

# FT-ICR による炭素クラスター - の質量分析 ( 2 )

## FT-ICR Studies of Laser-Vaporized Carbon Clusters (2)

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Atomic and molecular clusters are being recognized as playing an important role in the thin-film deposition process and phase-change phenomena. Furthermore, small clusters are the most adequate system for the verification of quantum molecular dynamics calculations such as the interference of light and matter, since a cluster is the unique small atomic system with a physically clear boundary condition. Hence, experimental treatments of such atomic and molecular clusters are now desired. In order to examine such clusters, we have implemented a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer directly connected to a laser-vaporization supersonic-expansion cluster beam source.

The heart of the FT-ICR spectrometer was made of ICR cell cylinder centered in a strong homogeneous magnetic field of a 6 Tesla superconducting magnet. The side plates of the ICR cell were composed of four sectors of a 42 mm i.d. cylinder, 150 mm in length. Two opposing 120° sectors were used for excitation of the trapped cluster ions, while the other two 60° sectors were used for detection of the image current induced by the cyclotron motion. The atomic cluster beam was generated outside of magnetic field by the laser vaporization of a solid sample disk, followed by cooling with supersonic expansion of pulsed helium gas. The ionized cluster was carried by helium gas and directly injected to the magnetic field. The radial ion motion was confined by the magnetic Lorentz force which determines the cyclotron motion. Along the magnetic central axis the confinement of the cluster ions was accomplished by two conical-shaped electrodes: the “front” and “back” doors. With appropriate electrical potential in both doors, cluster ions were completely confined in the center of the magnetic field for a few minutes. Furthermore, by measuring the ion-cyclotron frequency, which was inversely proportional to the mass, a very high-resolution mass spectrum could be obtained.

Examples of mass spectra measured by the direct-injection FT-ICR apparatus are shown in Fig. 1. Here, a graphite sample was vaporized by the 2nd harmonics of Nd: YAG laser

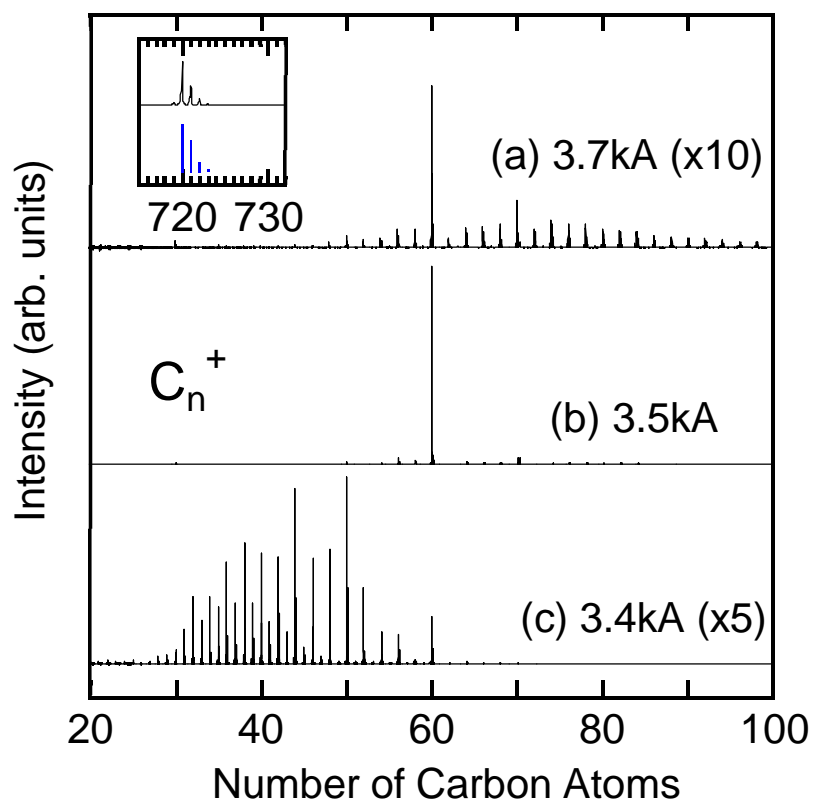


Fig. 1. Dependence of Helium gas pressure on the carbon cluster mass distribution. Insert panel is the expanded mass spectrum around  $C_{60}$  (in amu mass unit) compared to the theoretical isotopic distribution in the bottom.

and the positive carbon clusters were trapped and analyzed by the FT-ICR spectrometer. Fig.1 (a) is very much similar to the well known positive carbon mass distribution which lead to the discovery of spherical  $C_{60}$  structure [H. W. Kroto et al., Nature 318, 168 (1985)]. The high resolution of the FT-ICR mass spectrometer can be readily observed by the insert panel in which the mass scale was expanded to show the isotope distribution of  $C_{60}$  cluster compared with the theoretical distribution predicted from the natural isotope abundance of 1.108 %  $^{13}\text{C}$ . We can observe completely different aspects of mass spectra for less amount of source helium gas in the nozzle of the laser-vaporization cluster source. At the condition of Fig.1 (b) almost only  $C_{60}$  is observed and the even less pressure lead to the odd number of carbon atoms, which can be regarded as the non-closed structures of positive carbon clusters. These findings of intermediate stage of the fullerene formation must be very important for the understanding of the fullerene formation mechanism.

A mass spectrum shown in fig.2 was obtained by the laser vaporization of La-carbon composite disk (La:C = 1:130 atomic ratio) . In this mass spectrum, we can observe some

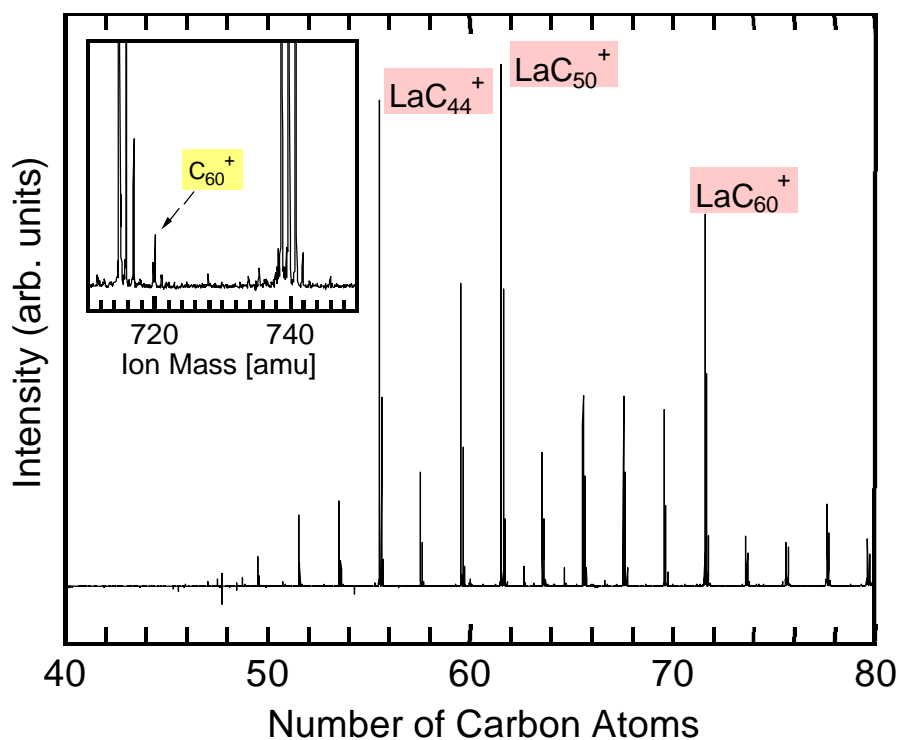


Fig.2 A mass spectrum obtained by the laser vaporization of La-carbon composite disk. interesting findings as follows. First, throughout the experiment,  $\text{LaC}_{44}^+$ ,  $\text{LaC}_{50}^+$  and  $\text{LaC}_{60}^+$

were usually observed as magic numbers. Second, the positive empty carbon clusters ( $\text{C}_n^+$ ) were not observed except for a tiny amount of  $\text{C}_{60}^+$  (see inserted figure). From this result, it is suggested that the attachment of the La atom to small carbon clusters occurs very easily and as a result, the chance of the growth of carbon clusters to the medium sized range is very small. Third, the odd-numbered La-carbon clusters ( $\text{LaC}_{2n+1}^+$ ) were not observed in the spectrum: only even-numbered La-carbon clusters ( $\text{LaC}_{2n}^+$ ) were produced in our source, just as same as positive empty carbon clusters ( $\text{C}_n^+$ ) in the size range  $n \geq 30$ . This can be explained by the hypothesis that all carbon atoms have  $\text{SP}^2$  bondings. At this stage we consider that those  $\text{LaC}_{2n}^+$  ( $2n \geq 40$ ) are imperfect ball-like structures with metal atom inside. In order to study the formation process of metallofullerenes, experiments of  $\text{YC}_n$  and  $\text{ScC}_n$  are now in progress.

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