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## LASER DESORPTION/IONIZATION OF FULLERENES: EXPERIMENTAL AND THEORETICAL STUDY

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*Experimental and theoretical aspects of fullerene C<sub>60</sub> ionization, fragmentation and aggregation are discussed by laser desorption/ionization mass spectrometry and quantum chemistry. Ion formation and chemical reactions of fullerene molecule depend essentially upon the nature and properties of the surface where it is deposited as well as upon the conditions of deposition and the mechanisms of ion-molecular reactions which occur in the ion source of mass spectrometer. It has been shown that the energy of single photon is enough to ionize an adsorbed fullerene molecule due to transition of single electron to the Fermi level of support and consequent overcoming the barrier of image forces. Nevertheless, this mechanism cannot explain the observed mass spectra completely, in particular the high level of fullerene fragmentation, because of lack of photon energy. Plasmon resonance resulted from multi-photon excitation of fullerene molecule in condensed state is the initial stage and the main mechanism of energy supply for fullerene laser induced ionization, fragmentation, aggregation, and chemical reactions which take place in both adsorbed state and ion plume. Explanation of observed experimental results concerning fullerene fragmentation and aggregation is proposed based on the results of quantum chemical calculations and on heuristic considerations.*

### INTRODUCTION

First image of fullerene C<sub>60</sub> was published in more than forty years ago in Japan by Z. Yoshida and E. Osawa in 1971 [1]. Then Harold W Kroto with co-workers showed that C<sub>60</sub> molecule might be assembled spontaneously from hot nucleating plasma [2]. New stage of investigation came in 1990 when possibility of synthesis of pure fullerenes in gram amounts was shown and soon the structure and physicochemical properties of C<sub>60</sub> – the most stable and easy to obtain fullerene – were investigated, mostly by efforts of R.F. Curl Jr., H.W. Kroto, R.E. Smalley who were awarded Nobel Prize in Chemistry 1996 “for their discovery of fullerenes”.

It should be noted that the first unequivocal experimental evidence of fullerene existence was obtained by means of mass spectrometry.

A number of fullerenes and fullerene-like systems is found at the moment but the most widely popular is fullerene C<sub>60</sub>, named also in literature as buckminster fullerene, in honor of famous American architect Buckminster Fuller who was the first to use the idea in his constructions. Simple nicknames buckyball and

soccerball are also widely used. C<sub>60</sub> molecule is the main subject of present article.

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<sub>60</sub> 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 [3], there are the principal differences between 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 postionic-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<sub>3</sub> fragment whereas fullerene C<sub>60</sub>, when interacting with laser radiation, demonstrates the intense

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loss of neutral fragments  $C_2$  which is typical of fullerene molecules only.

In [4] 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 paper, 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 [5]. The authors, 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 electron volts), 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.

From the moment of Nobel lecture pronounced by Harold W. Kroto entitled "Symmetry, Space, Stars and  $C_{60}$ " it has become clear to everybody that fullerenes may be interesting and useful not only in symmetry, space and star problems but also in completely earth and human problems of nanotechnology, as far as fullerene is not only a specific molecule but a nanoparticle as well, that with very promising properties.

Below the Table 1 is presented from the article by the President of the National Academy of Sciences of Ukraine B.E. Paton with co-authors titled "Nanoscience and nanotechnology:

technical, medical and social aspects" [6] summarizing the number of publications concerning nanoparticles of various kinds.

**Table 1.** Number of publications concerning nanoparticles [6]

Nanometals	Total	Up to 2000	2006-2009	First publication
carbon	1917	588	1329	1992
gold	1302	743	559	2000
titanium	430	127	303	2002
silver	414	191	223	2000
lead	412	156	250	1997
aluminum	398	155	243	2001
iron	362	192	170	1978
zinc	365	122	243	2000
sodium	353	140	193	2000
copper	220	118	112	2002

Carbon nanoparticles, including fullerenes, occupy the first position in this Table, in both the number of publications and the rate of increase during recent years. It is clear from this analysis that applications of carbon nanoparticles, fullerenes in particular, in nanotechnology, biotechnology, nanomedicine, and nanopharmacology [7] are most topical and important lines of scientific interest.

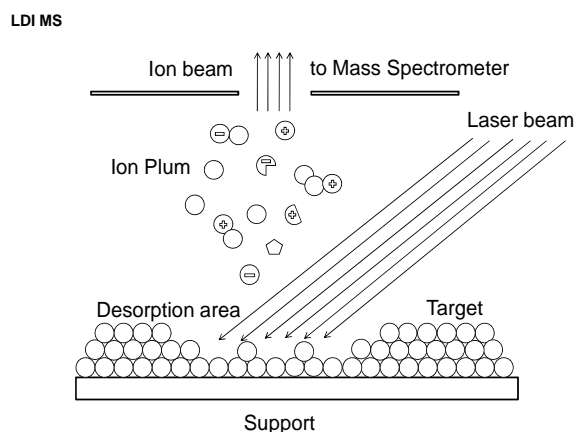
Nevertheless, no technological and application aspects will be discussed in this article. The main attention will be concentrated on the physical principles and mechanisms of fullerene ionization, fragmentation, and aggregation as well as on surface chemistry of the fullerene films deposited on surfaces of various kinds under effect of ultraviolet laser irradiation. Laser desorption mass spectrometry was the main tool of our experimental studies and obtained results were partially published in [8].

## EXPERIMENTAL

**Laser Desorption/Ionization.** In 2002 John Fenn, Koichi Tanaka and Kurt Wutrich were awarded Nobel Prize with motivation: "for the development of methods for identification and structure analyses of biological macromolecules". Among them, Koichi Tanaka was the first person to develop and to prove outstanding possibilities of matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) in studies of biological (and not only biological) macro-molecules. Further development of this experimental approach resulted in matrix-free laser desorption/ionization mass spectrometric (LDI MS) technique and some

other variations of the method, such, for example, as the most wide spread surface assisted laser desorption/ionization mass spectrometry (SALDI MS), desorption/ionization on silicon surface mass spectrometry (DIOS MS) and many others.

In Fig. 1 one can see how does the ion source work used in a matrix-free LDI mass spectrometer.



**Fig. 1.** The principal scheme of LDI ion source

The molecules under investigation (fullerene molecules in our case) are deposited on the surface of sample plate (so-called “support”). Any way of deposition is acceptable, the most wide spread being deposition from fullerene solutions with consequent evaporation of solvent or, in some cases, direct thermal deposition of fullerene molecules in vacuum on the surface of support. Most frequently used materials of support are stainless steel (standard support) or specially prepared silicon plates with chemically or physically modified surface. It should be noted that obtained mass spectra, as a rule, essentially depend upon the support material, procedure of deposition, and thickness of deposited sample.

The support with deposited sample is called “target” and in the course of experiment is irradiated by UV laser pulses concentrated in the middle of target to achieve intensity of irradiation enough to start laser ablation in desorption area. Laser-induced ablation of the target results in formation of ion plum located between the target surface and the entrance to mass analyzer.

As it is shown in the Figure 1, ion plum contains not only molecular ions, positive and negative, but also neutral and charged fragments, aggregates and products of their interaction. Mass

spectra obtained in positive and negative mode of registration (positively and negatively charged ions) provide an additional information concerning the mechanism of ionization, fragmentation, aggregation, and ion-molecular reactions. Ion-molecular reactions occur in the ion plum during the period called “extraction time” which is the time shift between the start of ionizing laser pulse and the start of the pulse allowing ions to enter mass analyzer. Thus, the result of ion-molecular reactions in a hot plum depends not only upon preparation procedure but also upon ion source parameters: laser power, pulse duration, pulse frequency and extraction time.

**LDI TOF mass spectrum of fullerene  $C_{60}^+$  and mechanism of fullerene ionization.** The LDI mass spectrum of molecular ion  $C_{60}^+$  contains molecular mass of  $12 \times 60 = 720$  Da as the main component. Next, heavier ions of 721, 722, 723 etc. of less intensity are explained by contribution of  $C_{13}$  isotope to total molecular mass. As the comparison of experimentally obtained intensities of molecular mass spectrum lines with those calculated from isotopic distribution shows complete coincidence, there is no doubt that the mass spectrum contains nothing except molecular ion  $C_{60}^+$ . This was the fact which allowed Nobel Prize winner Harold W. Kroto be sure that he really observed ion  $C_{60}^+$  in his mass spectrometric experiments.

The first possible mechanism of  $C_{60}^+$  formation is the mechanism of surface ionization. The electron in this case leaves molecule by tunneling to the Fermi level of metal support, so necessary energy of ionization in this case is only about  $I_p - \Phi = 2.8$  eV ( $I_p$  – ionization potential,  $\Phi$  – work function).

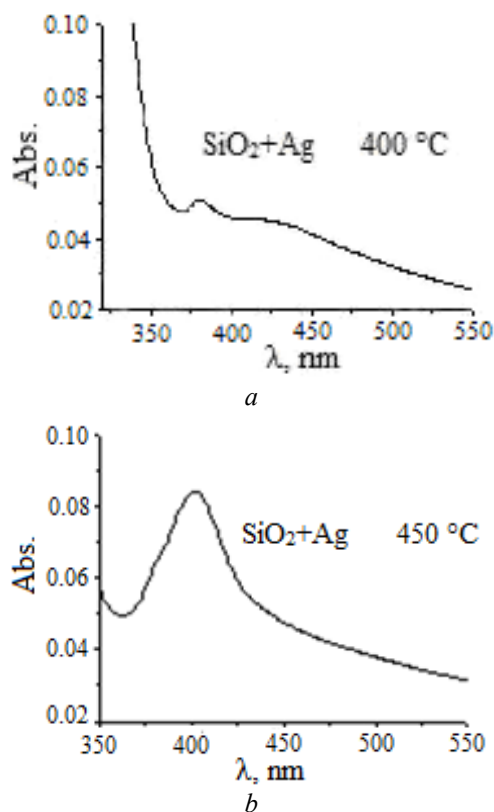
As far as the energy of a single UV photon in our experiments is about 3.7 eV, we have enough energy for single-photon ionization of isolated fullerene molecule resulting in formation of molecular ion  $C_{60}^+$ . Nevertheless, as it will be shown below, in desorption/ionization experiment, fullerene mass spectra include not only molecular ion  $C_{60}^+$  but also a large number of fragment and aggregate ions, what is impossible to be explained within the framework of single-photon mechanism because of lack of energy. It means, from our point of view, that multi-photon mechanism should be involved to explain experimental results.

Fortunately, independent experiments [5] point at existence of plasmon resonance for fullerene

molecule in the energy interval of 16–26 eV, so the multi-photon excitation mechanism may be reasonably assumed to explain the composition of mass spectra observed.

Important role of plasmon excitation of nanoparticles in LDI experiments has been already shown in our previous mass spectrometric experiments with silver nanoparticles [9].

**Effect of silver nanoparticles on methylene blue ion formation on mesoporous titania/silica surface.** The support for laser desorption ionization in our experiments was mesoporous titania/silica film doped with silver nanoparticles in amount of 3 %, 5 %, 10 % and heat treated at two temperatures.

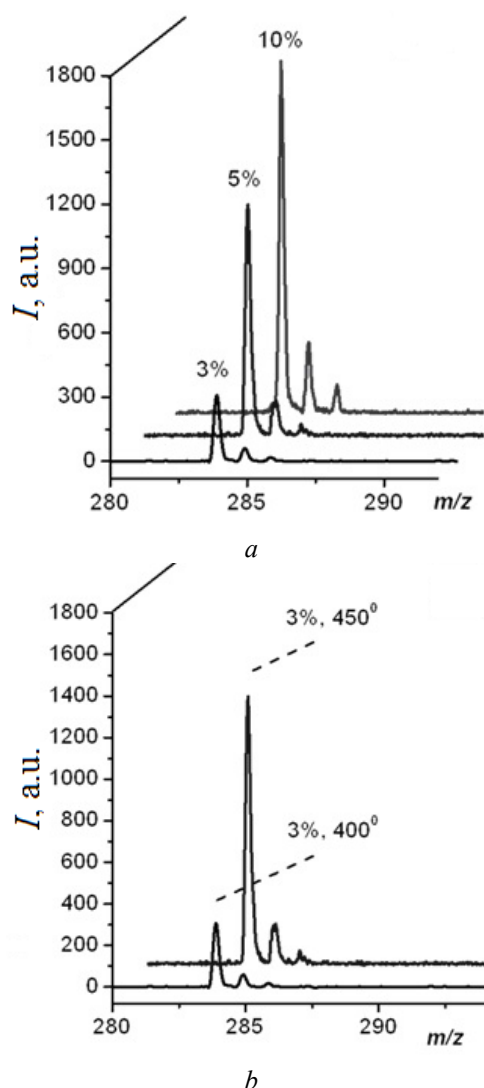


**Fig. 2.** UV absorption of TiO<sub>2</sub>/SiO<sub>2</sub> films: *a* – heat treatment of the film at 400 °C (no plasmon resonance); *b* – the same film treated at 450 °C (plasmon resonance is present)

It means that surface plasmon appears as a result of thermally stimulated structure rearrangement of incorporated silver nanoparticles.

Fourfold increase in intensity (Fig. 3, *b*) gives direct evidence of plasmon resonance important role in ionization mechanism of methylene blue molecule.

Considering all above mentioned, we can suppose a series of photo-induced interdependent processes that leads to the collective coherent electron excitation in the conduction band of silver nanoparticles and to other attendant complex effects on the surface of substrate during mass-spectrometric experiment. Photodesorption is directly dependent on the quenching rate of electronic excitation. It rises substantially at the resonance of optical radiation with plasmon oscillations of metallic nanoparticles due to light wave field gain on their surface.



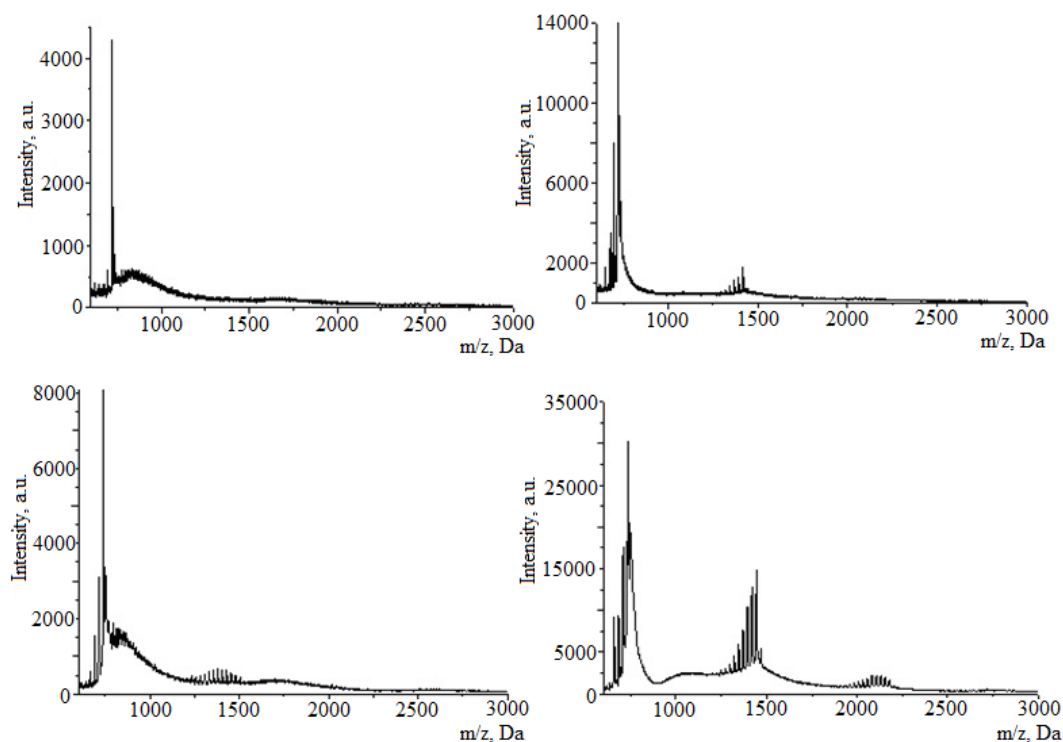
**Fig. 3.** Laser desorption/ionization mass spectra of methylene blue molecule for upper cases: *a* – 3 %, 5 %, 10 % of silver treated at 400 °C (in absence of plasmon resonance); *b* – 3 % of silver in mesoporous titania/silica film in absence (400 °C) and in presence (450 °C) of plasmon resonance

Resonant processes cause the maximum enhancement of local electric fields close to the surface of the particles and provide an efficient transfer of plasmon excitation energy to dye molecules. It was found that the contribution of the plasmon mechanism to the total rate of energy transfer dominates (exceeds by one to two orders of magnitude the rate of transfer in the absence of conducting bodies in system) when the molecules are located close to the metal surface.

Taking into account that fullerene molecule may undergo multi-photon plasmon excitation [5], we can reasonably assume an important role of plasmon mechanism in the processes of ionization, fragmentation, and aggregation as a result of laser ablation in the LDI MS experiment. Several examples of LDI mass spectra of fullerenes are presented below.

**Mass spectrometry of fullerene fragmentation and aggregation on steel and silicon surfaces.** Fullerene  $C_{60}$  samples (Fullerene Technologies, Russia, purity

> 99.5 %) were deposited on standard stainless steel target and on silicon monocrystal surface from solutions in  $CCl_4$ , in  $CH_3I$  and in  $C_5H_5N$  (all from Merck, purity > 99.5 %) and preliminary treated in an ultrasonic bath for twenty minutes. The concentration of fullerene in the solution was 0.13 mg/ml. Laser desorption/ionization time-of-flight mass spectrometry was performed on a MALDI TOF Bruker Daltonics Autoflex II instrument (5 shots per 3 ns pulse; laser fluence 70 %; extraction field 20 keV; laser wavelength 337 nm). All the fullerene solutions (in amount of 4 ml) were deposited on the target; then samples were kept for 20 min in air at room temperature to be completely dried and put into vacuum in the instrument chamber for 5 minutes before measurements. The extraction time was 40 ns to get the highest ion yield and the signal to noise ratio. Between these experiments, the solutions were kept in dark at room temperature.



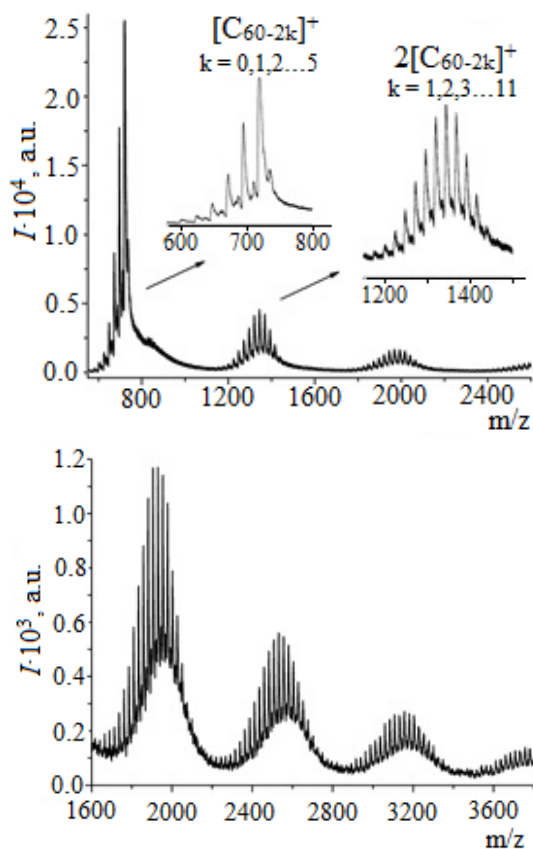
**Fig. 4.** LDI mass spectra of  $C_{60}/CH_3I$ , and  $C_{60}/C_5H_5N$  deposited on stainless steel support (left) and on Si support (right)

In all the mass spectra presented in Fig. 4 both aggregation of fullerene molecules and fragmentation of aggregates due to elimination of  $C_2$ ,  $C_4$ ,  $C_6$  etc. fragments may be observed.

Both aggregation and fragmentation preferentially take place in the experiments with fullerenes desorbed from silicon surface unlike with those desorbed from standard steel target.

This effect may be explained by efficient laser beam absorption in silicon surface layer. It can be seen that the effect of aggregation-fragmentation for the same target is more expressed for deposition from  $C_{60}/CH_3I$  ( $\epsilon = 7.0$ ) and less for  $C_{60}/C_5H_5N$  ( $\epsilon = 12.3$ ). Thus, aggregation/fragmentation of fullerene particles during laser desorption is pronounced for the most saturated  $C_{60}$  solutions in both cases (steel and silicon). Laser desorption mass spectra of fullerene have proved that aggregation/fragmentation processes are mostly enhanced for silicon support as compared to those for steel one.

**Detailed LDI mass spectra of  $C_{60}$ .** The detailed mass spectrum of  $C_{60}$  deposited on steel support from the solution N-methyl-pyrrolidone is presented in the Fig. 5. The procedure of deposition, post-deposition treatment, and experimental conditions of MS measurements were optimized to reach maximum intensity of ion current in order to obtain detailed quantitative information concerning mechanisms of ionization, fragmentation, and aggregation of fullerene ions and molecules.



**Fig. 5.** Mass spectra of  $C_{60}$  deposited on steel support from solution in N-methylpyrrolidone

The following regularities may be observed in Fig. 5.

1. The molecular ion  $C_{60}^+$  is, as usual, gives the most intensive signal in the mass spectrum.
2. Fragment ions  $[C_{60-2k}]^+$  are present, also as usual,  $k=0-5$ .
3. Aggregate ions  $2[C_{60-2k}]^+$  are observed in the mass spectrum,  $k=1-11$ .
4. Within the large masses area, groups of aggregates are also observed corresponding to 3, 4, 5 and even more fullerene molecules, with maximum of intensity distribution shifted to lower masses from the mass of corresponding aggregate. Despite results close to presented here were already observed and published, no satisfactory explanations are available in the literature.

From our point of view, a theoretical, first of all quantum chemical, approach is necessary to explain the rather complicated regularities observed in the fullerene mass spectra.

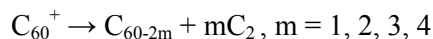
#### THEORETICAL STUDIES

##### *Extraction energies of neutral fragments from fullerene $C_{60}$ obtained by quantum chemical calculations.*

Fragmentation of fullerenes  $C_{60}$  is one of the methods of preparing fullerenes with defect structures  $C_n$  ( $n = 60, 58, 56, 54, 52$ ). Taking into account that experimental examination of the effect of defects in fullerenes  $C_n$  on their structural and energy characteristics is difficult, comparative quantum chemical studies of such systems become actual. Calculations were carried out within the B3LYP density functional theory [10, 11] with basis set 6-31G(d) by means of the software program USGAMES [12]. The energy characteristics have calculated of molecular  $C_n$ , cationic  $C_n^+$ , and anionic  $C_n^-$  forms of fullerenes ( $n = 52, 54, 56, 58, 60$ ) produced due to fragmentation of  $C_{60}$ , the energy values have been found of the frontier molecular orbitals ( $E_{HOMO}$  and  $E_{LUMO}$ ) as well as adiabatic ionization potentials ( $I_{ad} = (E(C_n^+) - E(C_n)) \cdot 27.2116$ , eV), electron affinities ( $E_a = (E(C_n^-) - E(C_n)) \cdot 27.2116$ , eV), and dipole moments  $\mu$  (see Table 2). The calculation method seems to be valid due to theoretical values of such fundamental characteristics of  $C_{60}$  molecule as adiabatic ionization potential  $I_p = 7.421$  eV, electron affinity  $E_a = 2.202$  eV, and chemical bond lengths  $d_{66} = 1.393$  Å (between two hexagonal rings) and  $d_{56} = 1.465$  Å (between heptagonal and hexagonal rings) that

agree well with respective experimental ones ( $I_p = 7.57 \pm 0.01$  eV [13],  $E_a = 2.667 \pm 0.001$  eV [14],  $d_{66} = 1.401$  Å and  $d_{56} = 1.458$  Å [15]).

It is known [16–18] that the reaction of  $C_{60}$  fragmentation occurs according to the scheme



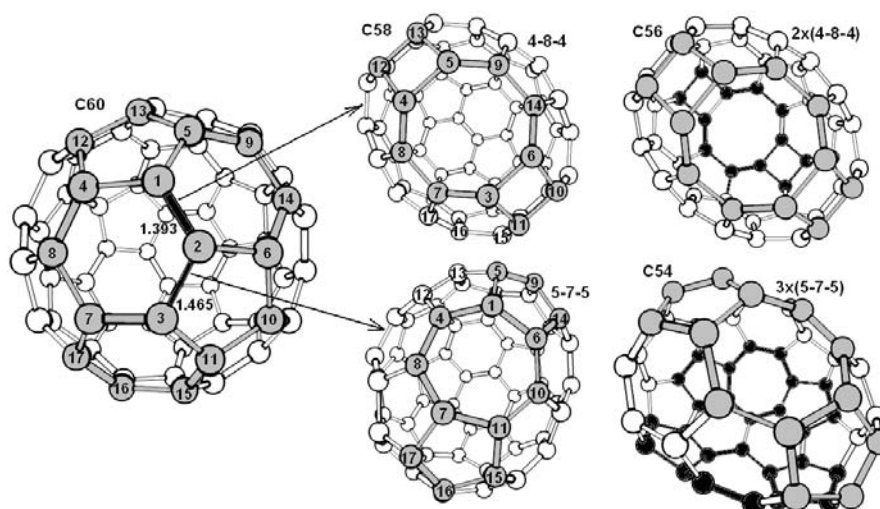
due to elimination of  $C_2$  fragment involving a 6–6 bond or a 5–6 one. In the first case, 4–8–4 defects are formed (an 8-member cycle is formed binding tetragonal, pentagonal, and hexagonal rings) whereas in the second one – 5–7–5 defects (a 7-member cycle is formed binding only pentagonal and hexagonal rings). As an example, the Fig. 6 shows some structures  $C_{60-mC_2}$  with 4–8–4 defects ( $m = 1, 2$ ) and with 5–7–5 ones ( $m = 1, 3$ ).

It follows from the analysis of the energy parameters of  $C_{60-2m}$  and  $C_{60-2m}^+$  clusters (Table 2) that:

1) Fragmented fullerenes and their cations  $C_{60-mC_2}^+$  with 5–7–5 defects are more stable (as for total energy  $E(C_n)$  and  $E(C_n)^+$  values) (more negative  $E(C_n)$  and  $E(C_n)^+$  values) as compared with those with 4–8–4 ones what agrees the presence of more strained 4-member carbon cycles in the structures. The total energy  $E(C_{58}^+)$  of cation  $C_{58}^+$  formation with involving a 5–6 bond (Fig. 6, a 5–7–5 defect) is more negative for 1.588 eV as compared with that involving a 6–6 one (Fig. 1, a 4–8–4 defect).

**Table 2.** Energy characteristics of fullerene cations  $C_{60}^+$  and of its defect structures  $C_n^+$  as well as energy effects of  $C_2$  fragment elimination

Defects	$C_n^+$	$-E(C_n^+)$ , a.u.	$-E(C_{n-2}^+ + C_2)$ , a.u.	$\Delta E(C_2)$ , eV	$I_{(C_n^+)}/I_{(C_{60}^+)}$			$\Delta E_n^+$ , eV
					30%	50%	70%	
	60	2285.1619	2284.8695	12.16	1.000; 1.000; 1.000		0.000	
(4–8–4)	58	2208.9470	2208.5089	11.92	0.370; 0.305; 0.280		0.090	
(4–8–4)s	56	2132.5713	2132.1455	11.59	0.081; 0.128; 0.130		0.190	
	60	2285.3162	2284.8695	12.16	1.000; 1.000; 1.000		0.000	
(5–7–5)	58	2209.0053	2208.5704	11.84	0.370; 0.305; 0.280		0.063	
(5–7–5)s	56	2132.6833	2132.2510	11.76	0.081; 0.128; 0.130		0.135	
(5–7–5)as	56	2132.6740	2132.2458	11.65	0.081; 0.128; 0.130		0.139	
(5–7–5)as	54	2056.3570	2055.9380	11.41	0.052; 0.091; 0.045		0.215	
(5–7–5)as	52	1980.0645	1979.6468	11.37	0.021; 0.011; 0.018		0.284	



**Fig. 6.** The structures of fullerene  $C_{60}$  and of defect fullerenes  $C_{58}$  and  $C_{56}$  derived due to elimination of  $C_2$  fragments involving 6–6 bonds (4–8–4 defect) and those of  $C_{58}$  and  $C_{54}$  derived due to elimination of  $C_2$  fragments involving 5–6 ones (5–7–5 defect)



2) The formation of several defects due to  $C_{60}$  fragmentation (both 5–7–5 and 4–8–4 ones) results in increase of both electron donor (decreased  $I_p$  value) and electron acceptor (increased  $E_a$  value) properties of  $C_{60-2m}$ , and fragmented fullerenes with symmetric defects have better donor-acceptor characteristics and smaller forbidden gaps ( $\delta E = I_p - E_a$ ) as compared to those with asymmetric ones  $C_{60-2m}$  (aS). Really, if a  $C_{56s}^+$  cation is formed, the total energy values  $E(C_{56s}^+)$  relative to symmetric defects differ for 3.047 eV whereas those for asymmetric ones in  $C_{56as}^+$  – for 3.087 eV.

3) The fragmented fullerenes  $C_{60-2m}$  with asymmetric defects have dipole moments ( $\mu$ ) what testify to both irregular electron density distributions over molecular cores and formation of sites of electrophilic and/or nucleophilic attacks.

4) An analysis of the electron density distribution over molecular core of the fragmented fullerenes  $C_{60-2m}$  and  $C_{60-2m}^+$  shows that for all the fullerenes examined the average value of electron density at carbon atoms is equal to  $5.992 \pm 0.010$  ( $C_{60-2m}$ ) and to  $5.982 \pm 0.008$  ( $C_{60-2m}^+$ ). This gives reason to believe carbon atoms in these systems to be very likely equivalent.

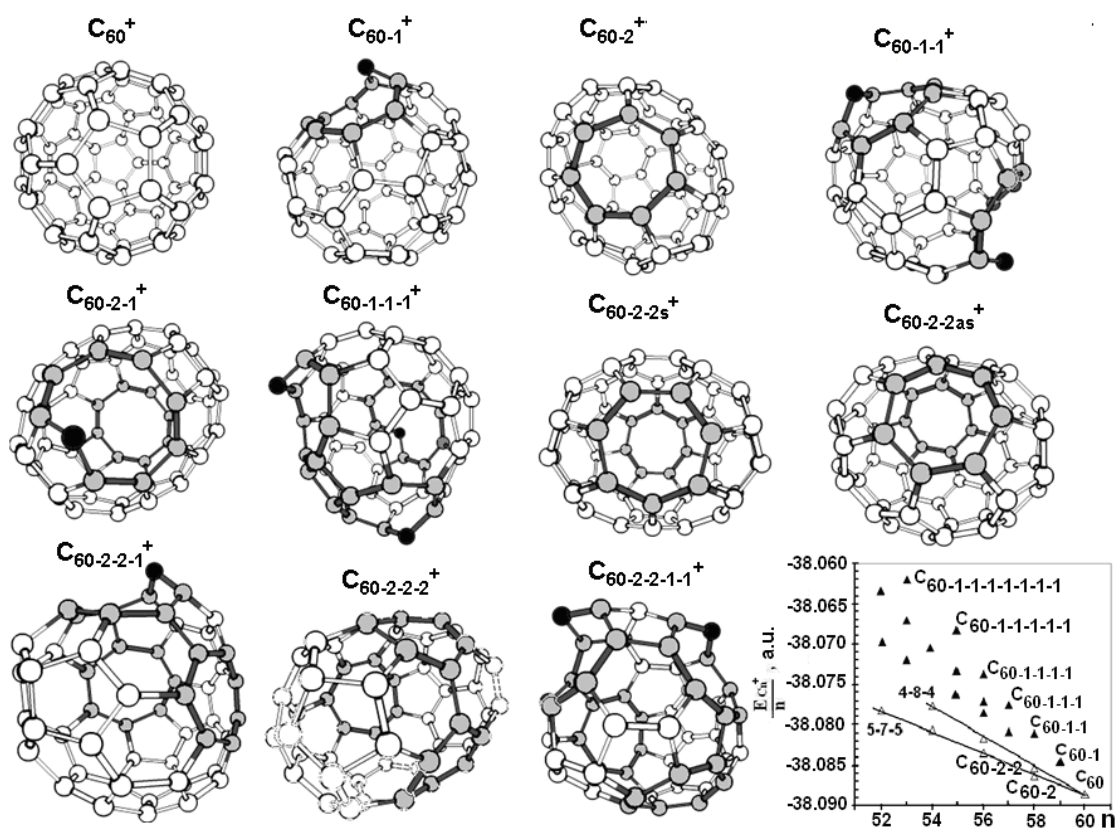


Fig. 7. Structures and total bonding energy values  $E_{C_n^+}/n$  normalized for the number of carbon atoms of defect (4–8–4) and (5–7–5) fullerene structures  $C_{60-2m}^+$

We have calculated normalized to the number of carbon atoms average values of the atomization energy  $E(C_{60-2m}^+)/n$  in fragmented fullerenes (Fig. 7,  $m = 0, 1, 2, 3 \rightarrow C_{60}^+, C_{58}^+, C_{56}^+, C_{54}^+, C_{52}^+$ ). The results testify that due to formation of defect structures, a deformation of spatial structure takes place, its level being controlled by the number of defects, place and symmetry of their localization. One can see in the Fig. 7 (right lower corner) that due to

sequential elimination only  $C_2$  fragments from  $C_{60}^+$  (light dots), more stable defect structures are formed than those formed due to step-by-step elimination of single (1), double (1,1), triple (2,1) and (1,1,1) or more carbon atoms (dark dots) from different positions in  $C_{60}$ . The results of calculations also prove that due to formation of defect structures  $C_{60-2m}^+$  (Fig. 7), via successive elimination of  $C_2$  fragments only from  $C_{60}^+$  (lucid dots) more stable structures are



formed than those born via successive elimination of single (1), double (1,1), triple (1,1,1) or more carbon atoms (dark dots) from different positions in C<sub>60</sub>.

Indeed, the calculated values  $\Delta E_C = (E_{C(60-1)^+} + C) - E_{C60^+} = 13.72$  eV,  $\Delta E_{C_2} = (E_{C(60-2)^+} + C_2) - E_{C60^+} = 12.16$  eV and  $\Delta E_{2C} = (E_{C(60-1-1)^+} + 2C) - E_{C60^+} = 23.53$  eV give reason to suppose that fragmentation of C<sub>60</sub><sup>+</sup> under laser irradiation most probably (thermodynamically profitably) process occurs only via elimination of C<sub>2</sub> fragment because elimination of single carbon atom needs more energy for 1.56 eV, that of two carbon atoms from different positions in C<sub>60</sub><sup>+</sup> being greater for 8.81 eV. Besides, it is seen in the Fig. 7 that carbon atoms C (marked by dark cycles) with dangling valences appear in defect structures C<sub>59</sub><sup>+</sup>(60-1), C<sub>58</sub><sup>+</sup>(60-1-1), C<sub>57</sub><sup>+</sup>(60-2-1), C<sub>57</sub><sup>+</sup>(60-1-1-1) and so on what testify to greater reactivity and lesser stability of these systems. Probably, the latter can play an important role in the formation of aggregated defect structures like nC<sub>60-2m</sub><sup>+</sup> (m = 1, 2, 3..., n = 2, 3, 4... and so on).

The energy value for a C<sub>2</sub> fragment elimination from fullerene cations C<sub>60-2m</sub><sup>+</sup> (m = 0, 1, 2, 3, 4) was calculated as a difference between the total energy of these cations and the sum of total energy values for cation E(C<sub>n</sub><sup>+</sup>) (n = 60, 58, 56, 54, 52) and the E(C<sub>2</sub>) for C<sub>2</sub> fragment distant for 9–10 Å from the C<sub>n</sub><sup>+</sup> cation

what practically excludes direct interaction between their electronic systems. The attention is paid to the fact that the increase in the number of defects in C<sub>n</sub><sup>+</sup> structures somewhat decreases the elimination energy value for each next C<sub>2</sub> fragment ( $\Delta E_{C_2} = E(C_{n-2}^+ + C_2) - E(C_n^+)$ , see Table 2, n = 60, 58, 56, 54, 52) as independent on the origin of defect (4–8–4 or 5–7–5). We believe the decrease in energy barrier observed for such a reaction to be caused by both decrease in ionization potential and increase in electron affinity and to be connected with increase in electron mobility over molecular core in defect fullerenes (increase in forbidden gap,  $\Delta E_{fg} = I_p - E_a$ ).

We suppose that the amount of cations (the intensities of signals in the mass-spectrum) in the research chamber of mass-spectrometer is controlled by stability (life time) of these cations, i.e. by their energy state. Provided in defect fullerenes all carbon atoms are identical (we realize the approximate character of this assumption), a measure of change in quality of the energy states of C<sub>n</sub><sup>+</sup> cations may be the difference value

$$\Delta E_n^+ = E(C_n^+)/n - E(C_{60}^+)/60$$

between the bonding energy values in defect fullerenes C<sub>n</sub><sup>+</sup> and C<sub>60</sub> normalized for the number of carbon atoms (Table 3).

**Table 3.** Energy characteristics of fullerene cations C<sub>60</sub><sup>+</sup> and its defect structures C<sub>n</sub><sup>+</sup> as well as elimination energy values of C<sub>2</sub> fragment

Defect	C <sub>n</sub> <sup>+</sup>	-E(C <sub>n</sub> <sup>+</sup> ), a.u.	-E(C <sub>n-2</sub> <sup>+</sup> + C <sub>2</sub> ), a.u.	ΔE(C <sub>2</sub> ), eV	I <sub>(C<sub>n</sub><sup>+</sup>)</sub> /I <sub>(C<sub>60</sub><sup>+</sup>)</sub> 30% 50% 70%	ΔE <sub>n</sub> <sup>+</sup> , eV
	60	2285.3162	2284.8695	12.16	1.000; 1.000; 1.000	0.000
(4-8-4)	58	2208.9470	2208.5089	11.92	0.370; 0.305; 0.280	0.090
(4-8-4)s	56	2132.5713	2132.1455	11.59	0.081; 0.128; 0.130	0.190
	60	2285.3162	2284.8695	12.16	1.000; 1.000; 1.000	0.000
(5-7-5)	58	2209.0053	2208.5704	11.84	0.370; 0.305; 0.280	0.063
(5-7-5)s	56	2132.6833	2132.2510	11.76	0.081; 0.128; 0.130	0.135
(5-7-5)as	56	2132.6740	2132.2458	11.65	0.081; 0.128; 0.130	0.139
(5-7-5)as	54	2056.3570	2055.9377	11.41	0.052; 0.091; 0.045	0.215
(5-7-5)as	52	1980.0645	1979.6468	11.37	0.021; 0.011; 0.018	0.284

Really, relative distributions of the signal intensities observed in the mass-spectra of cations I<sub>(C<sub>n</sub><sup>+</sup>)</sub>/I<sub>(C<sub>60</sub><sup>+</sup>)</sub> with different levels of laser excitation (30, 50, and 70 %, see Fig. 5) and 5–7–5 defects are described by a common expression

$$I_{(C_n^+)}/I_{(C_{60}^+)} = 0.874 \cdot \exp(-13.71 \Delta E_n^+),$$

$$n = 18, r = 0.983,$$

that for 4-8-4 defects being

$$I_{(C_n^+)}/I_{(C_{60}^+)} = 0.964 \cdot \exp(-11.58 \Delta E_n^+),$$

$$n = 9, r = 0.985.$$

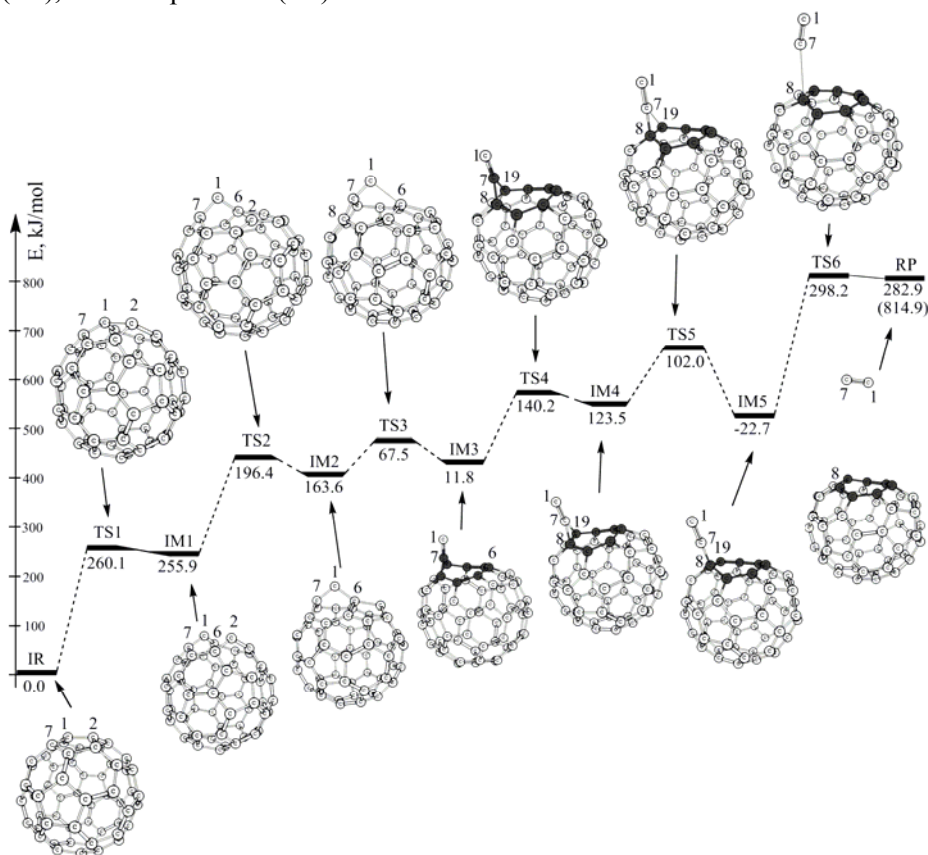
The relatively great correlation coefficient ( $r$ ) and close values of both pre-exponential and exponential factors in these equations give grounds to believe that the signal intensities of  $C_n^+$  cations observed in mass-spectra due to fullerene  $C_{60}$  fragmentation are determined by the energy states of defect  $C_{60-2m}^+$  structures, laser excitation energy, and, to a lesser degree, by the defect origin.

It is known from the results of quantum chemical calculations [19] that fragmentation of  $C_{60}$  fullerene occurs in several stages. A line is observed in the experimental mass-spectrum relative to cation-radical  $C_{58}^{+\cdot}$ . It can be formed due to laser irradiation effect on fullerene  $C_{60}$  molecule or on the neutral  $C_{58}$  fragment. It is interesting to determine the mechanism of formation of this fragment from  $C_{60}$  molecule and from cation-radical  $C_{60}^{+\cdot}$ , in order to justify the stage of destruction where  $C_{58}^{+\cdot}$  is formed.

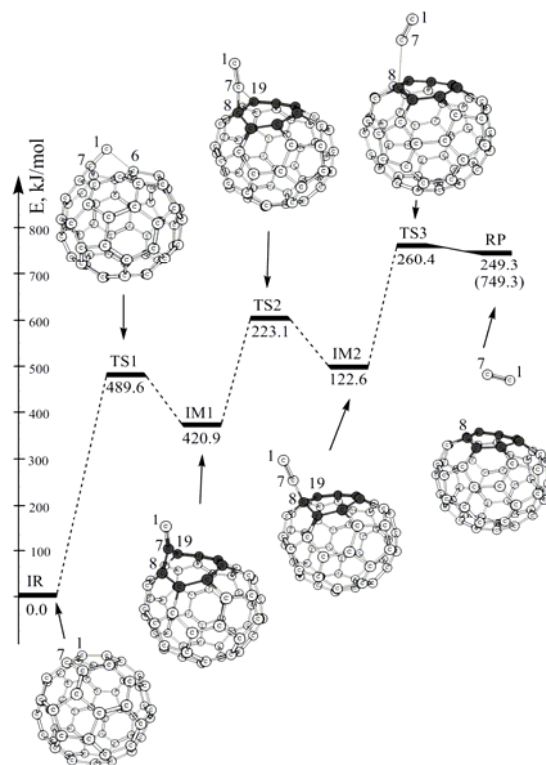
We have simulated destruction mechanisms of both  $C_{60}$  and  $C_{60}^{+\cdot}$  within the frameworks of *ab initio* Hatree-Fock method with basis set 3-21G(d) by means of USGAMESS program [12]. The equilibrium spatial structures of reactants (IR), intermediates (IM), reaction products (RP) as well

as of transition state (TS) configurations were found via gradient norm minimizing [20]. The energy minimum stationarities of corresponding structures obtained was proved by the absence of negative eigenvalues of relative Hesse matrices (force constant ones) whereas the presence of transition states was proved by existence of transitional vectors, according to the Murrell-Laidler theorem [21]. In order to verify accurate correspondence of the structures of both initial reagents and reaction products to those of transition states, the IRC method IRC [22] was used.

It follows from the results of our calculations (Fig. 8) that there are six stages of  $C_{60}$  destruction. The system becomes reactive in excited triplet state. Firstly, we examined the destruction mechanism [16] of neutral fullerene  $C_{60}$  molecule (Fig. 9). According to the literature data [23] on the bond strengths in  $C_{60}$  molecule, its fragmentation should start from the C1–C2 bond (between 5-member and 6-member rings) rupture resulting in the formation of the first intermediate (IM1). The formation energy of IM1 is equal to 255.9 kJ/mol (2.65 eV) and the process meets a considerable energy barrier of 260.1 kJ/mol.



**Fig. 8.** The energy diagram of destruction mechanism of fullerene  $C_{60}$  molecule



**Fig. 9.** Energy diagram of the destruction mechanism of  $C_{60}^{++}$  fullerene cation-radical

The second stage includes the change in hybridization of carbon (from  $sp^2$  to  $sp^3$ ) with formation of IM2. This stage is also endothermic one (163.6 kJ/mol) is characterized by a considerable value of the activation energy 196.4 kJ/mol. The covalent bond rupture between carbon atoms C1–C6 takes place at the next stage resulting in the formation of a cycle of eight carbon atoms (IM3). The activation energy of this process is relatively small (67.5 kJ/mol) and is characterized by an insignificant endothermic effect of 11.8 kJ/mol. The fourth stage is characterized by formation of a covalent bond between the atoms C8–C19, so the octagonal defect IM3 (Fig. 8) is rearranged into heptagonal one (IM4). The energy barrier of 140.2 kJ/mol is to be surmounted whereas the energy effect of the reaction is of 123.5 kJ/mol. The fifth stage is bond rupture between the atoms C7–C19. It should be noted that this stage is exothermic with the energy effect of -22.7 kJ/mol and a considerable value of the activation energy (102 kJ/mol). The last stage is connected with the bond C7–C8 rupture and formation of  $C_{58}$  and  $C_2$  fragments (Fig. 8, RP). The greatest values of both activation energy (298.2 kJ/mol) and energy effect (282.9 kJ/mol)

are characteristic of this stage, so it is the limiting one for the fragmentation way of  $C_{60}$  molecule considered. It should be noted that in the RP complex the  $C_{58}$  and  $C_2$  fragments are distant for 6 Å whereas the spin density is localized at the heptagonal defect of the  $C_{58}$  fragment. The total energy effect of the process is of 814.9 kJ/mol.

Unlike destruction of neutral  $C_{60}$  molecule (Fig. 8), the fragmentation of  $C_{60}^{++}$  cation-radical occurs in three stages (Fig. 9). At the first stage, the C1–C6 bond is ruptured with formation of an octagonal defect (IM1) similar to the neutral IM3 (Fig. 8). This stage is connected with overcoming the considerable energy barrier of 489.6 kJ/mol, the energy effect being 420.9 kJ/mol. It should be noted that direct connections have been found by the IRC method between TS1 and IR and also between TS1 and IM1 without intermediates and transition states. No intermediate has been found with changed for  $sp^3$  hybridization of carbon atom typical of the fragmentation of neutral  $C_{60}$  molecule (IM2, see Fig. 8). In this case, unlike the previous one, the first stage is limiting as it is characterized by the highest value of activation energy of 489.6 kJ/mol (Fig. 9).

This energy barrier is greater than those of the limiting stage of the neutral  $C_{60}$  molecule fragmentation for 298.2 kJ/mol (Fig. 8). The second stage is characterized by the activation energy of 223.1 kJ/mol; respective components of the transitional vector testify to the C7–C19 bond rupture and simultaneous formation of the C8–C19 one. As a result, the IM2 (Fig. 9) is formed with a heptagonal defect similar to the IM5 (Fig. 8). The energy effect of this stage is of 122.6 kJ/mol. The absence of intermediates has been also proved by the IRC method. The last (third) stage (Fig. 9) similar to the last stage of the fragmentation of neutral fullerene molecule (Fig. 8) is characterized by the C7–C8 bond rupture resulting in the formation of  $C_2$  and  $C_{58}$  fragments with overcoming a lesser energy barrier (260.4 kJ/mol). In the RP (Fig. 9), the distance between  $C_2$  and  $C_{58}$  is less than that in the analogous complex (Fig. 8) (about 4 Å). The spin density and positive charge are localized at the  $C_{58}$  fragment. The total energy effect of the  $C_{60}^{++}$  fragmentation is less (for 65.6 kJ/mol) than that of  $C_{60}$  (749.3 kJ/mol).

Thus, the results of calculations show destructions of both neutral  $C_{60}$  and cation-radical  $C_{60}^{++}$  to occur according to the similar mechanisms except different number of stages:  $C_{60}$  is decomposed into  $C_{58}$  and  $C_2$  in six stages whereas  $C_{60}^{++}$  is transformed into  $C_{58}^{++}$  and  $C_2$  in three stages. The energy value of the limiting stage of  $C_{60}^{++}$  fragmentation is greater for 191.4 kJ/mol. As the laser irradiation results in a local heating of the surface with adsorbed  $C_{60}$  molecules, their destruction should be believed to occur at a high temperature. This means that the main controlling factor of the reaction is its thermodynamic effect, i.e. a thermodynamic control takes place. The total energy effect of  $C_{60}^{++}$  destruction is greater for 65.6 kJ/mol than that of  $C_{60}$  neutral molecule.

**The origin of multiple fullerene  $C_{60}$  mass spectra: heuristic interpretation.** The unexpected satellites observed in mass spectra of  $C_{60}$  fullerene with the  $m/z$  values corresponding to aggregation of initial species and/or its fragments  $C_x$  ( $50 < x < 60$ ,  $x$  seems to be even) can be explained as follows. According to the ideas set out in writing by Z. Slanina [24], the intensity of spectra should depend on the probability of unifying initial species into a combined one. Thus, there is a unique way to obtain a  $C_{120}$  particle from two  $C_6$  species (one of

them being charged) or to form a  $C_{118}$  particle from  $C_{60}$  and  $C_{58}$ . At the same time, a  $C_{110}$  particle can be formed by  $C_{60} + C_{50}$ ,  $C_{58} + C_{52}$ , or  $C_{56} + C_{54}$  species (three variants). This circumstance can be used as a tool for explaining observed spectra.

Theoretical spectra of dimeric (a), trimeric (b) and tetrameric (c) particles are pictured below (Fig. 10). Their maxima correspond approximately to  $C_{55n}$  particles in a good agreement with the experiment. If normalized over the total number of probable combined species, a theoretical distribution of the intensities in mass-spectra closely mimic the experimental one (Fig. 5).

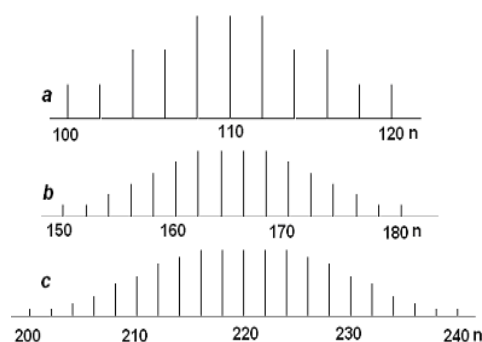


Fig. 10. Theoretical mass-spectra of dimeric (a), trimeric (b) and tetrameric (c) fullerene particles

## CONCLUSIONS

Laser desorption/ionization mass spectrometry seems to be the method of choice for investigation of physical processes occurring in condensed phase of fullerene molecules under laser ablation. Ion formation and chemical reactions of fullerene molecule depend essentially upon the nature and properties of the surface where it is deposited, upon conditions of deposition and upon mechanisms of ion-molecular reactions occurring in the ion plume.

Plasmon resonance, as the result of multi-photon excitation of fullerene molecule in condensed state, is the initial stage and the main mechanism of energy supply for fullerene laser induced ionization, fragmentation, aggregation, and chemical reactions occurring both in adsorbed state and in ion plume.

Quantum chemistry calculations are an efficient tool to clarify the nature, mechanisms, and details of processes under investigation, in particular fragmentation and aggregation of fullerene ions.

It has been shown that the energy of single photon is enough for ionization of adsorbed

fullerene molecule by transition of single electron to the Fermi level of support and consequent overcoming the barrier of image forces. Nevertheless, this mechanism cannot explain observed LDI mass spectra completely, in particular the high level of  $[C_{60}]^+$  fragmentation, because of the lack of photon energy.

We assume that possibility of multi-photon excitation of  $C_{60}$  by plasmon excitation mechanism should be taken in consideration, with consequent transformation of electron energy to vibration modes, in order to explain the distribution observed of fragment intensities in the mass spectra.

Dramatic and unexpected effects may be observed as a result of UV laser treatment of fullerene-containing nanostructured materials used in nanotechnological, biological, and medical applications of fullerenes and their derivatives.

It follows from the analysis of quantum chemical studies on the probable fragmentation mechanisms of fullerene molecule that destruction of  $C_{60}^{+\bullet}$  cation-radical is more probable thermodynamically than that or related molecular form. The results obtained may testify that the 5–7–5 defects and symmetry of their arrangement play more important role in the mechanism of defect formation due to  $C_{60}$  fragmentation under laser irradiation.

The origin of satellites observed in mass spectra of  $C_{60}$  fullerene may be successfully explained heuristically within the idea on formation of multiple species combined from initial and fragmented fullerene molecules and ions.

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### Лазерна десорбція/іонізація фуллеренів: експериментальні та теоретичні дослідження

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*Розглянуті та обговорені експериментальні та теоретичні аспекти іонізації, фрагментації та агрегації фуллерену  $C_{60}$ , вивченого методом мас-спектрометрії із застосуванням лазерної десорбції/іонізації та квантової хімії. Утворення іонів та хімічні реакції молекул фуллерену залежать переважно від природи та властивостей поверхні, на яку вони нанесені, від умов нанесення та від механізму іонно-молекулярних реакцій, які мають місце в іонному джерелі мас-спектрометра. Показано, що енергії одного фотона достатньо для іонізації адсорбованої молекули фуллерену шляхом переходу електрона на рівень Фермі підкладки та подальшого подолання бар'єру сил електростатичного зображення. Втім, цей механізм неспроможний пояснити одержані мас-спектри вичерпно, особливо високий рівень фрагментації фуллерену, внаслідок нестачі необхідної для цього енергії. Плазмонний резонанс, як наслідок багатифотонного збудження молекули фуллерену в конденсованому стані, є початковою стадією та основним механізмом постачання енергії для лазерно-індукованої іонізації, фрагментації, агрегації та хімічних реакцій, які відбуваються як в адсорбованому стані, так і в іонному джерелі мас-спектрометра. Запропонована інтерпретація спостережуваних експериментальних результатів, що стосуються фрагментації та агрегації фуллеренів, яка базується на результатах квантовохімічних розрахунків та евристичних міркуваннях.*

### Лазерная десорбция/ионизация фуллеренов: экспериментальные и теоретические исследования

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*Рассмотрены и обсуждены экспериментальные и теоретические аспекты ионизации, фрагментации и агрегации фуллерена  $C_{60}$ , исследованного методом масс-спектрометрии с применением лазерной десорбции/ионизации и квантовой химии. Ионобразование и химические реакции молекул фуллерена зависят преимущественно от природы и свойств поверхности, на которую они нанесены, от условий нанесения и от механизма ионно-молекулярных реакций, которые протекают в ионном источнике масс-спектрометра. Показано, что энергии одного фотона достаточно для ионизации адсорбированной молекулы фуллерена путем перехода электрона на уровень Ферми подложки и для дальнейшего преодоления барьера сил электростатического изображения. Однако, этот механизм не может объяснить полученные масс-спектры полностью, особенно высокий уровень фрагментации фуллерена, вследствие недостатка необходимой для этого энергии. Плазмонный резонанс как следствие многофотонного возбуждения молекул фуллерена в конденсированном состоянии является начальной стадией и основным механизмом поставки энергии для лазерно-индуцированной ионизации, фрагментации, агрегации и химических реакций, которые происходят как в адсорбированном состоянии, так и в ионном источнике масс-спектрометра. Предложена интерпретация наблюдаемых экспериментальных результатов, касающихся фрагментации и агрегации фуллеренов, основанная на результатах квантовохимических расчетов и эвристических соображениях.*