -containing fullerene materials.

Based on these experimental studies we summarize as follows: (1) The fragmentation pattern of the  $La$ - and  $Y$ -containing metallofullerene sequence with even number of carbon atoms shows the general feature of fullerenes, that is, the removal of carbon dimers from the cage skeleton without losing the metal atoms. (2) The termination of the  $C_{2n}M^+$  ( $M = La, Y$ ) sequence at around  $C_{44}M^+$  or  $C_{42}M^+$  was similar to the ‘shrink wrap’ behavior observed previously. Of course, the termination size depends also on the experimental

conditions. (3) The different behavior between  $C_{60}M_x$  ( $M = \text{La, Y}$ ) and  $C_{60}M_x$  ( $M = \text{Rh, Ni, Pt and Sm}$ ) shows that the metal atom La or Y is preferentially trapped inside the fullerene cage. We believe that the  $C_{2n}M$  ( $M = \text{La, Y}$ ) clusters appearing in our experiments take endohedral structures  $M@C_{2n}$ . These phenomena are very different from the case  $C_{60}Rh_x$ , which shows both the  $C_{2n-1}Rh$  and  $C_{2n}Rh$  sequences. The complicated laser ablation mass spectra of  $C_{60}Rh_x$  will be discussed in another paper.

We shall now discuss the formation of  $M@C_{2n}$  through the correlation between the odd-numbered ‘fullerene’ clusters and the endohedral metallofullerenes  $M@C_{2n}$ . We have optimized the structures of odd-numbered carbon clusters  $C_{51}$ – $C_{59}$ , using the genetic algorithm with the Brenner potential. Based on the obtained ground state structure, optimization at Hartree–Fork 3-21G level has been performed using GAUSSIAN 94. Fig. 5 displays the structure of  $C_{55}$ . Although the structure of the odd-numbered ‘fullerene’ given by theoretical calculations does not have the window of 7-membered or even bigger rings for the easy entrance of the metal atom as we expected, the presence of the two-fold coordinated appended carbon atom in the structure is interesting. It provides a weak point for the cage opening. For such structures, only an energy for breaking the two bridge-forming bonds is required to cleave off the appending carbon atom, forming a structure

with a 8- to 10-membered window. Such energy is much less than the energy required to build a window on an even-numbered fullerene cage as suggested by Murry et al. [8]. It is probable that when the metal-containing fullerene sample is subjected to laser ablation, the metal atom evaporated from the sample will have a chance to collide with the odd-numbered ‘fullerene’ fragment just formed in the plasma and enters the interior of the cage through the window opened by collision. The window will soon be closed after the metal insertion, forming endohedral fullerenes, which will further relax to the more stable fullerene isomers. Our experimental results seem to approve this argument. Comparison of the mass spectra between the positive and negative ion channels will show that, for  $C_{60}/La_2O_3$ , only very weak odd-numbered fragments were detected in the mass spectrum as shown in Fig. 4a. Correspondingly no metallofullerene clusters were observed in the positive ion channel as shown in Fig. 2a. While for the other samples studied under the same experimental conditions, enhanced odd-numbered ‘fullerenes’ were detected in the mass spectra as shown in Fig. 4. Correspondingly much stronger metallofullerene clusters were observed in the positive ion channel as shown in Figs. 2 and 3. Rigorously speaking the odd-numbered high carbon clusters in the fullerene mass regime are not closed cage fullerenes composed of hexagons and pentagons, but they can be regarded as imperfect fullerenes with defects as mentioned in [21]. Through their calculation the authors indicated that the barrier of inserting atoms into imperfect fullerenes would be much lower. In our case of laser ablation, the odd-numbered imperfect fullerenes are in excited nascent state, it is probable that the encapsulation process will be even easier. This might be the scenario of the enhancement of the formation of endohedral metallofullerenes by using derivatized fullerene materials.

In conclusion, we present results of the formation of metallofullerenes of lanthanum and yttrium by laser ablation of metal-containing fullerene composites and metal fullerenes. Experimental evidence shows that the metal atoms are trapped inside the fullerene cage forming endohedral fullerenes. Odd-numbered high carbon

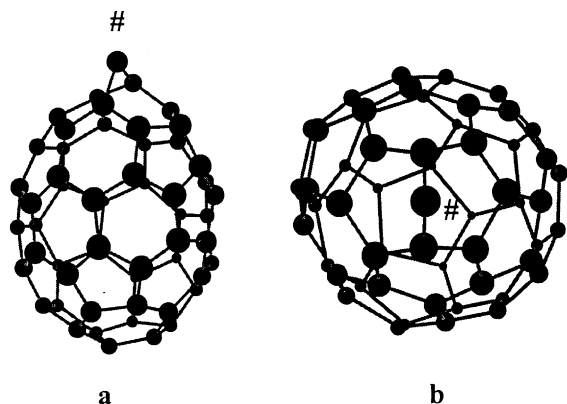


Fig. 5. Two views of the optimized structure of  $C_{55}$ , ‘#’ indicates the two-fold coordinated appended carbon atom.



clusters were observed in the fullerene mass regime in the negative ion mode. The structures of the odd-numbered species and their possible role in the formation of endo-metallofullerenes are discussed.

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### References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, *Nature* 347 (1990) 354.
- [3] H. Shinohara, *Adv. Metal Semicond. Clusters* 4 (1998) 205.
- [4] J.R. Heath, S.C. O'Brien, Q. Zhang, Y. Liu, R.F. Curl, H.W. Kroto, F.K. Tittle, R.E. Smalley, *J. Am. Chem. Soc.* 107 (1985) 7779.
- [5] D.S. Bethune, R.D. Johnson, J.R. Salem, M.S. de Vries, C.S. Yannoni, *Nature* 366 (1993) 123.
- [6] Z. Wan, J.C. Christian, S.L. Anderson, *J. Chem. Phys.* 96 (1992) 3344.
- [7] M. Saunders, H.A. Jimenez-Vazquez, R.J. Cross, R.J. Poreda, *Science* 259 (1993) 1428.
- [8] R.L. Murry, G.E. Scuseria, *Science* 263 (1994) 791.
- [9] S.H. Yang, R.B. Huang, W.Y. Lu, *Surf. Rev. Lett.* 3 (1996) 803.
- [10] Q.Y. Kong, J. Zhuang, L. Zhao, J.Y. Wang, S.X. Qian, Y.F. Li, X. Li, C.F. Zhong, R.F. Cai, Y. Yu, H.Q. Hou, *Chin. Phys. Lett.* 17 (2000) 419.
- [11] Q.Y. Kong, W.X. Zhang, J. Zhuang, L. Zhao, S.X. Qian, Y.F. Li, X. Li, R.F. Cai, Y. Yu, H.Q. Hou, *Int. J. Mass Spectrom.*, submitted.
- [12] F.D. Weiss, S.C. O'Brien, J.L. Elkind, R.F. Curl, R.E. Smalley, *J. Am. Chem. Soc.* 110 (1988) 4464.
- [13] K. Laasonen, W. Andreoni, M. Parinello, *Science* 258 (1992) 1916.
- [14] Lange's Handbook of Chemistry, 13th ed., J.A. Dean (Ed.), McGrawHill, New York, 1985.
- [15] S.Y. Wang, L. Zhu, J.Z. Lu, P.N. Wang, Y.F. Li, *Fullerene Sci. Technol.* 2 (1994) 49.
- [16] J. Deng, D. Ju, G. Her, C. Mou, C. Chen, Y. Lin, C. Han, *J. Phys. Chem.* 97 (1993) 11575.
- [17] L. Zhu, S.Y. Wang, Y.F. Li, *J. Chem. Phys.* 104 (1994) 3638.
- [18] A. VanCleempoel, R. Gijbels, M. Claeys, H. Vanden-Heuvel, *Rapid Commun. Mass Spectrom.* 10 (1996) 1579.
- [19] K.B. Shelimov, D.E. Clemmer, M.F. Jarrold, *J. Chem. Soc. Dalton Trans.* (1996) 567.
- [20] S. Nagase, K. Kobayashi, T. Kato, Y. Achiba, *Chem. Phys. Lett.* 201 (1993) 475.
- [21] S. Patchkovskii, W. Thiel, *J. Am. Chem. Soc.* 118 (1996) 7164.