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Reactions of excited fullerenes C_{60} and C_{70} studied by mass spectrometry

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The transformation of the mass spectra of the laser-desorbed C_{60} and C_{70} samples with a successive increase in the laser power, resulting in an increase in the degree of excitation of C_{60} (C_{70}) and in the number of the particles in the laser plume, was studied. Unusual metastable clusters ($C_{60} + C_2$) and ($C_{70} + C_2$) are formed even at a minimum laser power and begin to dissociate after ~0.5 μs following a short (3 ns) laser pulse. An increase in the laser power results in the appearance of peaks of metastable clusters C_{62} (C_{72}) with the statistically normal lifetime without a delay of dissociation. A further increase in the laser power produces metastable clusters C_{60k-2n} and C_{70k-2n} ($k = 2, 3$) formed without a lag from the dimers and trimers of C_{60} (C_{70}) by the ejection of a number of C_2 required for the stabilization of the C_2 molecules. The peak of C_{70} appears simultaneously with the appearance of the $(C_{60})_{2-2n}$ peaks upon the laser desorption of pure C_{60}. These findings provide evidence for the growth of the excited fullerene clusters by coalescence and subsequent stabilization due to the ejection of a small fragment rather than by the implantation of C_2 into the fullerene framework. This mechanism of cluster growth should be taken into consideration in modeling fullerene formation in an electric arc reactor, because the clusters formed under these conditions have a substantial excess internal energy.

Key words: fullerene, mass spectrometry, "hot" fullerenes, coalescence.

The theoretical and experimental studies of the mechanism of formation of fullerenes and nanotubes by carbon vapor condensation**[1—13]** did not pay proper attention to the nonequilibrium vibrational excitation of products formed by recombination. At the same time, each act of recombination of carbon particles results in the evolution of an energy, which is initially distributed over vibrational degrees of freedom of the product and then should be anyhow ejected to stabilize the latter. The complete vibrational-translatory equilibrium of recombination products is impossible under the conditions when the inert gas pressure in the recombination zone is comparable with the carbon vapor pressure. Therefore, vibrationally excited particles are involved in recombination. The laws of migration of an excess vibrational energy over the internal degrees of freedom and its transformation and relaxation determine the lifetime of the intermediate metastable particles formed and channels of their dissociation and recombination. Therefore, if the latter is ignored, the mechanisms of formation and growth of carbon clusters cannot be described correctly.

It is often assumed in the theoretical consideration of the growth mechanism of the fullerene clusters that the cluster containing at least 30 atoms, including the formation of C_{70} from C_{60}, grows due to the consecutive addition of small molecules**[11—13]** (C_2 **[13]** and C_3 **[11,12]** are considered as such particles). Accepting that in the zone of particle condensation the C_{60} molecules have an excess internal energy, the possibility of stabilization of the C_{62} cluster formed is determined by the probability of vibrational-translatory relaxation of this particle on the helium atoms during its lifetime. In order to stabilize this cluster, one has to discharge at least the energy of preliminary excitation and at least one quantum of the vibrational energy of the C_{62} cluster formed. The total released energy can be high. Therefore, in the analysis of the growth mechanism of the carbon clusters under these conditions the estimation of the lifetime of strongly excited clusters is significant.

One can model this stage of fullerene synthesis in both an electric arc and a laser reactor in which the first stable but still excited fullerene C^*_{60} or C^*_{70} is already formed in

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the condensation zone of carbon clusters by the laser desorption and ionization of the C_{60} or C_{70} sample in a time-of-flight mass spectrometer. Fullerene molecules can be obtained in different excited states, and the fraction of the C_2 molecules formed in the reaction $C^*_k = C_{k-2} + C_2$ can be controlled by increasing the laser power. The molecules and ions formed during the laser plume expansion collide with each other to form metastable clusters. The degree of excitation of fullerenes entering the reaction $C^*_k + C_2$ can be estimated from the number of fragments observed (C_{k-2}, C_{k-4}, C_{k-6}, ...). The ions of excited fullerene-like clusters C_k, C_{k-2}, C_{k-4}, and C_{k-6} formed under these conditions dissociate during acceleration,[14—16] resulting in the appearance of the characteristic metastable peaks with a long tail toward higher masses. The curve of this decay is directly related to the lifetime of the clusters.

In this work, we systematically studied metastable excited clusters formed due to the collisions of the $C_{60}{}^+$ ($C_{70}{}^+$) ions with "hot" C_{60} (C_{70}) molecules and products of their dissociation (mainly, C_2 molecules) at different degrees of excitation of the starting fullerene molecules. It was found that the low excitation of C_{60} and C_{70} produces unusual metastable clusters $(C_k + C_x)^+$, whose decay kinetics differs from that of the excited closed fullerene shells. It was also established that the excited dimers formed can be stabilized by the ejection of both one or several small fragments (C_2, C_4, ...) and C_{60} or C_{70}.

Experimental

Fullerenes were obtained in an electric arc reactor followed by chromatographic separation. A C_{60} sample was purified by sublimation (purity >99%) to remove admixtures of solvents. The purity of C_{70} was 98% (the sample contained heavier fullerenes) but C_{60} was found in this sample neither by mass spectrometry, nor spectrophotometrically.

A time-of-flight mass spectrometer with laser desorption (Finigan) was used. The laser pulse duration (337 nm) was 3 ns, and the maximum pulse energy was 250 μJ (this energy usually was 100 μJ, which corresponded to an energy density of 6 J cm^{-2} in the spot of the focused laser radiation). The beam was focused onto a mirror metallic target to the spot ~40 μm in diameter.

The samples were deposited on the target from a solution (the fullerene concentration was 1 mg mL^{-1}) as a ~2 μL droplet followed by solvent evaporation. The solvents were CS_2, C_6H_6 (C_6D_6), or toluene. The total laser desorption of the layer of C_{60} or C_{70} microcrystals in a chosen point of the crystal spot was achieved at three to four laser pulses. Each pulse resulted in the desorption of 10^{-9} g (~10^{-12} mol) of C_{60}. Accepting that the temperature of this gas is 3000 K,[17] then after 100 ns the diameter of the expanding gas plume would be ~80 μm and the volume of the plume of neutral particles would be ~$1 \cdot 10^{-10}$ L at an average pressure in this layer of ~1 atm and an average free path of a C_{60} molecule of ~$1.5 \cdot 10^{-2}$ μm.

The laser plume was expanded directly in the acceleration zone of the mass spectrometer: the accelerating voltage (6.2 kV) was applied between the target and an accelerating electrode. The electric field (if it was switched on without a delay relative to the laser pulse) accelerates ions to an energy of ~62 eV to ions after 100 ns, and the ions leave the plume zone where collisions are possible. Depending on the laser energy and taking into account errors of the estimates, the ions could experience from 10 to 1000 collisions. After the acceleration zone, the ions got into the field-free zone. The free flight time in this zone is directly related to the velocity gained by the ion in the accelerating zone and depends on its mass. The acceleration time of the C_{60} ion was ~1 μs, and the free flight time was ~100 or 200 μs, depending on the operating mode of the mass spectrometer (the linear mode or the operation with an electrostatic reflector). The numeralization system of the ion current of the instrument operated with a period of 5 ns.

Experiments are usually carried out at a minimum laser power, because in this case the destruction of the analyte substance and scatter of velocities of the ions formed are minimum. In our experiments, the laser energy was sequentially increased and that could decrease the resolution ability of the mass spectrometer due to an increase in the scatter of velocities of outgoing particles at laser desorption.

The initial scatter of the energy values of the ions formed in the laser plume can reach 5—10 eV in the standard operating mode. This results in the 0.2% scatter in the velocity gained by the ion at this accelerating voltage, which causes the broadening of the detected peaks toward lower masses. Two methods for space focusing of ions were used to eliminate this phenomenon. The controlled delay of accelerating voltage switch on relative to the laser pulse was used in the direct flight mode without a reflector. In the operating mode with a reflector, the field is switched on without a delay, and the ion scatter over velocities was compensated by the different depths of ion injection into the field of the electrostatic reflector. Each method provided a fourfold decrease in the peak width, and the final really observed instrumental resolution was 1000—2000 (according to the passport data, 2000).

For the maximum laser power used in experiments, the excitation energy of the fullerene molecules achieved 40 eV (this follows from the number of observed fragments). Since the excitation of the fullerene molecules by the laser radiation with a given wavelength occurs due to the multiphoton absorption of the radiation rather than by equilibrium plasma heating, 40 eV can be considered the upper boundary of the possible translatory temperature of the ions. For this energy, the peak broadening toward smaller masses without focusing could achieve 12 m.u. It was experimentally shown that no substantial peak broadening was achieved with an increase in the laser energy in all operating modes of the spectrometer, *i.e.*, either the methods used for focusing are sufficiently efficient, or the translatory temperature of particles in the plume is much lower than the estimate presented above.

During laser plume expansion, the particles collide to form metastable clusters, ions of which can decay during acceleration. As a result, peaks of metastable clusters appear in the mass spectrum. The longer time of ion staying in the metastable cluster, the longer time of its acceleration at the exit of the acceleration zone and, correspondingly, the later it is detected by the ion detector. As a result, the detected peak is broadened toward greater masses.

The ion of a strongly excited molecule of the initial fullerene, as the excited ion of its fragment, can also decompose during acceleration. An increase in the laser energy in the plume results in the appearance of ions with the energy storage sufficient for the ejection of one or several C_2 particles. This results in the appearance of the C_{60-2n} and C_{70-2n} peaks broadened toward greater masses. The decay curve of such a metastable cluster is related to the half-life of this cluster. The peaks of the formed fragments C_{k-2}, C_{k-4}, C_{k-6}, *etc.* look like metastable, because the internal energy of their parent cluster is sufficient for decomposition.

When a cluster, for example, $C_{60} + C_2$, decomposes before the end of the acceleration period, the remaining charged C_{60}^+ ion is detected between the masses of C_{60} and C_{62}. If the C_{62} cluster would live until the end of the acceleration period and decomposes already in free flight, the C_{62} mass is detected, although, in fact, the C_{60}^+ ion gets onto the detector. The wrong mass detection can be recognized when the operating mode of the mass spectrometer is switched from the linear mode to the mode with reflection. In this case, the energy of the C_{60} ions, which are formed during free flight and have the velocity corresponding to that of C_{62}, is lower than the energy of the real C_{62} ions due to the smaller mass. The depth of their injection into the electrostatic field of the mirror is smaller and, as a result, the peak of these C_{60} ions shifts toward smaller masses.

Results and Discussion

The transformation of the mass spectrum of C_{60} in the reflection mode is shown in Fig. 1. The mass spectrum obtained at the minimum laser energy (Fig. 1, *a*) distinctly exhibits three small peaks, which might correspond to the masses 730, 731, and 732. These peaks are present (but are not discussed) in the mass spectra described previously.[18,19]

The spectra obtained for the same sample but at the higher (by 8%) laser energy (Fig. 1, *b*) contains signs of C_{60} destruction as a small peak of C_{58} broadened toward greater masses, whereas the isotope structure of C_{60} is diffused and the rise at *m/z* 730—732 increases markedly. When the laser energy increases additionally by 10% (Fig. 1, *c*), broadened peaks of the metastable C_{58} and C_{56} clusters appear and the metastable character of the main C_{60} peak is designated. Nevertheless, the strongly grown peak in the region of *m/z* 730 is distinctly seen on the background of the general exponential decay of the main peak. The appearance of the peak at *m/z* 730 could be explained by the reactions of the fullerene molecules with solvent fragments, resulting in the addition of 10—11 hydrogen atoms to C_{60} or by the decomposition of the fullerene complexes with the solvent molecule. However, the replacement of toluene by deuterated benzene or CS_2 and purification of C_{60} by sublimation *in vacuo* had no effect on this peak. When the instrument is switched to the direct flight mode, the peak shifts toward greater masses, *i.e.*, it is caused by the metastable complex.

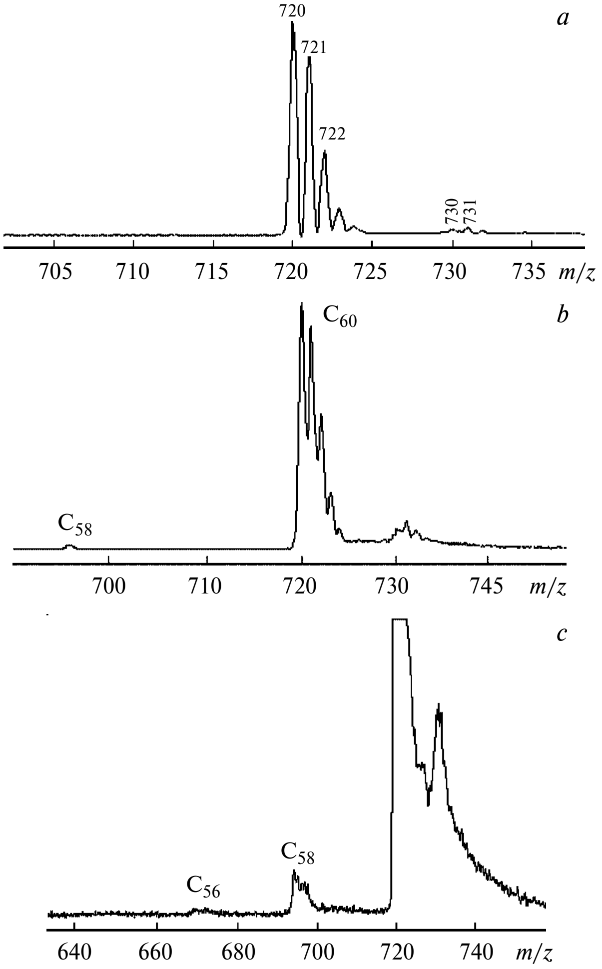

Fig. 1. Change in the shape of the mass spectrum of C_{60} with an increase in the laser pulse power: *a*, minimum power; *b*, 8% higher than the minimum power; and *c*, 18% higher than the minimum power.

At a still higher energy of the desorbing laser pulse, the fraction of the decomposed C_{60} molecules increases multiply, and rather intense peaks of the ions C_{58}, C_{56}, *etc.* appear (Fig. 2). The peaks of the products of partial decomposition of the C_{120} dimer cluster (*m/z* 1440, 1416, 1392, *etc.*) are also observed. The formation of the dimers upon laser desorption of fullerenes has been observed previously.[19,20] Coalescence has been studied earlier.[21—23] The study of the structure of the clusters using the ion mobility[24,25] has shown that the clusters with masses smaller than that of the full dimer (C_{120-2n}, n = 1, 2, 3, ...)... are closed, spherical shells.

The number of peaks of the products of dimer decomposition approximately corresponds to the doubled number of the peaks observed for the decomposition of the initial fullerene and is ~1.5-fold lower than the number of the peaks of the trimer (see Fig. 2). This indicates that the excess energy of the hot particles, which is quite sufficient

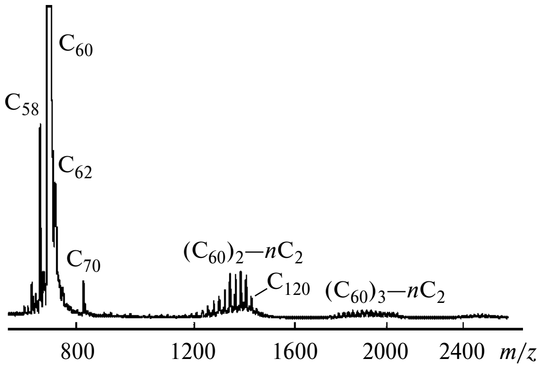

Fig. 2. Appearance of peaks of the dimers and trimers of C_{60} (m/z 1440, 1416, 1392).

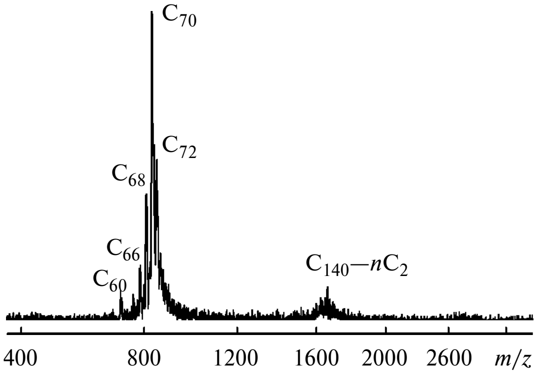

Fig. 4. Appearance of the first signs of formation of the dimers of C_{70}. The substantial peak of C_{72} appeared, and the peak of C_{68} increased strongly.

for their decomposition, does not prevent their coalescence; their overall internal energy can completely be transformed into the excitation energy of the dimer or trimer formed. In addition, the peak of C_{70}, which was absent in the spectrum of the initial sample, is distinctly seen. The presence of this peak, along with the C_{62} peak, at the anomalously high C_{58} peak indicates that the dimer can decompose to fragments almost equal in mass.

The laser desorption of C_{70} exhibits the same specific feature at *m/z* 851—853 as that for C_{60} at *m/z* 730—732. The mass spectrum obtained for the laser energy, at which the C_{70} molecules are already decomposed but the dimers are not formed yet, is presented in Fig. 3. The rise near *m/z* 852 and the peak of C_{60}, the height of which is greater than it should be expected from a decrease in the heights of the peaks in the series C_{68}, C_{66}, C_{64}, and C_{62}, are observed. No specific features are observed in the region of *m/z* 731.

At the laser energy corresponding to the appearance of the first signs of dimer formation, the peak at *m/z* 852 and the C_{60} peak increase (Fig. 4).

Since the metastable $C^*_{60(70)-2n}$ clusters formed upon the multiphoton laser excitation of fullerenes are known to be closed spherical shells,[14—16] we can conclude that the shape of the peaks observed for C_{k-2}, C_{k-4}, C_{k-6}, ... (k = 60, 70) reflects the decay kinetics of the excited spherical shells. The front edge of these peaks strictly corresponds to the masses of C_{k-2n}, *i.e.*, the excited "parent" begins to decay immediately after a laser pulse or even during irradiation, without a delay. The decay curve reflects the kinetics of decreasing concentration of these excited particles. A similar deduction is also valid for the products of decomposition of the dimers and trimers, which are also closed shells. Since the positions of these peaks also exactly correspond to their masses, one can assert that the excitation of the initial fullerenes and their coalescence to dimers and even trimers occur during within 40—50 ns (in the instrument used, 1 μs corresponds to the range of 24 m.u.), after which the metastable complexes immediately begin to decompose with some half-life. The decrease in the C_{k-2}, C_{k-4}, and C_{k-6} peaks corresponds to approximately 200—600 ns (see Fig. 3). Thus, the constant of the decay time of these clusters is one—two orders of magnitude higher than the laser pulse duration. Excitation of all the particles occurs during the laser pulse (3 ns) and is completed with the end of the pulse. These excited particles have time to collide and form dimers and trimers, and only after this all excited particles are stabilized with a higher life time by the successive ejection of C_2 or several fragments (C_2, C_4, C_6, *etc.*). It should be noted that when the C_{k-4} peak appears, the "tail" of the large C_{60} and C_{70} peaks extends further than *m/z* 744 (see Figs. 1, *c* and 3), indicating the formation of metastable complexes heavier than C_{62}, namely, C_{64}. This implies that the C_4 particles appear in the plume and, hence, C_{k-4} can be formed either due to the consecutive ejection of C_2 during irradiation or also by the elimination of C_4.

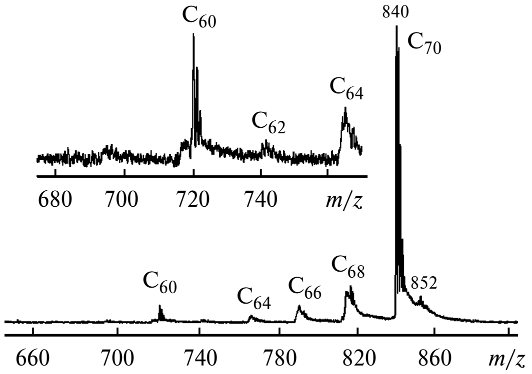

Fig. 3. Formation of C_{60} from the C_{70} molecules. The laser power is insufficient for a remarkable formation of the dimers. The increased pattern of the peak of C_{60} is shown in the insert.

Thus, the results obtained are indicative of the following mechanism. A small portion of the starting fullerenes gains the necessary energy under irradiation and ejects the C_2 particles. A smaller portion ejects the C_4 particles at a sufficient radiation power. Perhaps, a small portion of the formed C_{k-2} has time to absorb photons and again ejects the C_2 particles, *etc*. All formed particles undergo collisions in the laser plume to form various metastable coalescence products. The peaks corresponding to the full-mass dimers are comparatively small, although the number of nondecomposed but excited C_{60} and C_{70} particles in the plume is much greater than the number of the fragment molecules. This means that the coalesced excited C_{60} and C_{70} molecules can also produce dimers, which are rapidly stabilized by the ejection of at least one C_2 particle. Most likely, C_4 can also be ejected in this case, because the peak with *m/z* 1392 (C_{120-4}) shows the highest intensity. The main reason for the decomposition of the coalescence products is the excess internal energy rather than the laser radiation, because the dimers observed were not irradiated and were formed already after the end of the laser pulse.

The peaks of the filial C_{60} and C_{70} particles formed from the excited initial fullerene C_{70} and excited dimer C_{120}, respectively, have no long tail and, hence, their formation is not delayed in time. Figure 3 clearly exhibits the isotope structure of the C_{60} peak, which is much higher than the adjacent peaks of C_{62} and the weak peak of C_{58} at *m/z* 696. This indicates that at a sufficient laser radiation density the C_{10} fragment is singly ejected without any half-life (otherwise, the isotope structure would be diffused). The pedestal of this peak is likely related to the cascade decomposition of the C_{70} molecule.

Let us consider the shape of the peaks of the initial fullerenes C_{60} and C_{70} in more detail, namely, their specific features in the regions of *m/z* 731 and 851. The delayed signal after the peak of the initial fullerene can be explained only by the formation of metastable clusters due to collisions of the ions with the fullerene molecules and their fragments. At a low laser energy, the neutral reactant of this ion-molecular reaction can be either "hot" fullerene molecules (because they are present in the largest amount), or active particles C_2. Therefore, in this case, the $C_k^+ + C_2$ or $C_k^+ + C_k$ clusters decompose, which results in the appearance of peaks in the regions of *m/z* 731 and 851.

Thus, the unusual clusters are formed at a low excitation energy. When the mass spectrometer operates in the reflection mode, the peaks of these clusters lie at *m/z* 731 and 851 and look like completely isolated. When the mass spectrometer is switched to the direct flight mode, these peaks shift toward *m/z* 736 and 856, and the distance between them increases. It can be concluded that this unusual cluster does not decompose at all during approximately the half an acceleration period. Naturally, its position on the mass scale depends on the specific features of a particular instrument, the distance between the target and the accelerating electrode, and the voltage at this electrode. This behavior of the metastable cluster can seem surprising. After coalescence of the collided particles, the cluster possesses an internal energy, which is sufficient for inverse decomposition. Since the particles in the laser plume are separated in the mass spectrometer within ~10—100 ns, then the maximum number of the clusters is formed not later than 10—100 ns after the laser pulse. From this moment, if assuming the equiprobable decomposition, their number should decrease according to an exponential law. According to the peak shape, the clusters corresponding to the peaks of C_{k-2}, C_{k-4}, and C_{k-6}, which are obtained upon the excitation and decomposition of fullerenes, behave in precisely the same way. They begin to decompose immediately after the laser pulse.

The clusters in the regions of *m/z* 736 and 856 behave in a different way: the main part of the clusters begins to decompose after ~500 ns, which is much longer than the time of attainment of their maximum concentration. It is clear that these clusters require much longer time to concentrate the energy at the cleaved bonds than the normal spherically symmetric clusters. This can reasonably be explained assuming that the cluster decomposes precisely *via* the bonds that are formed at the moment of coalescence. As shown by the quantum-chemical simulation of the interaction of the C_{60} and C_2 particles, at the first step C_2 joins the fullerene framework at one end to form a "ball with fork structure." **[26]** This is the bond that is isolated and weaker. Since these peaks are observed at a low laser energy, the internal energy of this complex does not strongly exceed the dissociation energy of this bond. The concentration of the energy in the specific site demands much longer time than that for the spherically symmetric framework of fullerene, when all units of the framework are almost equivalent and any C_2 fragment can be ejected.

Thus, a possible mechanism of decomposition can be presented as follows. The chemisorption of the C_2 particle (or C_{60} molecule) on fullerene deforms its framework at the site of addition. The perturbation wave propagates along the framework. Therefore, at the first moment, the energy in the site of joint is already insufficient for inverse decomposition. The velocity of perturbation propagation is, first, finite and, second, different over different directions and types of vibrations. Therefore, different waves should pass multiply around the framework sphere until they are again gathered in the phase in the insertion site. Then the added particle is ejected. These discussions are also valid for the assumption about the coalescence of the C_k^+ ion with the "hot" fullerene molecule without formation of a unified spherical shell. In this case, the dumbbell-like structure also contains a specific site, in which an excess energy should be concentrated, and much more degrees of freedom. A noticeable growth in the peaks at *m/z* 731 (see Fig. 1, *b*) with the appearance of the C_{58} peak (this implies an increase in the content of the C_2 particles in the plume) confirms the first assumption about the formation of the unusual C_{60+2} complex. Thus, C_2 is not completely inserted into the fullerene framework even at the noticeable excitation of the C_{60} molecules (when some of them gain an energy of 10 eV necessary for the ejection of the C_2 particle).

When the energy of the reacting fullerene ion is high, the C_2 particle is completely inserted into the framework (or two spheres are completely coalesced), and then the spherical shell formed decomposes *via* the standard mechanism of statistical decomposition. However, even in this case, the peak at *m/z* 731 is clearly seen (see Fig. 1, *c*), *i.e.*, all bonds are not identical in a noticeable fraction of the metastable complexes formed, and many of them have a specific weak site. It can be concluded that a substantial internal energy excess is required for the irreversible insertion of the C_2 particles into the fullerene framework.

In Fig. 2, the C_{70} peak is seen and the C_{68} peak is not seen. This indicates that the channel of C_{70} formation from the C_{60} molecule by the successive addition of five C_2 particles is less probable than the formation of the C_{120} dimer followed by the formation of C_{70}.

Thus, the excited fullerene shells (as well as the dimers and excited C_{70} molecules) can be stabilized due to both the ejection of small particles C_2, C_4, C_6, *etc.* and decomposition with the formation of lighter stable fullerene C_{60} or C_{70}. Note that the possibility of coalescence of the hot fullerene shells followed by their decomposition has been assumed previously.[27]

The reactions of coalescence followed by decomposition to different fragments provide an efficient method of the growth of excited clusters, which does not require deactivation collisions with other particles. Such a stabilization of a cluster does not necessarily result in the complete discharge of the internal energy and, therefore, the nonequilibrium-high internal energy of the growing particles can retain for a long time during cluster growth. At the same time, the irreversible insertion of the C_2 particles into the fullerene framework needs a substantial internal energy excess. Therefore, the channel of C_{70} formation from the C_{60} molecule by the successive addition of five C_2 particles is less probable than the formation of the C_{120} dimer followed by decomposition with the formation of C_{70}.

This growth mechanism should be taken into account in models describing the synthesis of both fullerenes and single-wall nanotubes.

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