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Formation and Coalescence of Fullerene Ions from Direct Laser Vaporization

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A series of carbon cluster ions have been created by direct laser vaporization of elementary carbons and organic compounds with different structures and compositions. The mass spectra of the carbon cluster ions were recorded *in situ* by a time-of-flight mass spectrometer and the experimental results showed that the formation of fullerenes and their relative abundances are closely related to the surface structure of the sample. Under direct laser vaporization, the products from a perfect (0001) surface of graphite were mainly C_{60} and C_{70}. The surface perpendicular to the (0001) plane of graphite could not produce C_{60}, other fullerene ions or compounds containing six-membered aromatic carbon rings. The products of amorphous carbon and aromatic compounds included C_{60} and other fullerenes, among which those with a mass twice that of C_{60} were most abundant. Furthermore, C_{60} and C_{70} could also be aggregated from direct laser vaporization. Based on these experimental results, mechanism for formation of C_{60} and other fullerenes is suggested.

C_{60} has attracted extensive attention in the chemistry community,[1–7] but to a certain extent its formation mechanism is still a puzzle. Although C_{60} and other fullerenes are now commercially synthesized by arcing and other techniques,[8,9] C_{60} was first created by laser vaporization of graphite in the throat of a supersonic nozzle.[10] Recently, a coalescence reaction of C_{60} and C_{70} was carried out under similar conditions.[11,12,13] The relative abundance of C_{60} among carbon clusters and the aggregation of C_{60} were found to be strongly enhanced by increasing the density of the helium carrier gas[10] which suggests that C_{60} was mainly produced from carbon atoms or small fragments of graphite which were confined, 'cooked' and cooled by collisions of the buffer gas.[14,15,16] However, generation and aggregation of C_{60} and other fullerenes were later found to succeed from direct laser vaporization in high vacuum without the introduction of carrier gas.[17,18] Under these conditions aggregation of the species in the laser plasma should be rare and the mechanism of formation of carbon clusters might be much simpler. To understand the process and reveal the mechanism of C_{60} formation, a series of direct laser vaporization experiments were designed and carried out on a home-made apparatus. Various carbon-bearing samples, such as elementary carbons with different structures and polycyclic aromatic compounds, were ablated by a pulsed laser beam in high vacuum and their products were analysed by a time-of-flight (TOF) mass spectrometer.

Experimental

The experimental apparatus has been previously described in detail.[19] A vacuum of 10^{-6} Torr was maintained during the experiments performed under vacuum. The ion source for the TOF mass spectrometer was set up so that the sample was located 8 cm from the acceleration electrodes of the mass spectrometer. The vaporization laser beam passed through the acceleration zone perpendicular to the acceleration field. The laser generated plasma diffuses into the acceleration zone with the initial kinetic energy of the ions and the mass is determined by the flight time of the ions.

A pulsed laser beam of wavelength 532 nm and pulse width 7 ns was chosen for these experiments. Graphite, highly oriented pyrolytic graphite (HOPG), amorphous carbon, glassy carbon, C_{60}, C_{70}, and many aromatic compounds such as anthraquinone and purine were used as samples. Their vaporization products and relative abundance were recorded *in situ* by the TOF mass spectrometer. The scanning tunnelling microscopy (STM) images were taken using a home-built system with $I_t = 1$ nA and $V_{bias} = 100$ mV.

Results and Discussion

It is intriguing that very large clusters could be produced without the confinement of a buffer gas. Since buffer gas was not introduced during these experiments, the formation and distribution of the clusters could only be affected by the incident laser power density and the incident area on the sample surface. A general explanation is that the ablating laser beam focuses on a tiny area of the sample with very high power density so as to drill a hole in the sample. The hole may confine the laser plasma, in the same way that the helium flow in the throat of a supersonic nozzle does, and provides greater possibilities for aggregation reactions.[17] In our experiments, however, the laser beam was gently focussed, with a diameter of 3–5 mm on the sample surface, and its energy was generally adjusted in the range 15–30 mJ per pulse, so that the laser power density was not high enough to cause such a 'small-hole effect'. Unduly high laser-power density has been found to disfavour the generation of C_{60} and other fullerenes. Hence, carbon clusters generated from direct laser vaporization should be directly converted from the fragments of the sample and their structures should be related to the original structure of the sample.

Fullerenes generated from Six-membered Aromatic Carbon Rings

C_{60} and other fullerenes are produced almost exclusively from graphite. Evidently, there is some relationship between the sheet of graphite (hexagonal structure) and the cages of fullerenes which are composed of six-membered and five-membered rings. If a sample which does not contain aromatic carbon rings is directly vaporized by a pulsed laser beam, could it produce fullerenes?

Glassy carbon consists of long carbon microfibrils that twist, bend, bind and randomly orient and which contain no six-membered-rings. The positive-ion mass spectrum from glassy carbon [Fig. 1(*a*)] shows that no C_{60}^+ or C_n^+ with $n > 16$ was produced from direct laser vaporization. The carbon cluster anions observed were somewhat larger, but

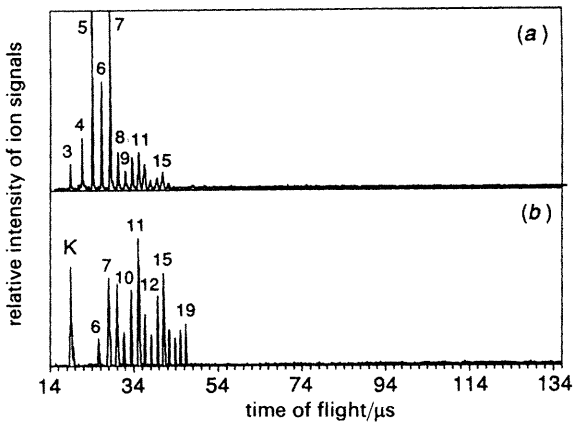

Fig. 1 TOF mass spectra of carbon cluster cations produced by direct laser ablation of (*a*) glassy carbon and (*b*) perpendicularly orientated HOPG (perpendicular to hexagonal sheet) using a 532 nm, 15 mJ per pulse laser beam focussed onto 0.2 cm^2 of sample surface

their sizes did not exceed 30 carbon atoms. The highly oriented pyrolytic graphite (HOPG) can be considered as a single crystal of graphite and its (0001) plane is a sheet composed of six-membered rings. If the HOPG was oriented with its (0001) plane perpendicular to the incident laser beam no fullerene ions were observed in the mass spectrum [Fig. 1(*b*)]. During the experiments, the vaporization laser energy was scanned from 10 to 60 mJ and the vaporization area on the sample was adjusted from 0.5 to 5 mm, but all carbon cluster ions recorded had low masses and very low signal intensities, even after extended laser ablation.

Amorphous carbon is composed of mainly microcrystals of graphite and so consists of six-membered aromatic rings. The negative ion mass spectrum taken from the sample [Fig. 2(*a*)] reveals a 'forbidden zone' in the intermediate mass region which corresponds to carbon clusters with planar ring configuration. They were unstable owing to an excessive number of dangling bonds around the rings. The smaller carbon clusters, up to a few tens of atoms, are considered to be linear chains and the larger clusters are C_{60} and other fullerenes. The intensities of the larger clusters exhibit a normal distribution with a maximum at C_{112}. Fig. 2(*b*) is the mass spectrum from anthraquinone ($C_{14}H_8O_2$). Although anthraquinone consists of hydrogen and oxygen atoms in addition to six-membered carbon rings, its mass spectrum is extremely similar to that of amorphous carbon in the higher mass section. Fullerenes are the unique products in the higher mass ions and oxygen is only included in the lower mass ions.

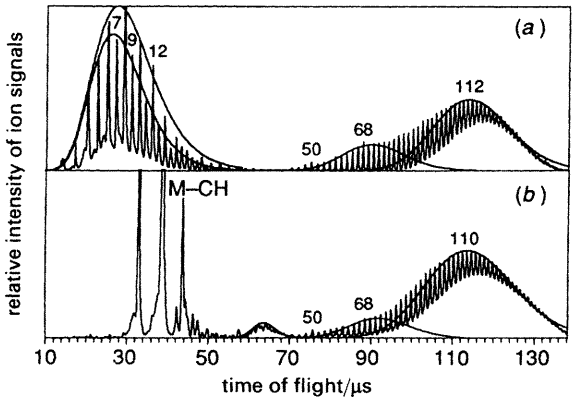

Fig. 2 TOF mass spectra of carbon cluster anions produced from direct laser vaporization (532 nm, 15 mJ per pulse focussed onto 0.2 cm^2 area) of (*a*) amorphous carbon (coal) and (*b*) anthraquinone. M – CH represents the ion formed by dissociation of a CH group from molecular anthraquinone.

Aromatic compounds without six-membered carbon rings such as purine, however, produced no fullerences or other large carbon clusters by direct laser vaporization using the same experimental parameters.[20]

From the above experimental results, it can be concluded that, at least under the conditions of direct laser vaporization, fullerenes are more probably generated from aromatic carbon rings instead of C_2 units or carbon atoms. Similar mechanisms have been found by Taylor *et al.* for the formation of fullerenes from naphthalene in an argon atmosphere.[21] The normal distributions of C_{60} and other fullerenes in Fig. 2(*a*) and Fig. 2(*b*) imply that these fullerenes have similar structural configurations and stabilities according to the statistical model of laser-generated clusters.[22,23] Because C_{60}^- is no more stable than other fullerene anions, most of those fullerenes, including C_{60} itself, may not have the spherical cage structure if they are generated from samples with unconjugated aromatic rings, such as coal and polycyclic aromatic compounds, and by direct laser vaporization.

Cage Fullerenes generated from HOPG

The mass spectra shown in Fig. 3 were recorded over different ablation periods on the same HOPG sample orienteted with (0001) plane perpendicular to the laser beam. Fig. 3(*a*) is the mass spectrum taken after a short period of laser ablation. The mass peak of C_{60} is remarkably high and that the peak due to C_{70} is the next most abundant. Carbon clusters with mass less than C_{54} or greater than C_{84} were not observed. However, distribution of the products changed with different ablation periods and Fig. 3(*b*) and (*c*) are the mass spectra from the same sample taken after *ca.* 1500 and 3000 laser pulses. Note that besides the peaks of C_{60} and C_{70}, the peaks of larger fullerenes appear, and their abundances grow with time of ablation. Their distribution is very similar to that in Fig. 2. The STM images (Fig. 4) show that the HOPG surface became rough, and platforms and steps of various sizes formed after laser ablation. Some platforms that contained enough six-membered rings could also generate

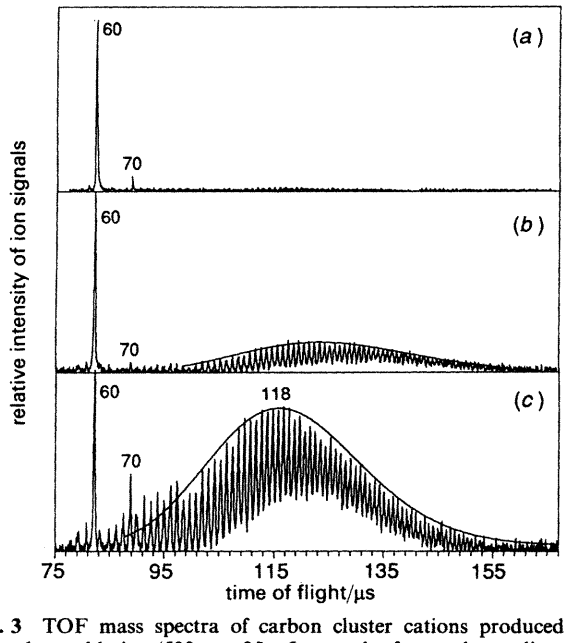

Fig. 3 TOF mass spectra of carbon cluster cations produced by direct laser ablation (532 nm, 25 mJ per pulse focussed to a diameter of 4 mm) of the (0001) plane of HOPG after *ca.* (*a*) 200, (*b*) 1500 and (*c*) 3000 laser shots. Mass spectra were measured during continuous laser vaporization of the same sample and the laser shots were counted from the beginning of the experiment.

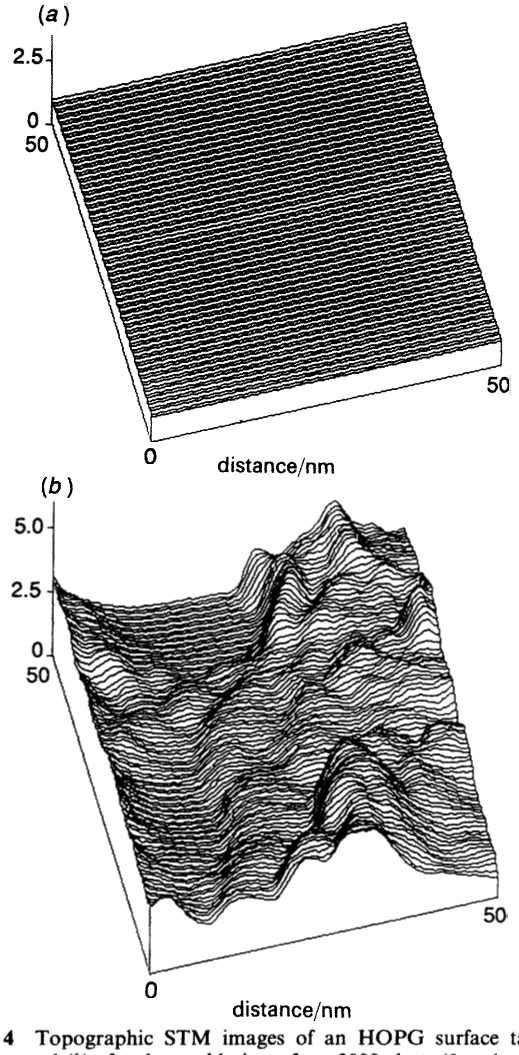

Fig. 4 Topographic STM images of an HOPG surface taken (*a*) before and (*b*) after laser ablation of *ca.* 3000 shots (I_t = 1 nA, V_b = 100 mV). The images show that the sample surface was roughened by the ablation.

C_{60} and C_{70}. However, most of the platforms did not contain enough six-membered rings, and like the amorphous carbon and some polycyclic aromatic compounds, they formed the larger fullerenes.

An 'ordinary' graphite is polycrystalline, so that the exposed hexagonal sheets on the surface are of different sizes. The mass spectrum generated from ordinary graphite (Fig. 5)

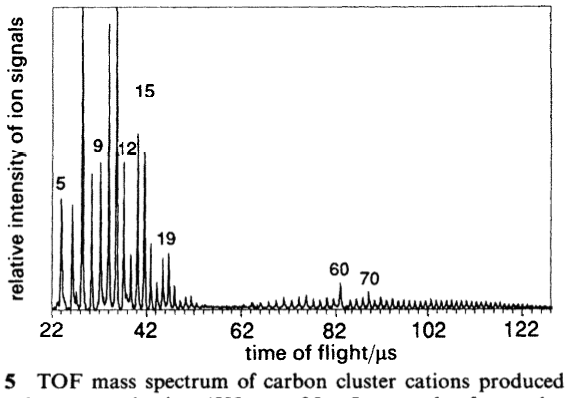

Fig. 5 TOF mass spectrum of carbon cluster cations produced by direct laser vaporization (532 nm, 25 mJ per pulse focussed to a diameter of 4 mm) of a polycrystalline graphite

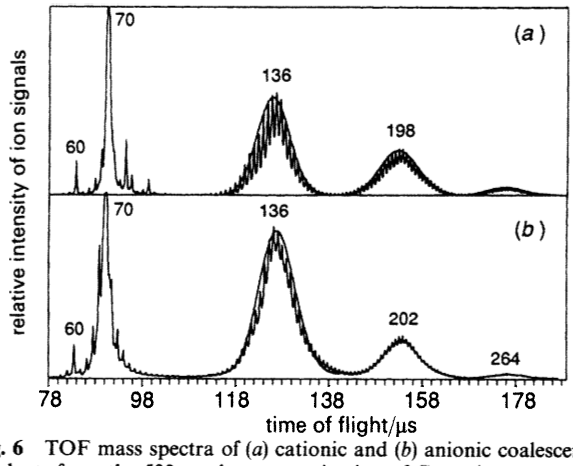

Fig. 6 TOF mass spectra of (*a*) cationic and (*b*) anionic coalescence products from the 532 nm laser vaporization of C_{70} using no carrier gas. The laser flux is *ca.* 100 mJ cm^{-2}.

shows that the relative abundances of C_{60} and C_{70} are higher than that of other fullerenes but not as high as for HOPG [Fig. 3(*a*)]. In addition, carbon clusters of different sizes can be observed, and relative abundances of carbon clusters with low masses are higher than those of fullerenes.

The C_{60} and C_{70} observed in ref. 10 are known to have cage structures and C_{60} exhibits a very high signal intensity owing to the icosahedral symmetry of its soccer ball structure. C_{60} and other fullerenes produced from the (0001) plane of HOPG obviously have this structure, because of their remarkable signal intensity, especially when the HOPG surface is perfect. Thus direct laser vaporization, buckminsterfullerene and other fullerenes with closed-sphere structure are probably formed from a self-assembling process by a 'rolling up' of the graphite sheet; fullerenes could also be produced from the smaller or separate hexagons, but their sizes are generally larger than 60 and their size distribution can be described by a log-normal curve.

Aggregation of Fullerenes

Fig. 6 shows the mass spectra of both positive and negative ions from C_{70}. The sizes and the abundances of aggregates are greater than those of their fragments. The most abundant coalescence products are not those whose sizes are multiples

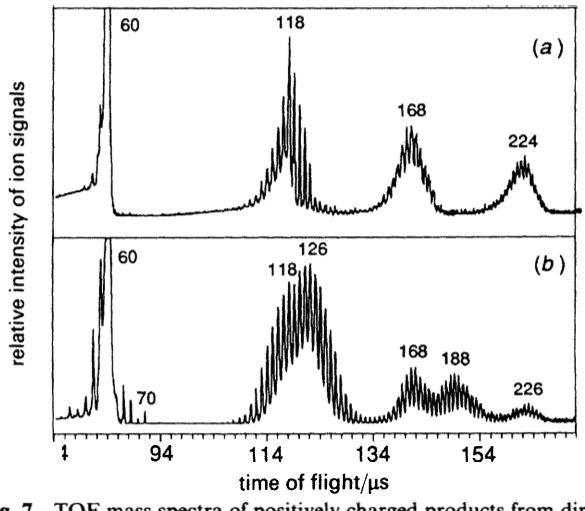

Fig. 7 TOF mass spectra of positively charged products from direct laser ablation of C_{60} with a laser of flux (*a*) 100 mJ cm^{-2} and (*b*) *ca.* 1 J cm^{-2}

of C_{60} or C_{70}, but those of $60n - 2m$ and $70n - 2m$. For example, the dimer with the highest signal intensity is C_{136}^+ for C_{70} or C_{118}^+ for C_{60}. In addition, the relative abundances of aggregates can vary with the experimental conditions, such as laser power density. For example, in Fig. 7(*b*), two humps can be found for the trimers of C_{60} when the vaporization-laser energy density is near 1 J cm^{-2}, but the size distribution of the coalescence products is still very smooth.

The previous research on fullerene coalescence by direct laser ablation has indicated that these coalescence products are still single-shell fullerenes.[13,24] From the size distribution of the aggregates shown in the mass spectra above, it can be seen that their relative abundances are in accordance with the normal distribution, indicating their similar structural configurations and stabilities.

Summary

From direct laser vaporization, carbon clusters of different sizes, including C_{60} and other fullerenes, could be produced without using a confining gas. Precursors with selected surface structures and compositions were used and their formation products and mechanisms studied by direct laser vaporization. C_{60} and other fullerenes with closed-sphere structure would be more probably produced from the self-assembly of the graphite sheet. Smaller fragments of six-membered carbon rings can also form fullerenes, but with relatively larger sizes. Samples without aromatic carbon rings would not be able to generate fullerenes. Finally, C_{60} or C_{70} can also aggregate to form larger fullerenes.

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