The Simplest Process in the Growth of Carbon Clusters: C_2 Formation from C_1 following Laser Vaporization of Graphite

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C_2 formation from C_1, as the simplest growing process of carbon clusters, can be observed from the time-resolved emission spectra of C_2 (the Swan bands) generated by the laser vaporization of graphite.

In connection with the study of the mechanism of formation of a stable large carbon cluster, especially of a fullerene, considerable attention has been paid to the reactivity and structure of a small carbon cluster; for example, photofragmentation properties of the carbon clusters[1] and chemical reactivity of the carbon clusters with hydrogen, oxygen[2] and various organic compounds.[3] It is, therefore, surprising to find very little direct experimental evidence for growth of a carbon cluster as shown in eqn. (1). We have confirmed experimentally the formation of C_2 from $2C_1$ as the simplest growing process of carbon clusters.

$$C_m + C_n \rightarrow C_{m+n} \qquad (1)$$

The formation of C_2 from $2C_1$ was shown by time-resolved emission spectra of C_2 generated by the laser vaporization of graphite. When the second harmonic from a YAG laser [532 nm, 10 Hz, 10 ns full width at half maximum (FWHM), 3.4 mJ per pulse] was focused on the graphite surface through a 30 cm focal length lens under an argon atmosphere, the time-resolved emission spectra on the irradiated graphite surface were measured by a photodiode array detector with a gated system and are shown in Fig. 1. The emission bands around 470 and 515 nm observed in Fig. 1 are in good agreement with the $\Delta v = 1$ and $\Delta v = 0$ sequences of the $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ Swan bands.[4]

In Fig. 1 the emission spectra from 1.5 to 8.5 μs after the laser irradiation decay through a single exponential function† and the decay time (apparent lifetime) was estimated to be 3.3 μs independent of the wavelength. The lifetime of $C_2(d^3\Pi_g)$ has been determined to be about 110 ns through the selective excitation of $C_2(a^3\Pi_u \rightarrow d^3\Pi_g)$ by using a pulsed dye laser.[5] The decay time observed in Fig. 1 is much longer than this; therefore, the decay profile observed in Fig. 1 does not show the true lifetime of $C_2(d^3\Pi_g)$, but it shows the change in the number of $C_2(d^3\Pi_g)$ produced after the laser vaporization.

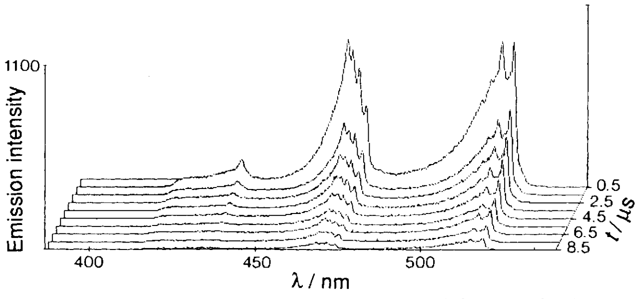

Fig. 1 Time-resolved emission of spectra of $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ Swan band observed on a graphite surface irradiated with the second harmonic from a YAG laser (532 nm, 10 ns FWHM, 3.4 mJ per pulse) under an argon atmosphere at room temp. The gate width for the photodiode array detector is 100 ns and the time indicated in the spectra corresponds to the time from the laser irradiation to the mid-point of this gate width. The time-resolved spectra were obtained by changing the delay time between the laser irradiation and the gate opening.

Furthermore, the observed decay time was increased with increasing the laser power. At the lower power of 2.5, 3.4 and 5 mJ per pulse, the resulting values of the lifetime were 2.3, 3.3 and 4.3 μs, respectively. If $C_2(d^3\Pi_g)$ or a much higher excited-stated C_2 is formed directly by the laser vaporization of the graphite, the observed decay time will become much shorter, and decrease with increasing the laser power due to the annihilation between $C_2(d^3\Pi_g)$ or much higher excited-state C_2 molecules.

When the 2.5 mJ per pulse laser was focused on the graphite surface under vacuum [10^{-7} Torr (1 Torr ≈ 133.3 Pa)], we observed emission due to C^+ ($2s^24f \rightarrow 2s^23d$) at 426 nm and predominant formation of C^+ by time-of-flight mass spectrometry.‡ This means that higher excited-state C_1 is formed immediately after the laser vaporization and subsequently ionized. Under an argon atmosphere (760 Torr), however, the emission due to C^+ ($2s^24f \rightarrow 2s^23d$) could not be observed even at higher laser power. The deactivation of higher excited-state C_1 occurs through interaction with argon, and the resulting C_1 is thought to form $C_2(d^3\Pi_g)$. Three possible mechanisms for $C_2(d^3\Pi_g)$ formation through the dimerization of C_1 can be written as eqns. (2)–(4) depending on the rate-determining step.

$$2C_1{}^* \Rightarrow C_2(d^3\Pi_g) \qquad (2)$$

$$2C_1{}^* \rightarrow 2C_1 \Rightarrow C_2(d^3\Pi_g) \qquad (3)$$

$$2C_1{}^* \Rightarrow 2C_1 \rightarrow C_2(d^3\Pi_g) \qquad (4)$$

($C_1{}^*$: higher excited-state of C_1, $\Rightarrow$: rate-determining step)

If the dimerization process is the rate-determining step [eqns. (2) and (3)], the decay profile of the observed emission intensity will be analysed through second-order kinetics. However, the decay profile shown in Fig. 1 is through the first-order kinetics; accordingly, mechanism (4) is the most probable, *i.e.* the observed much longer decay time in Fig. 1 than the lifetime of $C_2(d^3\Pi_g)$ is due to the relaxation of the highly excited-state C_1. The lifetime of excited-state C_1 as being longer than microseconds is reasonable because the transitions $^1S \rightarrow {}^1D$ and $^1D \rightarrow {}^3P$ are forbidden,[6] and $C_2(d^3\Pi_g)$ formation from $2C_1(^3P)$ is energetically allowed.[7] Accordingly, the decay profile observed in Fig. 1 corresponds to the concentration change of C_1 at low-energy states.

To confirm this, the time-resolved emission spectra were measured under an argon–benzene mixed atmosphere, because benzene is known to react with C_1 vapour.[8] The graphite sample was set above a liquid-benzene surface in a transparent cell. Other conditions were the same as those for the spectra in Fig. 1. The obtained spectrum shape was the same as that shown in Fig. 1. To see the effect of benzene on the decay time, the values of the emission intensity at 470 nm observed under an argon and under an argon–benzene mixed

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† Only the first point (0.5 μs after the laser irradiation) deviated from the first-order kinetics, which may be due to a possible faster relaxation process of C_1 occurring immediately after the laser irradiation. Detailed analysis is now in progress.

‡ To see the mass distribution immediately after the laser vaporization without any integration and cooling, the graphite sample was located between the acceleration electrodes of the time-of-flight mass spectrometer.

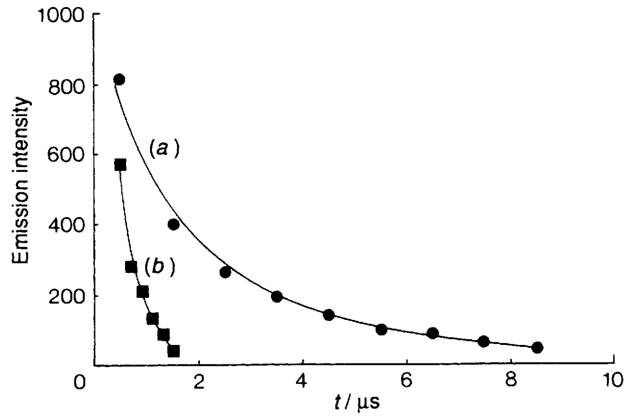

Fig. 2 Plots of the emission intensity at 470 nm when graphite was irradiated with the second harmonic from a YAG laser (532 nm, 10 ns FWHM, 3.4 mJ per pulse) under an argon (*a*) and under an argon–benzene mixed atmosphere (*b*) as functions of time after the laser irradiation

atmosphere are plotted as functions of time in Fig. 2. The decay of the emission intensity under an argon–benzene atmosphere can also be analysed completely by a single exponential function because the benzene-vapour concentration does not change owing to it being in equilibrium with the liquid, and the decay time is estimated to be 0.42 μs, which is much shorter than that under an argon atmosphere. This indicates that the C_1 concentration is reduced more quickly in the presence of benzene through the reaction of C_1 with benzene; therefore, the number of $C_2(d^3\Pi_g)$ molecules produced from C_1 is also reduced more quickly in the presence of benzene than in the absence of benzene.

Thus, all of the results suggest that we have observed the simplest growing process of a carbon cluster namely $2C_1 \rightarrow C_2$.

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