Carbon Clusters Vaporized Directly from Graphite through Laser Vaporization

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The laser-power dependence on the formation of carbon clusters through the laser vaporization of graphite confirms the direct vaporization of carbon clusters from the graphite.

Laser vaporization of graphite is one of the most general methods used to produce carbon clusters.[1,2] In this method, carbon clusters, especially fullerenes, are thought to grow through the aggregation of the species vaporized from the graphite.[2,3] The identification of the primary products from the laser vaporization of the graphite is indispensable for studying the mechanism of carbon-cluster growing. It is, therefore, surprising that there has been little information about this. We have confirmed experimentally that carbon-cluster ions, with linear or ring structure, were vaporized directly from the graphite surface, when the laser was focused on it.

In order to see the mass distribution of the primary products for laser vaporization of graphite, the graphite sample was placed between the acceleration electrodes of a time-of-flight (TOF) mass spectrometer. In this condition, the resulting carbon cluster ions were analysed without any integration and cooling. When the fundamental wave [1064 nm, 10 ns full width at half maximum (fwhm)] from an Nd-YAG laser was focused on the graphite surface at 14 different laser powers between 5.75×10^{-3} and 28.2×10^{-3} J pulse^{-1}, the TOF mass spectra were measured without using any other laser for ionization.

Fig. 1 shows typical mass spectra observed. The mass distributions changed with varying laser power, and the larger clusters were predominant at the lower laser powers. At a laser power of 5.75×10^{-3} J pulse^{-1}, C_3^+, C_5^+, C_7^+, C_{11}^+ and C_{15}^+ were observed as prominent peaks (magic number) as reported previously.[1] The C_n^+ with $n > 20$ could not be observed, which means that the carbon clusters with the linear and the ring structures are generated,[4] but the three-dimensional cage structure (fullerene structure) is not. With an increase of laser power to 6.8×10^{-3} J pulse^{-1}, the intensity of every peak was increased. At a laser power of 8.2×10^{-3} J pulse^{-1}, however, the C_n^+ with $n \geqslant 7$ was decreased remarkably. The C_n^+ with $n \leqslant 6$ was also decreased with further increase of the laser power.

Fig. 2 shows the plots of the logarithmic ion intensity of C_n^+, $\ln I_{C_n^+}$, for $n = 1, 3, 5, 7$ and 11 as functions of the logarithmic laser power, $\ln E_L$, which indicates that the intensity of each C_n^+ attains a maximum with increasing the laser energy. The internal energies of the resulting carbon-cluster ions reach the dissociation limit with increase of the laser energy, and then they dissociate to the smaller clusters. The laser energy corresponding to the dissociation limit was found to be reduced with increased cluster size.

† STA (Science and Technological Agency in Japan) fellowship.

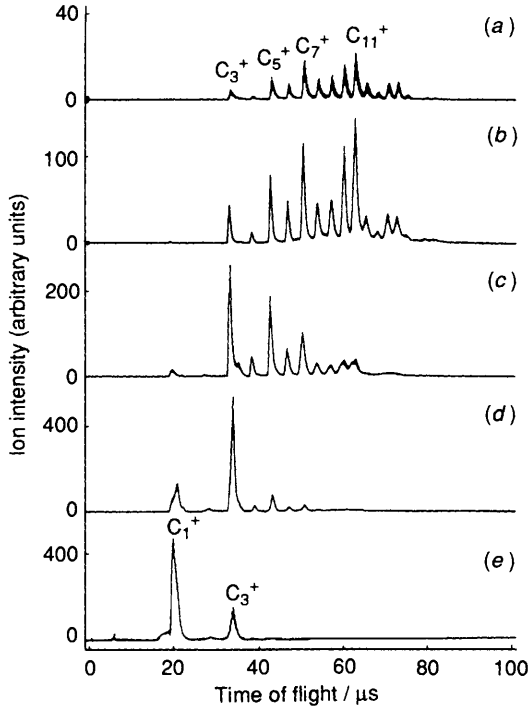

Fig. 1 Time-of-flight mass spectra of carbon clusters generated by the irradiation with the fundamental wave (1064 nm) from an Nd-YAG laser of graphite under vacuum (1.0×10^{-7} Torr; 1 Torr = 133.3 Pa). (*a*) 5.75×10^{-3}; (*b*) 6.80×10^{-3}; (*c*) 8.20×10^{-3}; (*d*) 10.0×10^{-3}; (*e*) 18.0×10^{-3} J pulse^{-1}

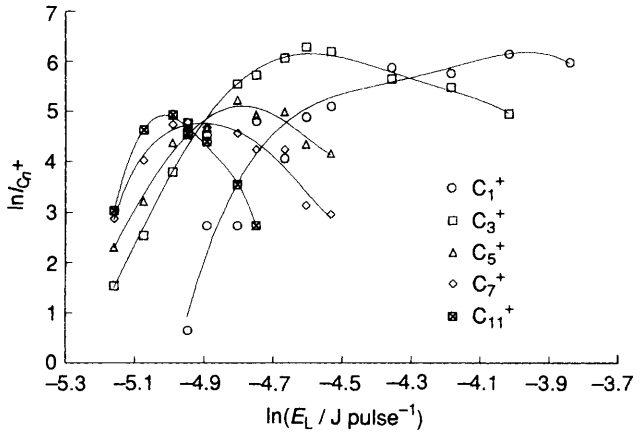

Fig. 2 Plots of the logarithmic ion intensity of C_n^+, $\ln I_{C_n^+}$, for $n = 1, 3, 5, 7$ and 11 as functions of the logarithmic laser power, $\ln(E_L$/J pulse$^{-1})$

Furthermore, as Fig. 2 shows, each $\ln I_{C_n^+}$ has linear relation to $\ln E_L$ before attaining the dissociation limit, that is, eqns. (1) and (2) are satisfied; where α and A are constant

$$\ln I_{C_n^+} = \alpha \ln E_L + \ln A \quad (1)$$

$$I_{C_n^+} = A E_L^{\alpha} \quad (2)$$

values. Eqn. (2) means that C_n^+ is generated through a multi-photon process. The constant α is obtained from the initial slope of the plots before attaining the maximum for each C_n^+ in Fig. 2. The values of α for C_1^+, C_3^+, C_5^+ and C_7^+ were 15.3, 13.2, 12.2 and 11.0, respectively.

Since α corresponds to the number of photons required to generate C_n^+, α can be estimated from the energy $E_{C_n^+}$ required to generate C_n^+ from graphite. $E_{C_n^+}$ is represented

Table 1 Energetics for carbon-cluster ion (C_n^+) formation

	C_1^+	C_3^+	C_5^+	C_7^+
$E_b(n)$/eV	7.4[a]	17.3	27.1	37.0
$E_s(n)$/eV[b]	—	−12.7	−23.9	−35.2
$E_i(n)$/eV[b]	11.0	11.4	10.7	10.0
$E_{C_n^+}$/eV	18.4	16.0	13.9	11.8
α(theoretical)	15.8	13.7	11.9	10.1
α(experimental)	15.3	13.2	12.2	11.0

[a] Ref. 5. [b] Ref. 6.

by the following three kinds of energy. (*i*) Bond-breaking energy to form *n* carbon atoms which are neighbouring in the graphite structure, $E_b(n)$: to vaporize a carbon atom from an atomic layer in graphite composed of six-membered rings (honeycomb structure), breaking three bonds is necessary; for *n* carbon atoms which are neighbouring, breaking $2n + 1$ is necessary. The heat of formation of carbon atom from graphite is available for $E_b(1)$;[5] therefore, $E_b(n)$ can be obtained from eqn. (3) on the supposition that every C–C bond on the atomic layer of graphite is equivalent.

$$E_b(n) = E_b(1) \cdot (2n + 1)/3 \quad (3)$$

(*ii*) Stabilization energy $E_s(n)$ for the bond formation among *n* carbon atoms. (*iii*) Ionization energy $E_i(n)$ for C_n. The reported values for $E_s(n)$ and $E_i(n)$ could be used for this purpose.[6] If the 1064 nm photon energy is completely converted into the thermal energy, $E_{C_n^+}$ [$= E_b(n) + E_s(n) + E_i(n)$] divided by the 1064 nm photon energy (1.165 eV) gives theoretical α values, which are recorded in Table 1 with $E_b(n)$, $E_s(n)$, $E_i(n)$, $E_{C_n^+}$ and experimental α values, for $n = 1, 3, 5$ and 7. The calculated α values are in good agreement with the experimental values described above.‡

These findings indicate that the formation energy of C_n^+ from graphite is characteristic of its size *n*; with increase of *n*, that energy decreases. Such laser-power dependence on C_n^+ formation strongly suggests that observed carbon clusters in Fig. 1 were directly vaporized from the atomic layer of graphite.§

Received, 30th November 1992; Com. 2/06397B

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‡ When 532 and 266 nm lasers were used for the vaporization of graphite, the difference between the experimental and the theoretical α values was larger than this result; this is owing to incomplete conversion of the photon energy into the thermal energy and/or the effect of photoelectronic excitation. Details will be reported soon.

§ At higher laser powers, C_1 is predominantly vaporized. If the resulting C_1 was cooled through collisions with inert atoms or molecules, it would grow into a larger carbon cluster.[7]