Endohedral fullerenes of different elements

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In this work we have studied the Li/C_{60}, Li/C_{70}, ^{99m}Tc/C_{60}, ^{99m}Tc/C_{70}, Gd/C_{60}, Gd/C_{70}, Nd/C_{60}, Nd/C_{70}, Y/C_{60} and Y/C_{70} systems by surface ionization mass spectrometry and investigated a possibility of the formation of endohedral fullerenes. Using the ion implantation technique (introducing negatively charged fullerene into a low temperature lithium, technetium, gadolinium, neodymium or yttrium plasma column by a strong axial magnetic field), the endohedral fullerenes Li≅C_{60}, Li≅C_{70}, Li_2≅C_{70}, ^{99m}Tc≅C_{60}, ^{99m}Tc≅C_{70}, Gd≅C_{60}, Nd≅C_{60}, Y≅C_{60}, Gd≅C_{70}, Nd≅C_{70} and Y≅C_{70} have been produced and ionization energies were measured. Their existence was demonstrated through the high sensitivity, magnetic mass spectrometer (TIMS- thermal ionization mass spectrometer). These metallofullerenes were identified as stable molecules. The reaction of the obtained endohedral fullerenes with oxygen compounds (H_2O, O_2 and N_2O) has also been investigated. The result showed that these metallofullerenes are very inert to all of these gas phase oxygen-rich molecules, leading support to the endohedral structure of the metallofullerenes. Observed ionization energies for Li≅C_{60}, Li≅C_{70}, Li_2≅C_{70}, ^{99m}Tc≅C_{60}, ^{99m}Tc≅C_{70}, Gd≅C_{60}, Nd≅C_{60}, Y≅C_{60}, Gd≅C_{70}, Nd≅C_{70} and Y≅C_{70} were 5.9eV, 5.1eV, 5.3 eV, 5.1 eV, 5.3eV, 6.2 eV, 6.5 eV, 6.6 eV, 6.4 eV, 6.5 eV and 6.7 eV, respectively.

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1. Introduction

Fullerenes have a unique type of inner empty space with their unusual cage-like structures. A wide variety of metal atoms may reside in this space and form endohedral metalofullerenes. The first evidence for endohedral metallofullerenes was reported soon after the discovery of C_{60} in 1985 [1]. However, only in 1991 endohedral metallofullerenes could be isolated in macroscopic amount. This was achieved by using laser- or arc-vaporization [2] of graphite-metal composites in helium. Endohedral metallofullerene compounds are stable by virtue of the transfer of electrons from the metal to the carbon cage.

These new series of materials with novel physical and chemical properties are very important for their potential application as new types of superconductors, organic ferromagnets, nonlinear optical materials, functional molecular devices, magnetic resonance imaging agents, biological tracing agents, etc., which will have great influence over electronics, optics, electromagnetic and medicine.

2. Experimental

The mass spectrometer used in this investigation was a 12-inch radius, 90° sector, magnetic instrument of local design. It was equipped with a combined electron impact Nier-type and surface ionization source. Pressures in the analyzer region were maintained below 10^{-8} Torr and operating pressures in the source region below $5 \cdot 10^{-7}$ Torr. The beam of the molecules to be investigated was produced by heating the sample in a Re canoe in the vicinity of a Re ionizing filament, where a certain fraction of the neutrals were ionized. The samples were: C_{60} or C_{70} / LiI for Li@C_{60}, Li@C_{70}, Li_2@C_{70}, C_{60} or C_{70} / Tc carbonile for Tc@C_{60} and Tc@C_{70}, C_{60} or C_{70} / $GdCl_2$ for Gd@C_{60} and Gd@C_{70}, C_{60} or C_{70} / $NdCl_2$ for Nd@C_{60} and Nd@C_{70}, C_{60} or C_{70} / YCl_2 for Y@C_{60} and Y@C_{70}. The ion beam was introduced into the Nier-type ion source. The ion source is shown in Figure 1. Surface ionization (SI) is a method for generating ions at a hot metal surface. When atoms or molecules from an atomic or molecular beam or from a surrounding vapor hit a hot metal surface, they are emitted partly as neutral species and partly as positive or negative ions. The formation of positive ions is called positive surface ionization (PSI) and the formation of negative ions is called negative surface ionization (NSI). PSI and NSI are quantitatively described by the Saha-Langmuir equations:

$$\alpha^+ = \frac{g^+}{g} e^{\frac{\Phi - IE}{kT}}, \qquad \alpha^- = \frac{g^-}{g} e^{\frac{EA - \Phi}{kT}} \qquad (1)$$

where α^+ and α^- are the ionization coefficients; g^+, g^- and g are the statistical weights of the ions and neutrals; Φ is the work function of the surface; IE is the ionization energy of atoms and molecules; EA is the electron affinity of atoms and molecules; k is Boltzman's constant; T is the temperature of the surface. It can be seen from Eqn(1), high yields of positive and negative ions can be obtained for atoms or molecules with low ionization energy and with high electron affinity, respectively. The high work function is suitable for PSI, while the low work function is suitable for NSI.

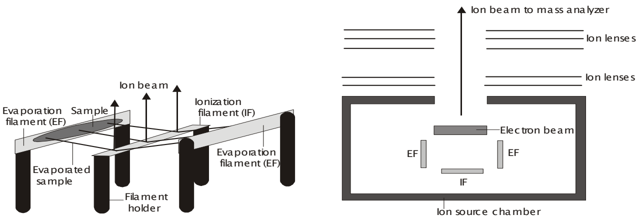

Fig. 1. Schematic diagram of a triple filament surface ionization ion source with electron impact source. Electron beam is perpendicular to the paper.

3. Results

Using the ion implantation technique (introducing negatively charged fullerene into a low temperature lithium, technetium, gadolinium, neodymium or yttrium plasma column by a strong axial magnetic field), the endohedral fullerenes Li≅C_{60}, Li≅C_{70}, Li_2≅C_{70}, ^{99m}Tc≅C_{60}, ^{99m}Tc≅C_{70}, Gd≅C_{60}, Nd≅C_{60}, Y≅C_{60} and Gd≅C_{70}, Nd≅C_{70} and Y≅C_{70} have been produced and ionization energies were measured. Observed ionization energies for Li≅C_{60} [3], Li≅C_{70} [4], Li_2≅C_{70} [4], ^{99m}Tc≅C_{60}, ^{99m}Tc≅C_{70}, Gd≅C_{60}, Nd≅C_{60}, Y≅C_{60}, Gd≅C_{70}, Nd≅C_{70} and Y≅C_{70} were 5.9eV, 5.1eV, 5.3 eV, 5.1 eV, 5.3eV, 6.2 eV, 6.5 eV, 6.6 eV, 6.4 eV, 6.5 eV and 6.7 eV respectively. We have also determined the electron affinities of C_{60} [5] and C_{70} by surface ionization mass spectrometry. Observed electron. affinities are 2.66 eV and 2.68 eV respectively. Following figures show theoretical and observed isotope pattern of produced endohedral ions.

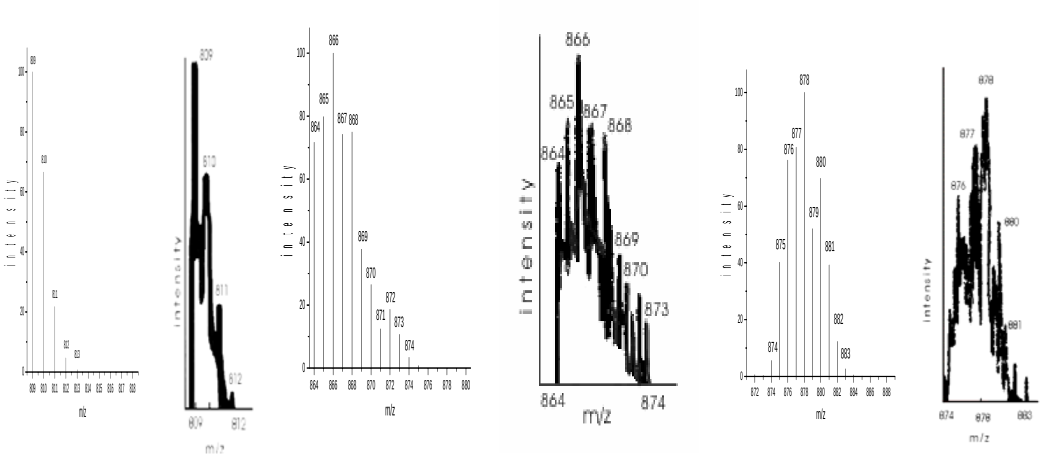

Fig. 2. Comparison of the theoretical and observed isotope pattern of Y≅C_{60}, Nd≅C_{60}, Gd≅C_{60} ions.

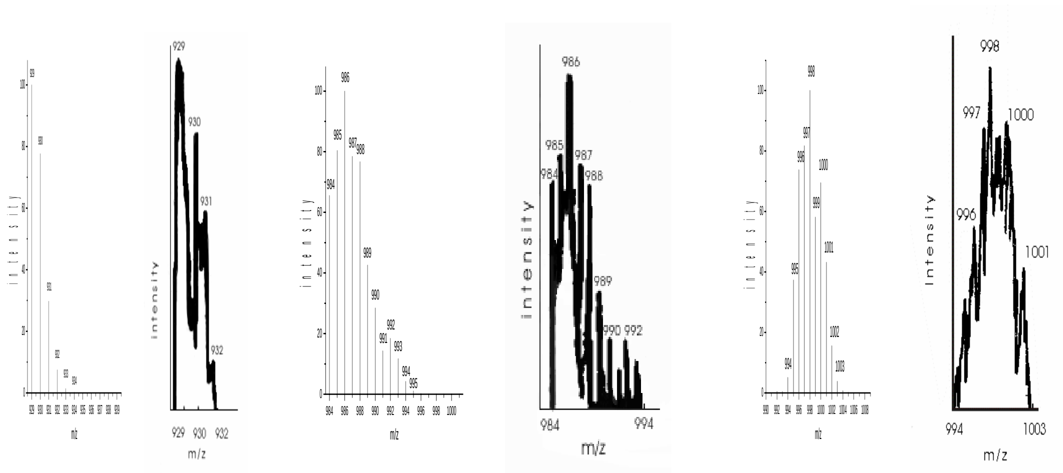

Fig. 3. Comparison of the theoretical and observed isotope pattern of Y≅C_{70}, Nd≅C_{70}, Gd≅C_{70} ions.

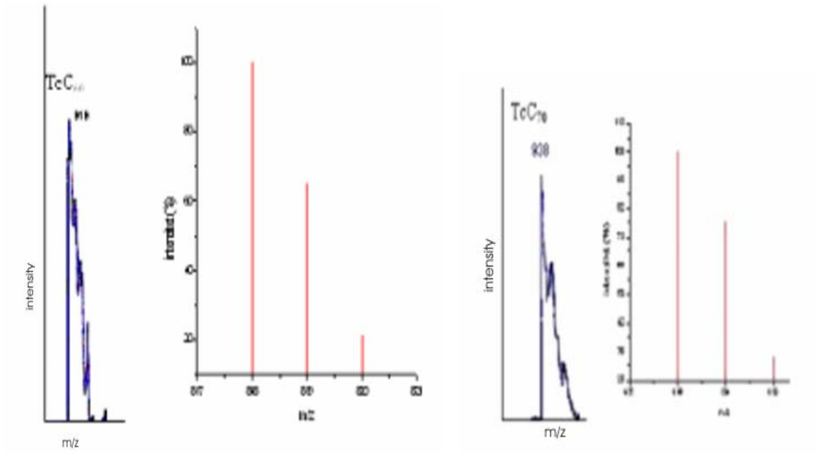

Fig. 4. Comparison of the theoretical and observed isotope pattern of $Tc{\cong}C_{60}$ and $Tc{\cong}C_{70}$ ions.

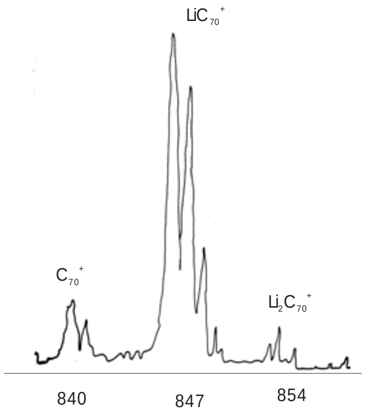

Fig. 5. Mass spectrum for a C_{70} / LiI sample containing C_{70}^+, $Li{\cong}C_{70}^+$ and $Li_2{\cong}C_{70}^+$ species.

4. Conclusions

TIMS is a very important mass spectrometry method for investigation of ionization energy of fullerenes and fullerenes derivates.

Acknowledgments

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References

[1] H. Kroto, J. Heath, S. O'Brien, R. Curl, R. Smalley, Nature **318,** 162 (1985).
[2] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J.M. Alford, R. E. Smalley, J. Phys. Chem., **95**, 7564 (1991).
[3] A. Djeric, M. Veljkovic, O. Neskovic, M. Miletic, K. Zmbov, Full. Sci. Tech., **8(6)**, 461 (2000).
[4] M. Veljkovic, O.Neskovic, T. Ivetic, S. Velickovic, T. Maksin, Mater. Sci. Forum, **480-481**, 351-354 (2005).
[5] A. Djeric, L. Vasic, M. Veljkovic, O. Neskovic, M. Miletic, K. Zmbov, Chem. Ind. **52(12)**, 524 (1998).

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