# REGULARITIES IN FULLERENE $C_{60}$ FRAGMENTATION ACCORDING TO LASER-DESORPTION MASS-SPECTROMETRIC AND QUANTUM CHEMICAL DATA

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Experimental and theoretical results concerning the regularities in the fullerene $C_{60}$ fragmentation are reported. The destruction of $C_{60}$ thermally deposited onto a silicon substrate is studied with the use of laser-desorption mass spectrometry and provided various values of laser radiation power. The intensity of $[C_{60}]^+$ ions in the mass spectrum is shown to increase linearly, when the laser radiation power grows from 30 to 70% of its maximum. At the same time, the relative degree of $C_{60}$ fragmentation first increases and then saturates at 50% of the laser power maximum. Two possible mechanisms of fullerene ionization are proposed. The electron structures of molecular, $C_{60-2n}$, and cationic, $[C_{60-2n}]^+$, fullerene forms, where the parameter $n = 0$ to 4 indicates the number of lost $C_2$ fragments, are calculated within the quantum chemistry method. The boundary molecular orbitals (EHOMO and ELUMO), adiabatic ionization potentials, and electron affinities are calculated.

## 1. Introduction

The laser desorption/ionization (LDI) technique in combination with a time-of-flight analyzer can be successfully applied to study the structure of carbon substances–in particular, fullerene $C_{60}$ and its derivatives–by analyzing the processes of their ionization and fragmentation. Moreover, this method allows new fullerene-like forms of carbon to be created, which were absent in the initial specimen. As was marked in work [1], there are the principal differences between the mass spectra obtained for different allotropic forms of carbon. As follows from the analysis of the mass spectra of graphite and diamond obtained by the method of post-ionic-source decay, their laser desorption/ionization does not give rise to the formation of particles with fullerene-like structures. This conclusion is connected with the observed tendency to the fragmentation of diamond and graphite evaporation products by means of the detachment of a neutral $C_3$ fragment, whereas fullerene $C_{60}$, when interacting with laser radiation, demonstrates the intense loss of neutral fragments $C_2$, which is typical of fullerene molecules only.

In work [2], it was shown that there is a threshold value of laser radiation power for fullerene $C_{60}$ deposited from a solution in toluene onto a polished silicon surface, at which the mass spectrum starts to reveal the ion $[C_{58}]^+$, the most intensive fragment of a fullerene molecular ion. In the same work, it was shown that an increase in the laser radiation power is accompanied by a monotonous increase in the relative intensity of ions-fragments characterized by the general formula $[C_{60-2n}]^+$, where $n$ varies from 1 to 4. Earlier, in experiments with the crossed beams of fullerene ions and electrons, a similar fragmentation of molecular ions was observed [3]. The authors of work [3], having analyzed the dependence of the transverse cross-section of molecular ion fragmentation, $[C_{60}]^+=[C_{58}]^++C_2$, on the electron energy made assumption that, if the energy of incident electrons is low enough (a few tens of electronvolts), the fragmentation of molecular ions can be a consequence of the plasmon resonance.

According to the observed mass spectra, fullerenes become fragmented in the course of LDI. This fragmentation can be regarded as a way to produce fullerenes with a defect structure, such as $C_{60-2n}$ with $n = 1$ to 4, the energy and the geometrical parameters of which differ from those for the initial molecules. It is a complicated task to make a complete description of energy parameters, structural factors, and the influence of defects on the formation of fullerene fragments with the corresponding composition on the basis of exclusively experimental data. Therefore, the obtained mass-spectrometric data are confronted below with the results of quantum chemical calculations.

## 2. Materials and Methods

In this work, we used a powder of fullerene $C_{60}$ (MER Corp., USA) with a purity grade of 99.5%. The method

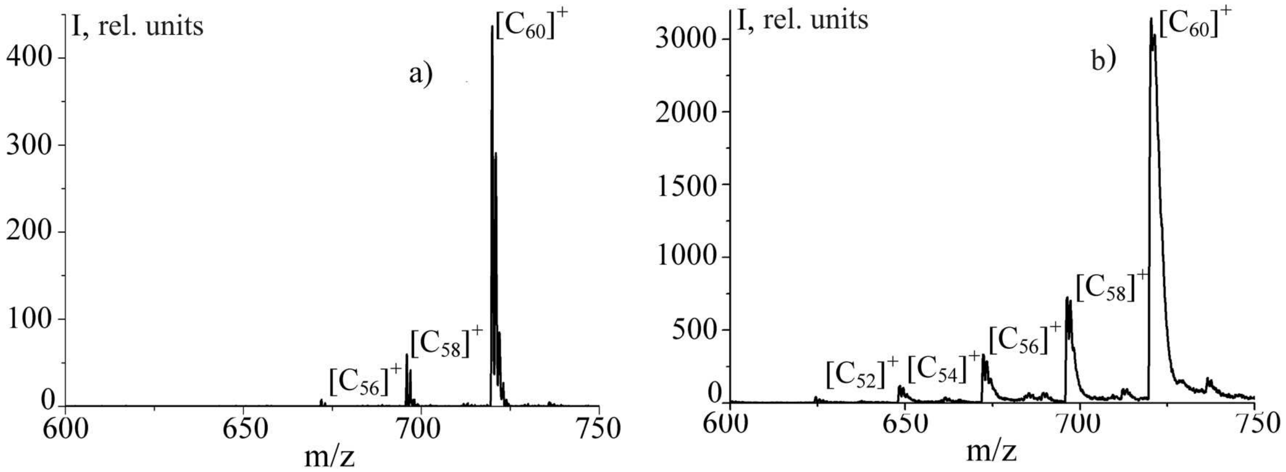

Fig. 1. LDI mass spectra of fullerene $C_{60}$ in the range of molecular masses of about 720 Da measured at two values of laser power: 30 (*a*) and 70% (*b*) of its maximum

of depositing the film onto a silicon (100) surface was described in work [4]. The measurements were carried out on a time-of-flight mass spectrometer Autoflex II LRF 20 (Bruker Daltonics) equipped with a pulse nitrogen laser with the wavelength $\lambda = 337$ nm and a pulse duration of 3 ns. The mass spectra presented in this work were recorded for positive ions in the linear mode of mass-spectrometric analysis and at the following device parameters: the number of pulses was 5, the pulse repetition rate was 10 Hz, and the delay time was 0 ns. The mass spectra were registered at various values of laser power ranging from 30 to 70% of its largest value with an increment by 10%. Quantum chemical calculations were carried out in the framework of the density functional theory, in the B3LYP approximation [5, 6] with the basis set 6-31G(d,p), and with the use of the software program USGAMESS [7].

## 3. Experimental Results and Their Discussion

In Figs. 1,*a* and *b*, the mass spectra of fullerene $C_{60}$ are exhibited for two values of laser power, 30 and 70%, respectively, of the maximum. The obtained mass spectra are characterized by the presence of fullerene molecular ion $[C_{60}]^+$. The figures demonstrate that its intensity increases with the laser power. The ionization energy for a fullerene molecule equals 7.6 eV, which is almost twice as much as the photon energy (3.68 eV). Therefore, we may assume that, in the course of molecular ion formation, two competing mechanisms of ionization take place.

One of them is connected with the single-photon absorption of laser radiation by a fullerene molecule and the subsequent tunneling of an electron into the conduction band of the substrate, on which the fullerene film is adsorbed. At the same time, the local heating of the surface allows the newly formed ion to overcome the electrostatic image forces to be desorbed from the surface in the form $[C_{60}]^+$, provided that the desorption rate exceeds the destruction one [8], i.e. when the magnitude of vibrational excitation of the generated ion is not sufficient for its fragmentation. In this case, the emergence of molecular ion $[C_{60}]^+$ in the mass spectrum seems to possess a threshold character, i.e. at a certain radiation power, followed by a subsequent monotonous growth of its intensity, provided that the fragmentation is absent. It is this type of the dependence of the molecular ion intensity on the laser power that was observed in our experiment at low radiation powers (see Fig. 2).

The other mechanism can be associated with the absorption of more than a simgle photon so that the electron structure of a $C_{60}$ molecule or ion falls within the range of its plasmon resonance [3]. This results in the ionization of the molecule, its desorption, and the probable subsequent fragmentation. The latter may take place owing to a vibrational excitation that arises in $[C_{60}]^+$ ion because of the difference in the equilibrium positions of carbon atomic nuclei in the initial molecule and the strongly excited molecular ion.

It follows from Fig. 3 that if the energy of laser radiation is high enough, the mass spectrum, besides the peak corresponding to the molecular ion $[C_{60}]^+$, contains also peaks associated with fragmentary ions $[C_{60-2n}]^+$, where the parameter $n = 1$ to 4 characterizes the degree of molecular ion fragmentation. Such a composition of

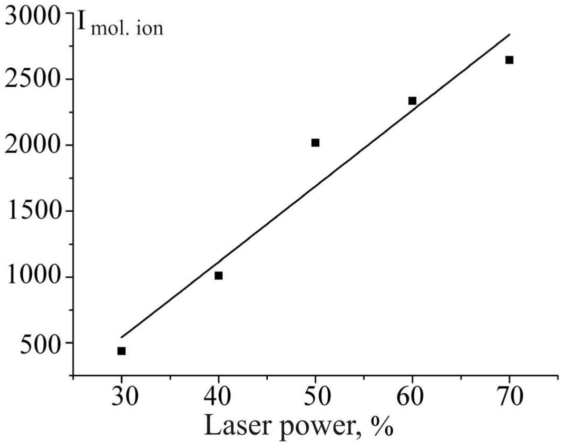

Fig. 2. Dependence of the intensity of a fullerene $C_{60}$ molecular ion on the laser power

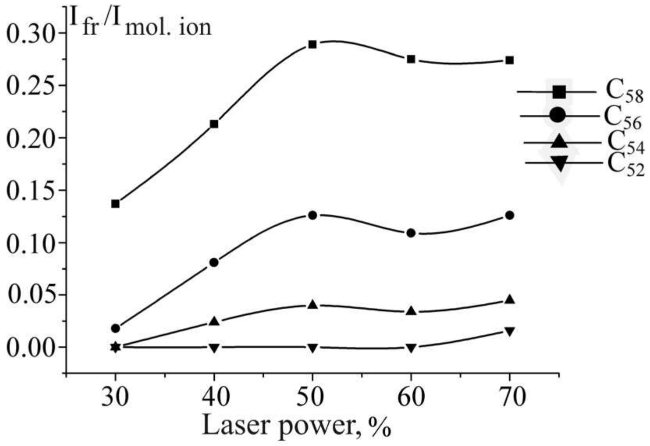

Fig. 3. Dependence of the relative intensity of fragmentary ions $[C_{58}]^+$, $[C_{56}]^+$, $[C_{54}]^+$, and $[C_{52}]^+$ on the laser power

the mass spectrum is always typical of the laser-induced ionization and fragmentation of fullerenes [10]. As one can see from Figs. 1,*a* and *b*, the number of fragmentary ions increases with the laser power from 30 to 70%. Moreover, as follows from Fig. 3, the more $C_2$ fragments are removed from the molecular ion, the higher laser power is required for $[C_{60-2n}]^+$ ions to emerge. The results of quantum chemical calculations, which are presented in the Table testify that the energy necessary for the detachment of $C_2$ from the molecular and subsequent fragmentary ions, $[C_{60-2n}]^+$, exceeds 10 eV in all cases, provided that the photon energy is 3.68 eV. Whence it follows that the most probable mechanism in the formation of the LDI mass spectrum of fragments is the multiphoton excitation of a molecule or ion of fullerene in the range of the plasmon resonance followed by the subsequent fragmentation.

The relative intensity of charged fragments first increases linearly with the laser power and then saturates in the power interval from 50 to 70%. In our opinion, this fact can testify that the molecular ions and fragments in a hot spot on the surfaces and over the target surface reach a quasistationary state in the indicated power interval. This dependence differs substantially from that obtained in work [2], where a monotonous increase, rather than a saturation of the relative intensity of fragmentary ions, was observed under the growing laser power. The observed discrepancy may stem from the difference between the structures of irradiated fullerene films, because they were formed using different methods. The absolute intensity of a fullerene molecular ion in work [2], as well as in our case, increased within the whole interval of variation of the laser power (see Fig. 2). The saturation typically observed for the relative intensity of fragments, when the laser power increases, can be supposedly explained by the fact that, from a certain moment, the growth of laser-induced ionic current begins to be governed by the geometrical extension of the hot spot over the substrate surface, provided that the physical conditions, under which $C_{60}$ molecules are ionized and ions are fragmented, are maintained constant.

## 4. Quantum Chemical Calculations

For the analysis of the fragmentation mechanism for a single-charged molecular ion of fullerene $C_{60}$ to be done in detail, we carried out quantum chemical calculations, the results of which are presented in Figs. 4 and 5 and also summarized in the Table.

It is known [11–13] that the reaction of $C_{60}$ fragmentation can run by the scheme

$$[C_{60}]^+ \rightarrow [C_{60-2n}]^+ + nC_2, (n = 1, 2, 3, 4)$$

in two ways: the removal of $C_2$ fragment from the 6-6 junction (bond 1-2 connecting two hexagonal rings, Fig. 4) and from the 5-6 junction (bond 2-3 connecting a hexagonal and a pentagonal ring, Fig. 4). Defects 4-8-4 in the former case and 5-7-5 in the latter one are formed. The results of calculations for the reaction

$$[C_{60}]^+ \rightarrow [C_{58}]^+ + C_2$$

show that the required energy is by 1.20 eV lower in the latter case (the removal of the $C_2$ fragment from the 5-6 junction and the formation of defect 5-7-5). The results obtained agree with both the literature data [6] and the fact that the 5-6 junction (bond 2-3, Fig. 4) is

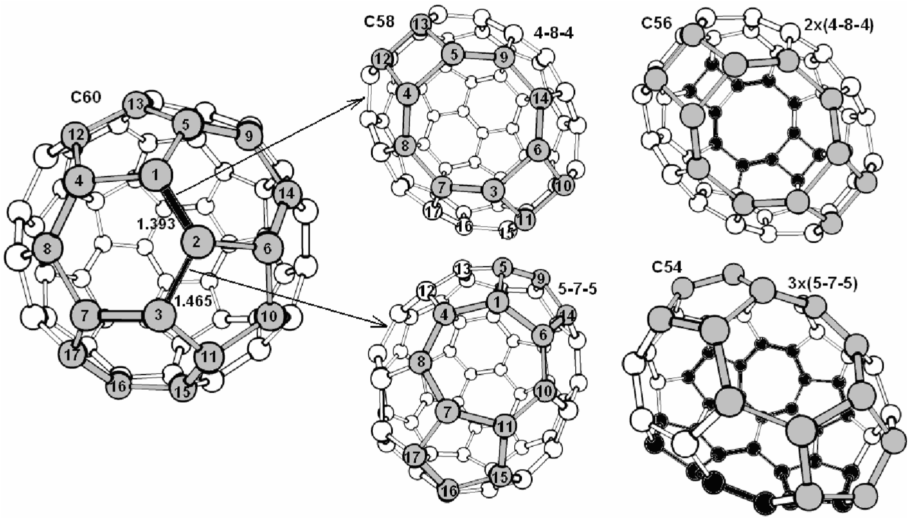

Fig. 4. Structures of defect fullerenes after the removal of $C_2$ fragments from 6-6 (bond 1-2, defect 4-8-4) and 5-6 (bond 2-3, defect 5-7-5) junctions

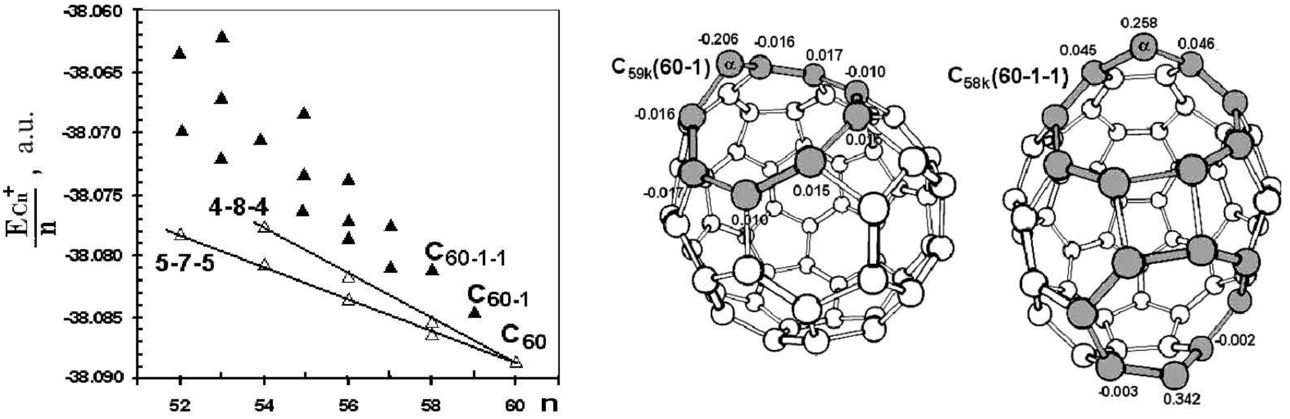

Fig. 5. Total binding energies $E_{C_n^+}$ of defect fullerene $C_{60}$ structures normalized to the number of carbon atoms $n$ ($a$) and the structures and spin densities at defects in single-charged cation clusters $C_{59}$(60-1) and $C_{58}$(60-1-1) ($b$)

**Table 1. Energy parameters of fragmentary ions $[C_{60-2n}]^+$**

| Defect type | $n$ | $E([C_n]^+)$, a.u. | $E([C_{n-2}]^+ + C_2)$, a.u. | $\Delta E_{C2}$, eV | $I_p$, eV | $E_a$, eV |
|---|---|---|---|---|---|---|
| | 60 | −2285.316191 | −2284.869506 | 12.16 | 7.42 | 2.20 |
| 4-8-4 | 58 | −2208.946997 | −2208.508949 | 11.92 | 6.94 | 2.91 |
| 4-8-4 | 56 | −2132.571277 | −2132.145456 | 11.59 | 6.64 | 3.85 |
| 5-7-5 | 58 | −2209.005346 | −2208.570367 | 11.84 | 6.78 | 2.88 |
| 5-7-5 | 56 | −2132.673980 | −2132.245814 | 11.65 | 6.57 | 3.46 |
| 5-7-5 | 54 | −2056.357003 | −2055.937697 | 11.41 | 6.40 | 3.89 |
| 5-7-5 | 52 | −1980.064956 | −1979.937367 | 11.20 | 6.02 | 4.48 |

The first column – type of defects; $n$ is the number of carbon atoms, $E$ the total energies of ions in the initial and dissociated states, $\Delta E$ energies of the $C_2$ adiabatic removal from the ion, $I_p$ the ionization potential, and $E_a$ the electron affinity longer and, hence, weaker than the 6-6 junction (bond 1-2, Fig. 4). In addition, this circumstance may testify that defects 5-7-5 rather than 4-8-4 play a more important role in the mechanism of defect formation in the course of $C_{60}$ fragmentation. The results of calculations also demonstrate (see Fig. 5,*a*) that, when the $C_2$ fragments are removed one-by-one from $[C_{60}]^+$, more stable defective structures are formed (hollow symbols) than those when one, two, three, or more carbon atoms are removed sequentially (solid symbols). Really, the values $\Delta E_{\mathrm{C}} = E_{[C_{59}]^+ + \mathrm{C}} - E_{[C_{60}]^+} = 13.72$ eV (Fig. 5,*b*), $\Delta E_{C_2} = E_{[C_{58}]^+ + C_2} - E_{[C_{60}]^+} = 12.16$ eV (Fig. 4), and $\Delta E_{2\mathrm{C}} = E_{[C_{58}]^+ + 2\mathrm{C}} - E_{[C_{60}]^+} = 23.53$ eV (Fig. 4, bond 2-3), which were calculated for the first time in the framework of the density functional approach, give us the basis to suggest that, for the fragmentation of $C_{60}$ formed under the action of laser radiation, thermodynamically more favorable is only the removal of $C_2$ fragment, because the removal of one carbon atom demands the energy expenses by 1.56 eV and the simultaneous removal of two carbon atoms from two different positions in $[C_{60}]^+$ by 8.81 eV higher. Moreover, as follows from Fig. 5,*b*, in defect structures $[C_{59}(60\text{-}1)]^+$ and $[C_{58}(609\text{-}1\text{-}1)]^+$, there appear carbon atoms $C_\alpha$ with noncompensated valences of $-0.206$ and 0.258, respectively, which evidences a high reactivity and instability of those states. The latter circumstance can play a substantial role at the aggregation of the excited fullerene and its fragments resulting in the formation of defect structures of the type $[C_{120-2m}]^+$, where $m = 1, 2, 3, \ldots$, which were observed in work [14].

## 5. Conclusions

In this work, the regularities in the ionization of molecules and the fragmentation of single-charged molecular ions of fullerene $C_{60}$ thermally deposited onto a silicon substrate are studied both experimentally (using the method of laser desorption mass spectrometry) and theoretically (in the framework of the density functional theory). It is shown that $[C_{60}]^+$ ions appear in the mass spectrum when the laser power reaches 30% of its maximum value. Then their intensity increases linearly. At the same time, the relative degree of fragmentation first grows and then saturates at a relative laser power of 50%.

The quantum chemical technique was used to calculate the total binding energies of $[C_{60}]^+$ and its single-charged fragmentary ions $[C_{60-2n}]^+$ normalized to the number of carbon atoms. The structure of and the spin density at defects in $[C_{59}]^+$ and $[C_{58}]^+$ obtained, when one and two, respectively, carbon atoms are removed one-by-one, were visualized. The structures of defect fullerenes are determined in the cases where the $C_2$ fragment is removed from two, different by their types, bonds in the fullerene $[C_{60}]^+$ molecular ion. The energy of a single photon is proved to be not enough to explain the observed mass spectrum of fullerene desorption ionization and fragmentation, so that the consideration of the multiphoton interaction between a $C_{60}$ molecule and laser radiation – presumably driven by the plasmon resonance mechanism – is required.

The molecular constants for neutral and charged $C_{60}$ molecules, as well as their fragments, are calculated; these are the total energies, ionization potentials, electron affinities of the $C_{60}$ molecule and its fragments, and energies of ion dissociation, when the $C_2$ molecule is removed from various positions. The calculated molecular constants may prove to be useful for the interpretation of experimental mass-spectrometric results dealing with the fragmentation of aggregated fullerenes in the course of their laser desorption ionization on the substrates of various nature.

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## ЗАКОНОМІРНОСТІ ФРАГМЕНТАЦІЇ ФУЛЕРЕНУ $C_{60}$ ЗА ДАНИМИ ЛАЗЕРНО-ДЕСОРБЦІЙНОЇ МАС-СПЕКТРОМЕТРІЇ ТА КВАНТОВОЇ ХІМІЇ

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Резюме

У роботі представлено експериментальні та теоретичні результати дослідження закономірностей фрагментації фулерену $C_{60}$. Деструкцію $C_{60}$, нанесеного методом термічного осадження на кремнієву підкладку, вивчено методом лазерно-десорбційної мас-спектрометрії при різних значеннях потужності лазера. Показано, що інтенсивність іонів $[C_{60}]^+$ в мас-спектрі лінійно зростає при збільшенні потужності лазера від 30% до 70% максимальної потужності, тоді як відносний ступінь його фрагментації спочатку збільшується, а потім досягає насичення при відносної потужності лазера 50%. Запропоновано два можливих механізма іонізації фулерену $C_{60}$.

Методом квантової хімії розраховано електронну будову молекулярних $C_{60-2n}$ і катіонних $[C_{60-2n}]^+$ форм фулеренів, де $n = 0, 1, 2, 3, 4$ визначає кількість втрачених фрагментів $C_2$. Визначено значення граничних молекулярних орбіталей ($E_{\text{ВЗМО}}$ і $E_{\text{НВМО}}$), адіабатичні потенціали іонізації і спорідненість до електрона.