International Journal of Mass Spectrometry 209 (2001) 69–79

Formation of odd-numbered fullerene-related species and its relation to the formation of metallofullerenes

Qingyu Kong[a,b,*], Li Zhao[a,b], Jun Zhuang[a,b], Jiong Xu[a,b], Shixiong Qian[a,b], Yufen Li[a,b], Ruifang Cai[c], Huiqi Hou[d], Jue Wang[e]

[a]*State Key Joint Laboratory for Materials Modification by Laser, Ion, and Electron Beams, Fudan University, Shanghai, China 200433*
[b]*Department of Physics, Fudan University, Shanghai, China 200433*
[c]*Department of Chemistry, Fudan University, Shanghai, China 200433*
[d]*Department of Environmental Science and Engineering, Fudan University, Shanghai, China 200433*
[e]*Pohl Institute of Solid State Physics, Tongji University, Shanghai China 200092*

Received 16 November 2000; accepted 31 May 2001

Abstract

Odd-numbered carbon clusters in the fullerene regime are formed through laser ablation of various fullerene-containing materials: organic fullerene derivatives, metal fullerides, and guest-host fullerene materials. The formation mechanism of odd-numbered “fullerene” species is briefly discussed. The structural properties are calculated with genetic algorithm and ab initio methods, and the results show that the odd-numbered fullerene species are pseudo-open-caged fullerenes. In the laser ablation of metal fullerides, substitutional or endohedral metallofullerenes are observed. A new way for metallofullerene preparation through the odd-numbered fullerene intermediates is suggested and realized experimentally. (Int J Mass Spectrom 209 (2001) 69–79) © 2001 Elsevier Science B.V.

Keywords: Fullerene derivatives; Odd-numbered carbon clusters; Metallofullerenes; Laser ablation; time-of-flight mass spectrometry

1. Introduction

Since the macroscopic production of C_{60} became possible, fullerene-based materials and their potential applications have attracted much interest in the fields of physics, chemistry and materials science [1,2]. The investigation of photoinduced fragmentation and aggregation dynamics of fullerenes and fullerene-related materials is of significance both in basic research and in exploring fullerene applications.

Laser desorption clustering dynamics of fullerenes has been studied extensively in the past decade, but the formation of odd-numbered carbon clusters in the fullerene regime has been only scarcely reported. In our earlier laser ablation studies of fullerenes [3,4], odd-numbered “fullerene” species were observed in the mass spectra of some fullerene derivatives, such as $C_{60}(C_6H_5CH_2)_n$ (n = 1–14), $C_{60}O_n$ (n = 1–6), $C_{60}CH_2$ and some others. The enhancement of odd-numbered carbon cluster formation through fullerene derivatization has attracted our interest. The reason is that only even-numbered carbon clusters can form closed cage fullerene structures comprised of pentagons and hexagons, the formation of odd-numbered species might be an evidence of carbon cage opening [5], which may provide new route to the preparation

---

*Corresponding author. E-mail: 980189@fudan.edu.cn

PII S1387-3806(01)00477-8

of endohedral, substitutional and giant fullerenes. Branz et al.[6] indicated that metal atoms can interact with fullerene cages to form three kinds of metallofullerenes: (1) the endohedral fullerenes with atoms trapped inside the hollow fullerene cage, (2) exohedral fullerenes with atoms located outside the cage, and (3) substitutional fullerenes with atoms incorporated into the fullerene network. Endohedral metallofullerenes have attracted much attention because of their unique structural and electronic properties [7–9]. The mostly used methods to produce endohedral metallofullerenes are laser vaporization and arc discharge of graphite-metal composite rod at high temperature [7]. Substitutional metallofullerenes were studied extensively over the past several years [10–12], general synthesis methods of substitutional metallofullerenes are also laser ablation and arc-discharge process.

Our motivation of studying the enhancement of odd-numbered fullerene formation is to explore novel efficient method for the preparation of metallofullerenes. In our recent laser ablation study of fullerene composite and metal fulleride materials, it is interesting to find that in addition to the enhancement of odd-numbered fullerene formation, substitutional and endohedral metallofullerenes was observed from the laser ablation of metal fulleride materials, which is consistent with our prediction that the odd-numbered carbon species might play a role in the formation of these metallofullerenes. The results obtained in these experiments might be an indication that searching for fullerene materials with efficient odd-numbered fullerene formation may open a new way of metallofullerene preparation.

In this paper, the samples studied are metal fullerides $C_{60}M_x$ (M=Sm, Rh, Ni, La) and fullerene doped silica aerogel. For comparison, the results on organic fullerene derivatives and pristine C_{60} are also given.

2. Experiment and theoretical calculation

2.1. Reflectron time-of-flight mass spectrometer

Fig. 1 is a schematic diagram of the reflectron time-of-flight (TOF) mass spectrometer. The sample

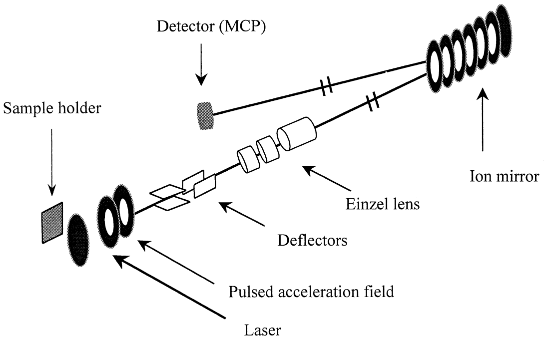

Fig. 1. Schematic diagram of the reflectron time-of-flight mass spectrometer (RTOF).

was placed in a position about 5 cm from the acceleration region, a 308 nm XeCl excimer laser beam (~20 ns) was focused to the sample surface in a direction perpendicular to the acceleration fields. The ions produced by laser ablation expanded into the acceleration region at right angles to the electric field direction after passing through a 2 mm aperture. For the detection of negative ions, a pulsed voltage of –1200 V was applied on the double stage ion source. After acceleration the ions then drifted along the axis of the field-free tube at ground potential. An Einzel lens was used to focus the ions into the reflector. This two-stage reflector 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° 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 paper have been averaged over 20 laser shots. The resolution of the reflectron TOF is $M/\Delta M \approx 1000$.

2.2. Sample preparation

The metal fulleride $C_{60}M_x$ (M=Sm, Rh, Ni, La) were prepared in the chemistry lab of Fudan University by organometallic methods, x is different for different metal fulleride, and ranges between 1–2.5.

$C_{60}O_n$ was generated by bubbling O_3 through C_{60} in toluene for 2.5 min (350–500ml/min and 6% O_3 in O_2). The $C_{60}C_5H_5CH_3$ adduct was synthesized by the reaction of freshly distilled methylcyclopentadiene ($C_5H_5CH_3$) with C_{60} in benzene at room temperature.

The C_{60}-doped silica aerogel sample was prepared by the sol-gel and supercritical drying techniques.

2.3. Structure optimization of carbon clusters

A genetic algorithm (GA) based on the Brenner potential is used to optimize the structures of odd-numbered carbon clusters C_{51}–C_{59} [13]. The genetic algorithm was run with a population of sixteen for several thousand generations until the structural isomer, which was believed to have the globally optimal geometry, was reached. Based on the GA calculation results, the structure of C_{55} and C_{54} was optimized at the Hartree Fock and B3LYP levels using 3-21G basis set, the single point energies of both the positive and negative ions of C_{54} and C_{55} was calculated at the same level using 3-21G basis set.

3. Results and Discussion

3.1. Formation of odd-numbered carbon clusters in the fullerene regime

Fig. 2 shows the typical negative ion TOF mass spectra of pristine C_{60}, fullerene derivatives $C_{60}O_n$, $C_{60}C_5H_5CH_3$, and C_{60}-doped aerogel (from top to bottom) with a laser fluence of about 650 mJ/cm^2. The general feature is that for these fullerene derivatives and the composite material, in the fullerene mass regime in addition to the usual even-numbered fullerene fragments C_{60-2n}, enhanced odd-numbered carbon clusters C_{57}^-, C_{55}^-, and C_{53}^-were also observed. It is interesting to find that the laser ablation of C_{60}-doped silica aerogel could give rise to extra strong odd-numbered fullerene species, with C_{55}^- even more intense than the neighboring even-numbered carbon clusters. Notice that different from our previous report, very weak [Fig. 2(a)] odd-numbered species were also observed in the spectrum of pristine C_{60}.

What is of particular interest is that in our recent laser ablation study of a variety of metal fullerides $C_{60}M_x$ (M=Sm, Rh, Ni, La), odd-numbered fullerene species were also observed in the negative ion mass spectra of all the metal fullerides being studied. Fig.3 shows the mass spectra of $C_{60}M_x$ with a laser fluence of about 650 mJ/cm^2. Odd-numbered carbon clusters C_{59}^-, C_{57}^-, C_{55}^- and sometimes even C_{61}^-, C_{63}^-, C_{65}^- can be clearly observed. This experimental result 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.

These results demonstrate that the formation of odd-numbered fullerene species is not a sparsely occurring phenomenon. It can be realized through the use of various fullerene-containing materials.

Deng and Beck [14,15] observed the formation of odd-numbered carbon clusters C_{59}^-, C_{57}^-, and C_{55}^- in the fullerene regime by laser ablation of $C_{60}O_n$, and attributed the formation of odd-numbered fullerene species to the evaporation of CO from the starting material $C_{60}O_n$. Gotts et al. [16] has also observed the formation of odd-numbered carbon clusters in the fullerene regime by laser ablation of graphite, but they considered C_1 or C_3 as odd fullerene precursors. In our opinion, the different formation processes of odd-numbered carbon clusters in the fullerene regime as suggested by these authors might originate from the different starting materials used in their laser ablation experiments. Since C_{60}-containing materials were used for laser ablation in our experiments, we think that the observed odd-numbered fullerenes mainly come from the fragmentation of the fullerene derivatives. Similar to Deng's case of CO evaporation, in our experiments on metal fullerides, the rupture of metal carbide cluster MC from $C_{60}M_x$ may be responsible for the formation of odd-numbered fullerenes. The observation of metal carbide SmC^+ from the laser ablation of $C_{60}Sm_x$ as will be discussed in Sec. 3.3 confirms this viewpoint. Certainly, formation of odd-numbered fullerene species through capture of

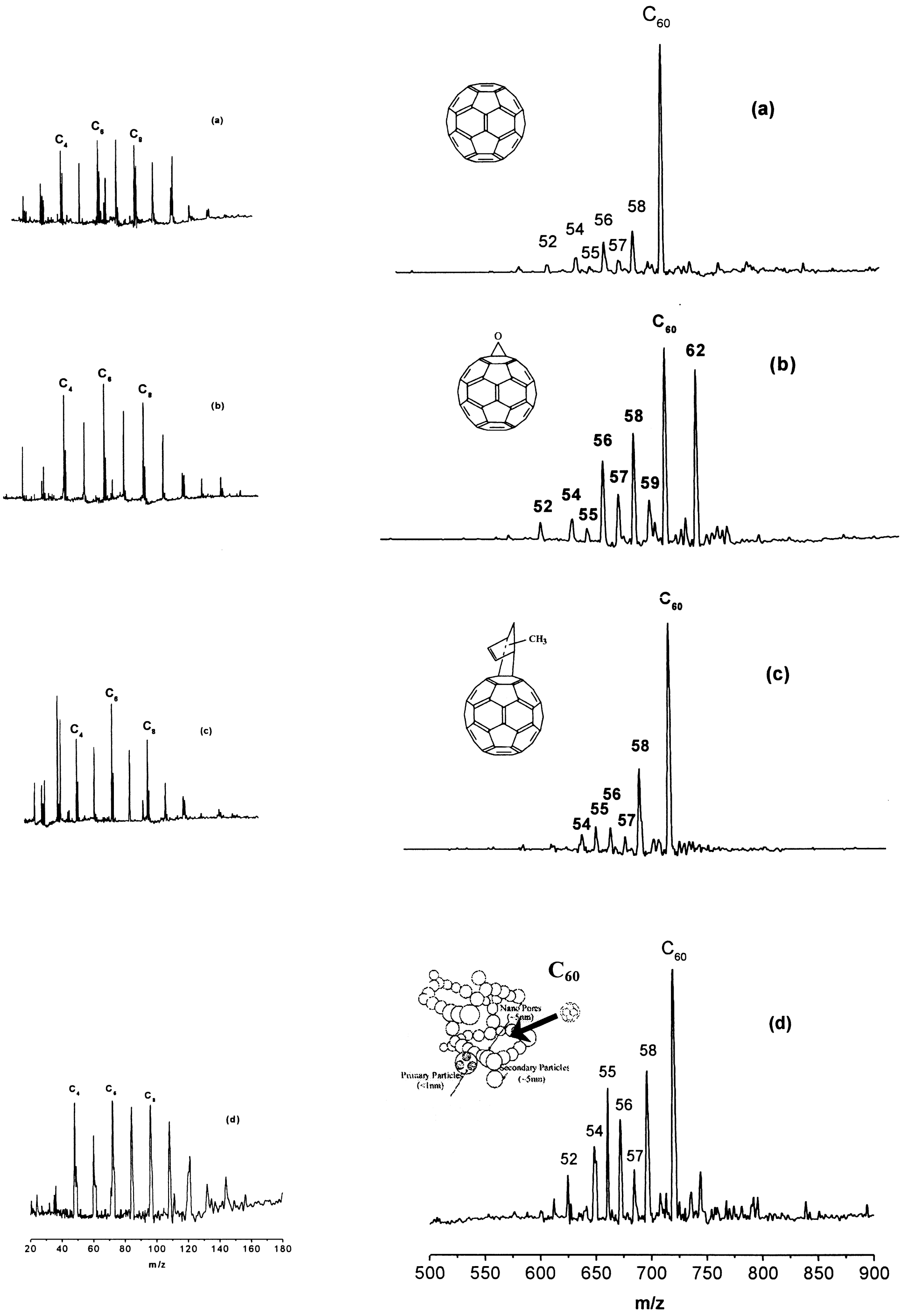

Fig. 2. Typical negative ion TOF mass spectra of (a) pristine C_{60}, (b) $C_{60}O_n$, (c) $C_{60}C_5H_5CH_3$, and (d) fullerene-doped silica aerogel with a laser fluence of about 650 mJ/cm^2. The inserts show the structures of (a) pristine C_{60}, (b) $C_{60}O_n$, (c) $C_{60}C_5H_5CH_3$, and (d) fullerene-doped silica aerogel.

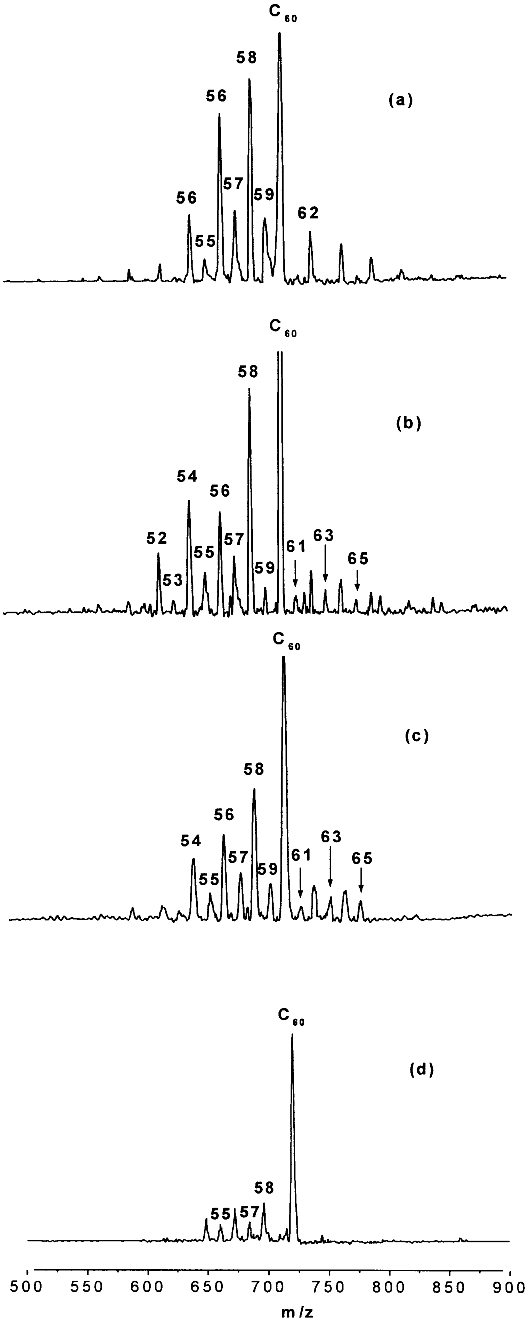

Fig. 3. Typical negative ion TOF mass spectra of (a) $C_{60}Sm_x$, (b) $C_{60}Rh_x$, (c) $C_{60}Ni_x$, and (d) $C_{60}La_x$ with a laser fluence of about 650 mJ/cm^2.

small odd-numbered carbon clusters C_1 or C_3 is another possibility. We recorded the small carbon clusters in the low mass region of the negative spectra and found that in all the negative mass spectra recorded for various fullerene materials, the intensities of the small carbon clusters C_n^- (n = 4–9) vary alternatively with the even-numbered clusters stronger than the odd ones. It is in accordance with the observation that the odd-numbered fullerenes are usually weak.

In the positive ion channel, all these samples behave similarly. Only normal photofragmentation, that is, the formation of even-numbered fragments due to loss of C_2 or C_{2n} were recorded, as shown in Fig. 4. Odd-numbered fullerene species have never been detected in the cationic mode, even though quite intense odd-numbered species, such as C_{55}^-, has been recorded in the anionic mode from fullerene doped in silica aerogel. Bowers et al.'s [16] experiments on graphite gave similar result. To our knowledge, no observation of odd-numbered fullerene cations in the laser ablation experiments has ever been reported, and no interpretation has been provided. VanCleempoel and coworkers reported the formation of odd-numbered carbon clusters in fullerene regime in both the negative and positive ion modes, but their experimental results were from collision-induced dissociation of C_{60} and C_{70} oxides [17]. From the formation mechanism of the cationic and anionic fullerene fragments, this phenomenon is thought to be related to the ionization potentials and the electron affinities of the fragments. As mentioned in the previous studies [16,18], we know that fullerenes with closed cage structures usually have lower ionization potentials (IP) and lower electron affinities (EA) than the smaller carbon clusters with chain or ring structures. Since odd-numbered carbon clusters in fullerene mass region cannot take closed cage structures as even-numbered fullerenes, their structures may be regarded as intermediates between chain/ring and cage structures. Theoretical calculation below indicates the case. It is reasonable to predict that the odd-numbered fullerenes will have higher IP as well as higher EA than the even-numbered fullerenes, favoring the formation of the former in the anionic mode. We have optimized the structures of C_{54} and C_{55} at the Hartree Fock and B3LYP level with 3-21G basis set. Based on the ground state structures of the neutral clusters, the

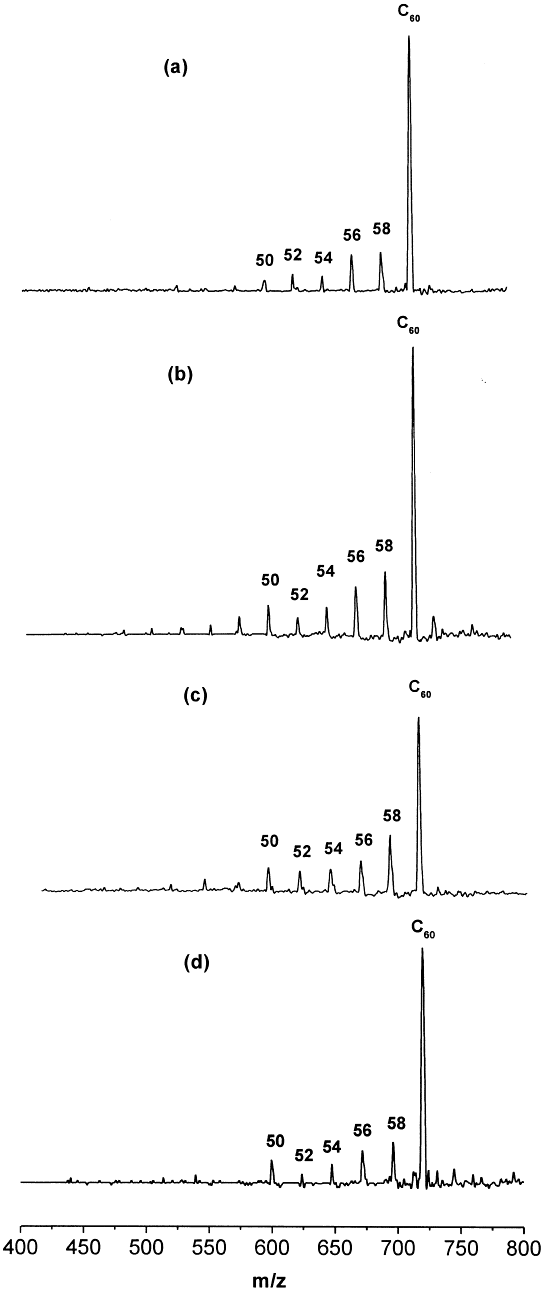

Fig. 4. Typical positive ion TOF mass spectra of (a) pristine C_{60}, (b) $C_{60}O_n$, (c) $C_{60}C_5H_5CH_3$, and (d) fullerene-doped silica aerogel with a laser fluence of about 600 mJ/cm^2.

single point energies of both the positive and negative ions of C_{54} and C_{55} were calculated at the same level to get the vertical EA and IP of C_{54} and C_{55}. The IP values of C_{54} and C_{55} are 6.85 and 7.27 eV respectively, at the HF/3-21G level and 7.18 and 7.25 eV respectively, at the B3LYP/3-21G level. As in our experiments the ions appearing in the mass spectra were all laser-induced, so it is reasonable to assume that the process is related to the vertical EA and IP. Although our calculation at both levels gives C_{55} higher IP than C_{54}, the differences are so small (especially for the calculation at B3LYP level) that it cannot explain the absence of the odd-numbered fullerene species in the positive ion channel. Therefore we cannot but say that the absence of odd-numbered fullerene cations is still an open question.

3.2. Structures of the odd-numbered fullerene species

Since only even-numbered carbon clusters C_n with $n = 20$ and $n \geq 24$ can take the trivalent closed cage polyhedral structures comprised of only pentagons and hexagons, the odd-numbered carbon clusters observed in the fullerene regime of our anionic mass spectra cannot take the usual closed cage forms of fullerenes. We have performed the structural optimization from C_{51} to C_{59} by the genetic algorithm with the Brenner potential to find the structures of the lowest energy isomers of these clusters. For C_{53} and C_{57} the minimal energy isomers we found have energies lower than those obtained previously [19] by 0.8 and 0.6 eV respectively, whereas the minimal energies for C_{51}, C_{55}, and C_{59} were the same as the previous ones within 0.2 eV. The structure of C_{55} was also optimized with Hartree Fock and B3LYP methods using 3-21G basis set. The structure remains the same, but with slightly different bond lengths. From our calculation it was found that all these odd-numbered clusters take cage-like forms as their lowest energy structures, but they are not the really closed cage fullerenes. The structures of the odd-numbered fullerene species have a general feature in that a twofold coordinated carbon atom appended to a pentagonal/pentagonal, pentagonal/hexagonal, or hexagonal/hexagonal interface appears in the structure. Figs. 5(a) and (b) show two views of the structures of the lowest energy isomers of C_{55} and C_{57}, in which a

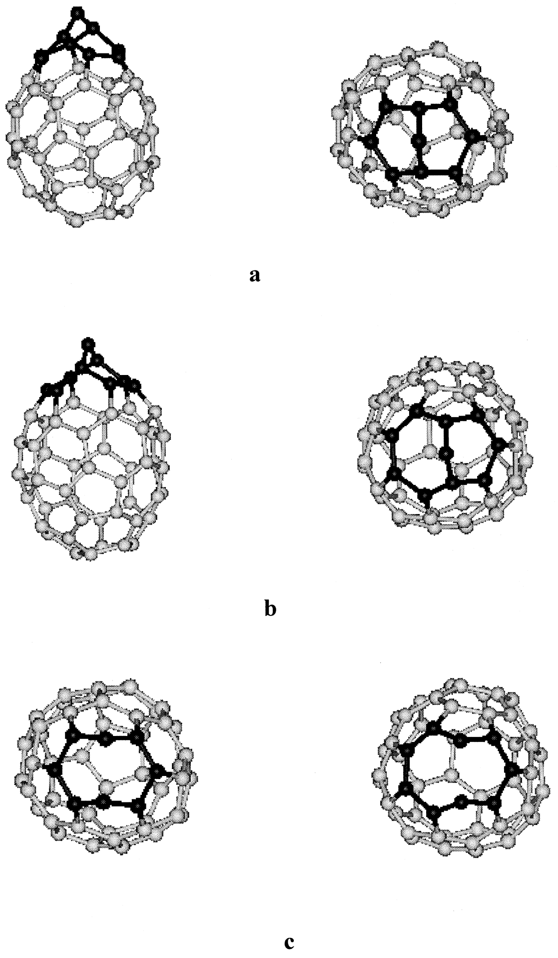

Fig. 5. Optimized structure of the odd-numbered carbon clusters: two views of (a) the lowest energy isomer of C_{55}, (b) the lowest energy isomer of C_{57}, and (c) the eight/nine-member window formed on C_{55}/C_{57} by removal of the appending C atom. The solid circles denote the window-forming carbon atoms.

carbon bridge is formed along the borderline of two pentagons and pentagon/hexagon respectively. Bowers et al. [16] have discussed the formation of the ring isomers of the odd-numbered carbon clusters in their laser ablation of graphite experiment. In our present study, however, the odd-numbered carbon clusters are mainly formed from the fragmentation of C_{60} as discussed in the above section, the possibility of forming ring isomers of the odd-numbered fullerene species should be very low. Kohno's experiment [20] supported this point of view. In their study, the comparison of the photoelectron spectra of C_{60} from different sources indicated that the fragments formed from fullerenes more probably preserve the ball-like structure of fullerenes, whereas laser vaporization of graphite produces clusters with ring-like structures.

Although the structures of the odd-numbered fullerene species do not have the "windows" of seven-membered or even bigger rings for the entrance of atom as we expected before, they are still interesting. Notice that for C_{55} the bond lengths between the appended carbon atom and the neighboring atoms (1.480Å) are intermediate between the longest (1.539Å) and the shortest (1.332Å) bond lengths of the molecule. This twofold coordinated appended carbon atom provides an active site for chemical reactions, because only two bonds of medium strength have to be broken instead of the usual three bonds. 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 an eight- or nine-membered window shown in Fig. 5(c) (for C_{55} and C_{57} respectively as examples). From this point of view, the odd-numbered carbon clusters in the fullerene regime can be regarded as pseudo-open-caged fullerenes.

3.3. Formation of metallofullerenes from metal fulleride $C_{60}M_x$

The main purpose of our study of the odd-numbered carbon clusters in the fullerene regime is to examine the possibility of finding a new way to prepare endohedral or substitutional metallofullerenes through the odd-numbered carbon clusters with pseudo-open-caged structures. In our laser ablation study of a series of externally doped metal fullerides, along with odd-numbered fullerenes, endohedral or substitutional metallofullerenes are formed in the gas phase. Fig. 6 shows the laser ablation mass spectra of $C_{60}Sm_x$ (a) in the negative ion channel and (b) in the positive ion channel with laser fluence of about 800 mJ/cm^2. Mass peaks corresponding to $C_{59}Sm$ are observed both in the negative and positive ion channels, which is confirmed by its isotopic distribution patterns shown in the inserts of Fig. 6. Based on the

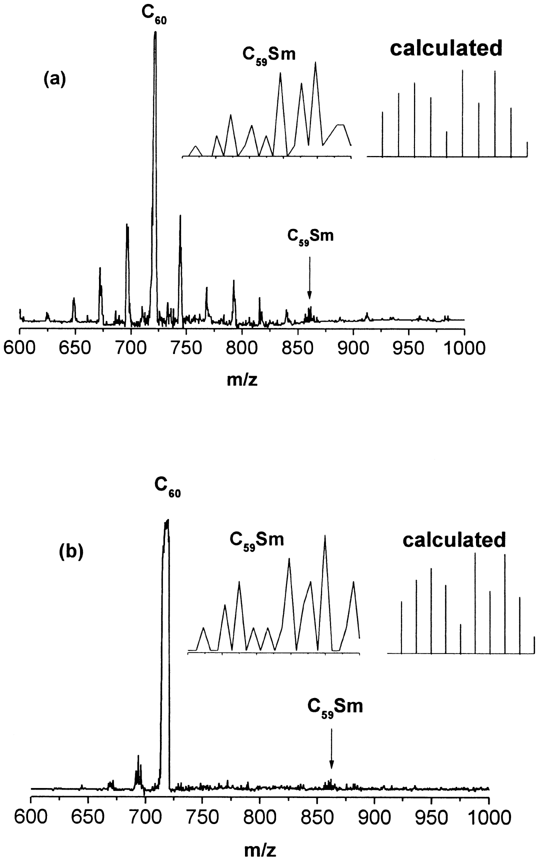

Fig. 6. Typical TOF mass spectra of metal-fullerene cluster $C_{60}Sm_x$ (a) in the negative ion channel, (b) in the positive ion channel with a laser fluence of about 800 mJ/cm^2. The inserts show the isotopic distribution patterns observed for $C_{59}Sm$ and comparison with the calculated spectra.

previous studies [6,21], we assign the metallofullerene cluster $C_{59}Sm$ with an odd-number of carbon atoms as substitutional heterofullerene with one carbon atom of the fullerene network replaced by metal atom Sm. The formation of $C_{59}M$ from the photofragmentation of the precursor metal fullerides $C_{60}M_x$ provides a new way for the preparation of metallofullerenes.

As suggested in the previous studies [6], the metal-substituted fullerenes come from photofragmentation of $C_{60}M_x$ through a transformation process from an externally doped to a substitutionally doped fullerene. To investigate the formation mechanism of the substitutional metallofullerenes $C_{59}M$, the evolution behavior of $C_{60}Sm_x$ under laser ablation with number of laser irradiation shots was investigated in the positive ion channel. The results are displayed in Fig. 7. Each spectrum was averaged over 30 laser shots. We found that at the beginning of laser irradiation strong mass peaks corresponding to the isotopic multiplet of Sm atom were observed in the low mass region, no metal carbide SmC appeared at that moment. In the high mass region, only mass peaks corresponding to $C_{60}Sm$ were observed, no mass peaks belonging to $C_{59}Sm$ appeared. As the laser irradiation continued to act at the same sample site, the laser ablation products changed gradually. In the low mass region, besides the isotopic multiplet of Sm atoms, mass peaks of the metal carbide SmC were observed. In the high mass region, $C_{59}Sm$ began to appear in the neighborhood of $C_{60}Sm$ [Fig. 7(b)]. With prolonged irradiation, $C_{60}Sm$ disappeared at last, leaving $C_{59}Sm$ as the only remained mass peaks in this high mass region [Fig. 7(c)]. Here we observed the concurrence of the metal carbide cluster SmC and the heterofullerene cluster $C_{59}Sm$.

Based on the above observations, a scenario about the transformation process from an externally doped to a substituationally doped fullerene might be drawn. The metal atoms located outside the fullerene cage were first evaporated from the precursor at the beginning of the laser irradiation due to the weak interaction between the metal atoms and the cage, resulting in the appearance of the mass peaks corresponding to C_{60} and the metal atoms in addition to $C_{60}Sm$. The dissociation of metal carbide SmC from the metal fulleride $C_{60}Sm_x$ requires higher energy to break chemical bonds and the ionization energy of SmC is higher than that of Sm. Therefore the formation of metal carbide is a slow and difficult process. It needs the accumulation of energy through continued laser irradiation at the same site of the sample. As the heating of the clusters $C_{60}Sm_x$ reaches a certain point metal carbide SmC is ruptured from the precursor, leaving behind the substitutional fullerene $C_{59}Sm$ in case the precursor $C_{60}Sm_x$ having $x > 1$. At the end of the evolution process, the metal atoms located outside of the fullerene cage are evaporated completely and no $C_{60}Sm$ remained in the mass spectrum.

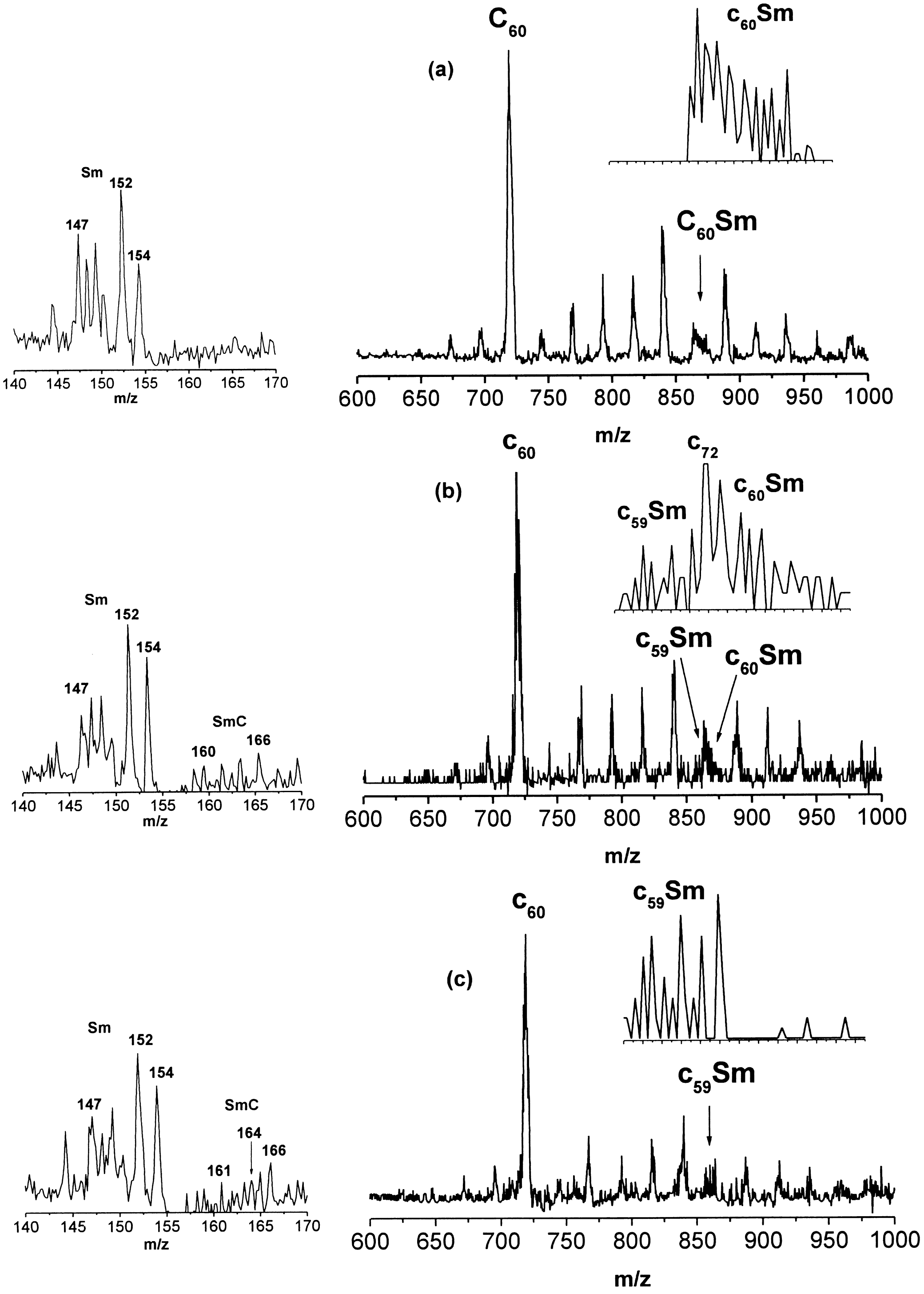

Fig. 7. The evolution behavior of $C_{60}Sm_x$ photofragmentation in the positive ion channel, each spectrum was averaged over 30 laser shots.

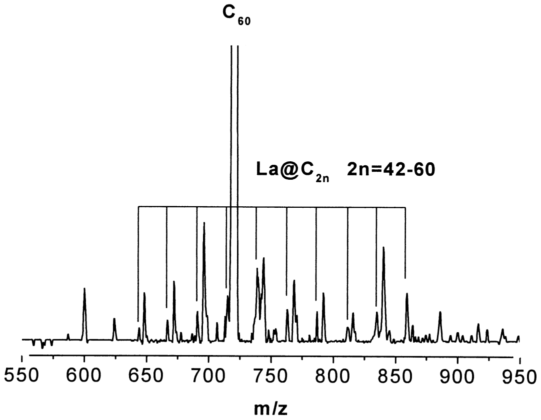

Fig. 8. Positive ion TOF mass spectra of $C_{60}La_x$ with a laser fluence of about 800 mJ/cm^2.

Another process for the formation of the substitutional metallofullerenes is through the odd-numbered carbon cluster C_{59}, which is formed when SmC is ruptured from $C_{60}Sm$. Since frequent collisions take place in the gas phase, C_{59} can then react with the evaporated Sm metal atom giving rise to the formation of substitutional metallofullerene $C_{59}Sm$, or the metal carbide SmC will have a chance to collide with C_{59} and replace the twofold coordinated appended carbon atom forming $C_{59}Sm$ with extrusion of a carbon atom. The reactions might be expressed

Insert displayed equation from msp 10

We have also observed the formation of endohedral metallofullerenes La@C2n from the laser ablation of externally doped metal fulleride $C_{60}La_x$ as shown in Fig. 8. Huang et al. [22] observed the formation of metallofullerenes M@C2n (M=La,Y) via laser ablation of M_2O_3/C_{60} composite materials, and they attributed the formation of endohedral fullerene to a window mechanism. The enhancement of the production efficiency of endohedral fullerenes in our case might be related to the window formation through odd-numbered fullerene species. The detail has been discussed in another paper [23]. As we have mentioned above, it is easier to form an eight- or nine-membered window on the odd-numbered fullerene cage than on the even-numbered fullerene cage, we think that endohedral fullerenes is more probable to be formed through the odd-numbered fullerene intermediates rather than through the even-numbered fullerene window mechanism as suggested by the previous study [22].

From our excimer laser ablation studies on a variety of fullerene derivatives, we have learned that the formation of odd-numbered fullerene species can be enhanced through derivatization of fullerenes, the enhancement is different for different derivatization. The formation of metallofullerenes, both substitutional and endohedral, may be closely related to the formation of the odd-numbered fullerene intermediates in the laser ablation of metal-containing fullerene materials. Therefore, it is reasonable to suppose that searching for fullerene derivatives, which can efficiently yield odd-numbered fullerenes might lead to novel route of efficient production of metallofullerenes. Our preliminary experiments have already given some confirmative results.

4. Conclusion

The formation and structural properties of odd-numbered carbon clusters in the fullerene regime were studied both experimentally and theoretically. Laser ablation study showed that odd-numbered fullerene clusters could be generated from various fullerene-containing materials: organic fullerene derivatives, metal fullerides, and guest-host fullerene materials. The calculated results indicate that odd-numbered carbon clusters in the fullerene regime are pseudo-open-caged fullerenes with a twofold coordinated carbon atom in the structure, which favors the formation of an eight- or nine-membered window on the odd-numbered fullerene cage upon collision. The high reactivity and the pseudo-open-caged fullerene structure of the odd-numbered species might be an ideal intermediate to form substitutional or endohedral metallofullerenes. Our experiments on metal fullerides provide valuable information on the formation of metallofullerenes through the participation of odd-numbered fullerenes.

Acknowledgements

The support to this work by National Natural Science Foundation of China (Project 29890216) is greatly acknowledged. The authors thank Prof. Zhang Yunwu, Prof. Sheng Liusi, and Dr. Gao Hui of the University of Science and Technology of China for their technical assistance in the reflectron TOF mass spectrometric experiments.

References

[1] C. Yeretzian, K. Hansen, F. Diederich, R.L. Whetten, Nature 359 (1992) 44.
[2] P.M. Ajayan, S. Iijima, Nature 361 (1993) 333.
[3] L. Zhu, S.Y. Wang, Y.F. Li, J. Chem. Phys. 101 (1994) 8592.
[4] 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.
[5] S. Yang, R.B. Huang, W.Y. Lu, Surf. Rev. Lett. 3 (1996) 803.
[6] W. Branz, I.M.L. Billas, N. Malinowski, F. Tast, M. Heinebrodt, T.P. Martin, J. Chem. Phys. 109 (1998) 3425.
[7] D.S. Bethune, R.D. Johnson, J.R. Salem, M.S. de Vries, C.S. Yannoni, Nature 366 (1993) 123.
[8] H. Shinohara, Adv. Met. Semicond. Clusters 4 (1998) 205.
[9] H. Shinohara, M. Tanaka, M. Sakata, T. Hashizume, T. Sakurai, Mater. Sci. Forum 232 (1996) 207.
[10] T. Guo, C. Jin, R.E. Smalley, J. Phys. Chem. 95 (1991) 4948.
[11] B. Nuber, A. Hirsch, Chem. Commun. (1996) 1421.
[12] R.Q. Yu, M.X. Zhan, D.D. Cheng, S.Y. Yang, Z.Y. Liu, L.S. Zheng, J. Phys. Chem. 99 (1995) 1818.
[13] D.M. Deaven, K.M. Ho, Phys. Rev. Lett. 75 (1995) 288.
[14] J.P. Deng, D.D. Ju, G.R. Her, C.Y. Mou, C.J. Chen, Y.Y. Lin, C.C. Han, J. Phys. Chem. 97 (1993) 11575.
[15] R.D. Beck, C. Stoermer, C. Schulz, R. Michel, P. Weis, G. Bräuchle, M.M. Kappes, J. Chem. Phys. 101 (1994) 3243.
[16] N.G. Gotts, G.V. Helden, M.T. Bowers, Int. J. Mass Spectrom. Ion Processes 149 (1995) 217.
[17] A. VanCleempoel, R. Gijbels, M. Claeys, H. VandenHeuvel, Rapid Commun. Mass Spectrom. 10 (1996) 1579.
[18] S.B.H. Bach, J.R. Eyler, J. Chem. Phys. 92 (1990) 358; J.A. Zimmerman, J.R. Eyler, S.B.H. Bach, S.W. McElvany, J. Chem. Phys. 94 (1991) 3556.
[19] S. Hobday, R. Smith, J. Chem. Soc. Faraday Trans. 93 (1997) 3919.
[20] M. Kohno, S. Suzuki, T. Kodama, D. Kasuya, H. Shiromaru, Y. Achiba, Eur. Phys. J. D 9 (1999) 359.
[21] J.M. Poblet, J. Munoz, K. Winkler, M. Cancilla, A. Hayashi, C.B. Lebrilla, A.L. Balch, Chem. Commun. (1999) 493.
[22] R.B. Huang, W.Y. Lu, S.H. Yang, J. Chem. Phys. 102 (1995) 189.
[23] Q.Y. Kong, Y.F. Shen, J. Xu, L. Zhao, J. Zhuang, S.X. Qian, Y.F. Li, X. Li, Y.H. Lin, R.F. Cai, Chem. Phys. Lett. 341 (2001) 447.