Phototransformation and photoinduced oxygen-uptake in C_{60} films irradiated by femtosecond laser pulses

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ABSTRACT

Photopolymerisation and photoinduced diffusion of the molecular oxygen in oxygen bearing C_{60} films by λ=459, 514 nm continious laser radiation and by 100 - fs, λ=395, 410 nm pulses were compared by visual observation of photodarkening spots and by recording the Raman spectra, in the range 200 - 1700 cm^{-1}, of the irradiated regions. It was found out that in the case of femtosecond pulses, the efficiencies of both photoinduced processes are significantly lower than those in the case of continious radiation.

Keywords: femtosecond pulses, photopolymerization, photoinduced oxygen diffusion, C_{60}, Raman spectra.

1. INTRODUCTION

Phototransformation of C_{60} under the action of UV and visible radiation creates materials with structural, chemical, and electrical properties different from those of the original substance[1]. One of the phototransformation processes is photopolymerisation (PP) occurring in the solid phase of C_{60} (films and crystals), which creates a photoproduct insoluble in toluene and consisting of dimers and polymers of covalently bound C_{60} molecules[2]. This process can be used in photolithography[1]. Moreover, similar structures appear when ultrahard fullerites are formed at high pressures and temperatures[3]. PP in C_{60} in both oxygen free and oxygen bearing films was widely studied in the case of continuous radiation of visible and UV ranges. The main ways of the photoexcited C_{60} molecules relaxation which leads to different photoproducts are shown in fig. 1. A lot of works concerns with the most intensive peak in Raman spectrum of C_{60}- tangential mode $A_g(2)$[1-6]. There are two processes attributed to PP: decrease of intensity of $A_g(2)$ mode and shift of its frequency from 1469 cm^{-1} to 1458 cm^{-1}.

It was proposed[4] that the PP mechanism is well known reaction of 2 + 2 cycloaddition, resulting in covalent binding of van der Waals molecules in a molecular crystal[4]. This reaction can occur in solid C_{60} if it contains a pair of fullerene molecules with parallel double bonds, separated by a distance not exceeding 4.2 Angstroms from one another. One of the molecules should be in

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the ground state and the other should be in the lowest excited triplet state[5]. The observed fall of PP efficiency in presence of oxygen is connected with effective energy transfer from C_{60} triplets (T_1) to the oxygen molecules which are in the lowest triplet state. The triplet oxygen transforms to singlet state and reacts with C_{60} in ground state with production of carbonyl $C_{60}O_2$ (dioxetane reaction), (fig. 1). Also oxygen occupying octaehedral voids in the *fcc* lattice between the C_{60} molecules impedes free spinning of C_{60} thus preventing PP as in the case of low temperatures.

Another process which can reduce the PP efficiency is a photoinduced increase of oxygen diffusion into the interior of a sample (uptake) observed on films irradiated by continuous wavelength (CW) radiation and leads to the formation of $C_{60}(O_2)_x$ clathrates[7] (fig.1) . It was found[8] that the spectrum of a sample impregnated with oxygen was the same, in the visible range, as the initial spectrum. On the other hand, PP increased the absorption at the red wavelengths and this made it possible to detect the process visually because of the appearance of characteristic dark spots [5].

The PP process is the most efficient when C_{60} samples are irradiated with CW UV radiation[9]. A typical average radiation intensity needed to initiate PP must be in the range 1 - 100 W cm^{-2}. An increase in the average intensity over 10^3 W cm^{-2} at 514 nm wavelength results in destruction of the core of the C_{60} molecules in C_{60} films and production of amorphous carbon[10]. Irradiation with 5 ns pulses of intensity 2 x 10^6 W cm^{-2} at λ=266 nm destroys C_{60} in presence of oxygen [11] . PP of C_{60} by femtosecond laser pulses had not previously been investigated experimentally, although the dark spots were observed in film and attributed to PP on irradiation of films with 230 fs pulses at λ=590 nm at intensities in excess of 10^{10} W cm^{-2} [12].

The interest in such investigations increased after the report that relaxation of the photoinduced absorption in oxygen-free C_{60} films was accelerated by irradiation during several minutes with femtosecond pulses of relatively low intensity (10^6 - 10^7 W cm^{-2}) repeated at a frequency of 82 MHz[13]. According to Ref.[13], it was PP of C_{60} during normal illumination, and also under the action of femtosecond pulses (FS) in the course of the experiment itself, that accelerated the observed relaxation. Moreover, it was stated in Ref.[13] that an increase in the intensity and a corresponding increase in the excitation density should increase the PP efficiency. Thus, therefore, practically all the published experimental results obtained by femtosecond spectroscopy of fullerene films should be reviewed. Nevertheless, no experimental proof was provided in Ref. [13] of the occurrence of PP (as manifested by changes in the Raman spectrum and in photodarkening of the sample). In contrast to Ref.[13], all the other published femtosecond spectroscopic investigations were carried out on films exposed to atmospheric oxygen. Some comments were made on this topic in Ref.[14], but the problem of the efficiency of PP of fullerenes irradiated with femtosecond laser pulses has not been previously studied.

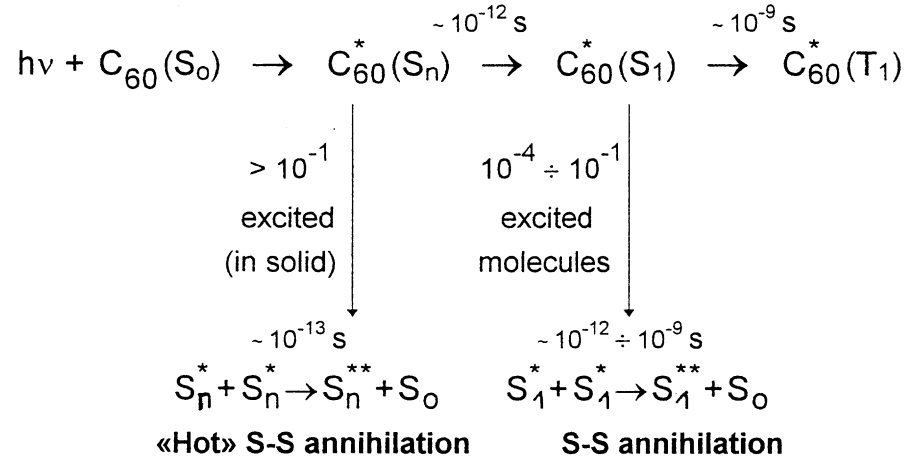
This work compares of photoinduced characteristic changes in C_{60} oxygen- bearing samples which have place with both CW and FS laser radiation.

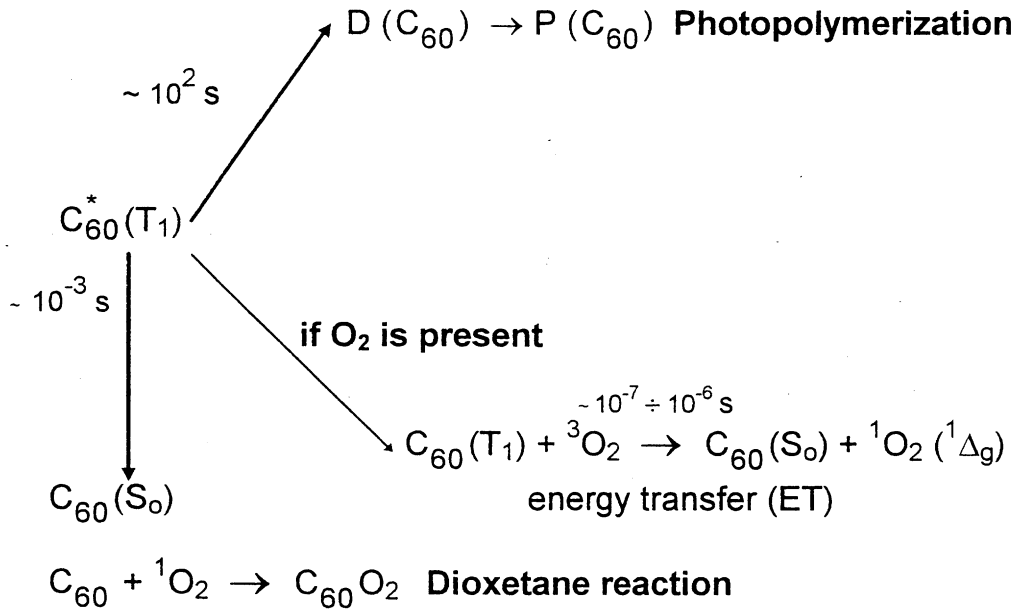
2. EXPERIMENT AND DISCUSSION

We investigated C_{60} films, of 140- 1000 nm thickness on quartz substrates, stored in air and in the presence of normal illumination for over a year. The Raman spectra of the original samples recorded were in the range 200 - 1700 cm^{-1}; they included the *Hg*(3), *Hg*(4), *Hg*(7), and *Hg*(8)

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PHOTOTRANSFORMATION OF C_{60}





Photoassisted diffusion of $^3O_2$ into the bulk of film (oxygen uptake)

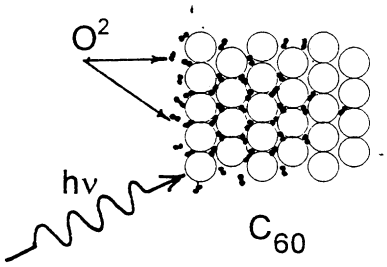


Fig. 1

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modes, as well as the strongest tangential *Ag*(2) mode. All modes are typical for C_{60} spectrum[2]. In the first experiments these films were exposed to CW argon laser radiation at λ=459 nm with average intensity of 19 W cm^{-2} and pulses train at a frequency of 82 MHz, representing the second harmonic of titanium sapphire laser with λ=410 nm (pulse duration 100 fs) of average intensity 13 W cm^{-2} [15]. As can be seen from the linear absorbtion spectrum (Fig. 2), the absorbed energy was practically the same for both regimes.

We studied the dynamics of appearance of the dark spots associated with PP in the irradiated region under various irradiation conditions, and we determined the exposure (radiation dose) needed for their appearance. After irradiation, we recorded the Raman spectra of the spots using the multichannel spectrometer[16] . Each spectrum was recorded during 5-6 min- the period of sample irradiation by argon laser at λ =514 nm with intencity less than 10 W cm^{-2}. We found that the method to observe dark spots by their visual appearance is more effective for PP detection than Raman spectra investigation.

CW irradiation at λ=459 nm produced a PP spot after 15 - 20 min, i.e. after a dose of 20 kJ cm^{-2}. The Raman spectra recorded for the dark spots revealed changes typical of PP: the intensity of the *Hg*(4) mode at ν=775 cm^{-1} decreased, the intensity of the *Hg*(3) mode at ν=710 cm^{-1} increased, and all the *Hg* lines were split. The greatest changes were observed for the *Ag*(2) tangential mode at ν=1469 cm^{-1}: the line of this mode broadened considerably and its intensity fell. However, complete disappearance of this line and its replacement with a line at ν=1459 cm^{-1}, typical of complete PP under oxygen-free conditions[5], was not observed. This was evidence of a reduction in the PP efficiency in the presence of oxygen.

When the 1μm C_{60} film was irradiated with FS, there was no evidence of PP after exposure for 8 h, although the radiation was of a shorter wavelength (λ=410 nm). The appearance of a PP spot under the action of FS was detected only at average radiation intensities of more than 50 W cm^{-2} and if the C_{60} film thickness was less than 0.15 μm. The radiation dose was of the order of 1 MJ cm^{-2}. However, even at these conditions the spot was so weak that we were unable to detect the difference between the Raman spectrum of this spot and the spectrum of the original sample.

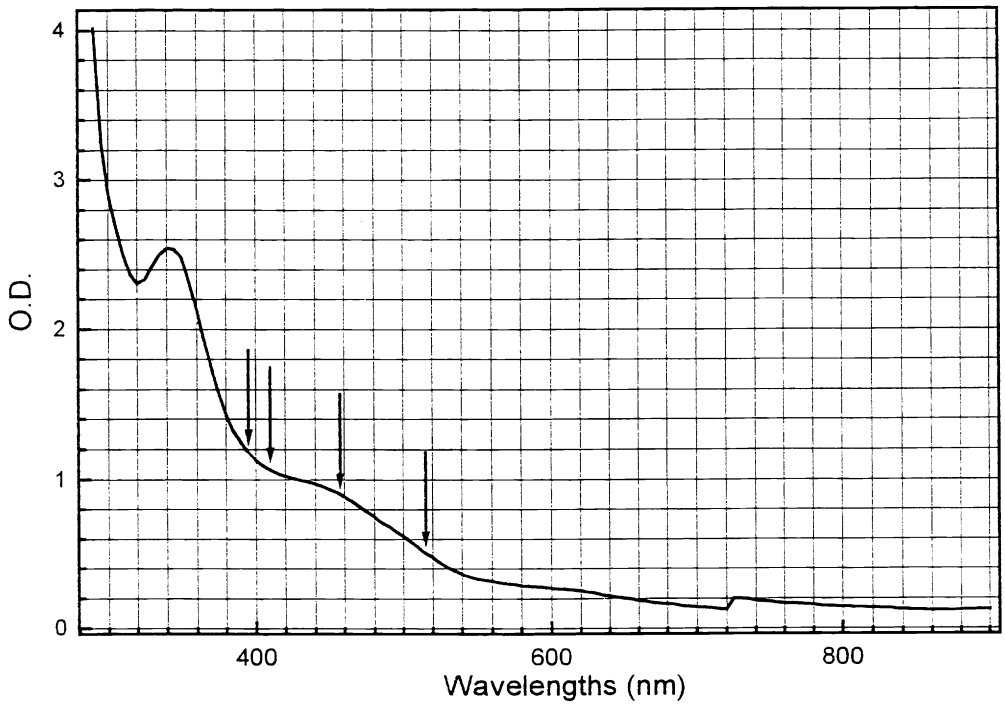
The appearance of the PP spots under irradiation of a C_{60} film with CW laser indicated that the film had oxygen-free regions where the PP occurred. This conclusion was confirmed by the equality between the threshold dose in the last case and that observed under oxygen-free conditions[1]. However, during CW irradiation the size of the oxygen-free region decreased rapidly because of photostimulated diffusion of oxygen into the interior of the sample[7], thus the number of the polymerized molecules was restricted. For this reason the PP efficiency was less in the presence of oxygen than under oxygen-free conditions.

These experiments have shown that PP in C_{60} films irradiated with FS was much less effective than that in the case of CW irradiation although the absorption was even a bit more for FS. Estimates based on the experimental results reported above indicated that PP during CW irradiation required only $2x10^6$ photons per molecule, whereas, in the case of FS it was not possible to observe PP even when $6x10^7$ photons per molecule were absorbed. It should be noted that due to low average intensity, FS radiation was focused into a smaller area than CW one. On

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ABSORPTION SPECTRUM OF C60 FILM

Wavelengths of irradiation are pointed by arrows



Laser radiation parameters:

CW	λ = 459 nm, average intensity 20 W/cm^2
	λ = 514 nm, average intensity 20 - 4000 W/cm^2
100 fs, 82 MHz	λ = 410 nm, average intensity 20 -50 W/cm^2
	λ = 395 nm, average intensity 10 -130 W/cm^2

Fig.2

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the other hand there was observed "size effect" (decrease of the threshold dose at increase of focal area) in the case of CW. To avoid ambiquities which can arise from "size effect"and sample quality there was performed one more set of experiments with more powerful femtosecond laser and using the same film for all irradiation regimes[17].

The following experimental results were found for C_{60} film of 150 nm thickness which was exposed to FS at 395 nm and to CW at 514 nm. The average power of radiation was in the range of 10- 1000 W cm $^{-2}$ in both cases. Irradiated area was the same in both cases: 200 μm in diameter. In these experiments the linear absorbtion of FS radiation was greater than that of CW (Fig. 2). It was found that PP takes place in the case of CW as well as in the case of FS. Minimal exposure time for the dark spot appearance was approximately 1- 2 min in the first case and more than 10 min in the second case. The threshold radiation dose for the appearance of PP spots with continuous radiation diminishes while the radiation intensity increases from 50 to 300 W cm^{-2}; that was close to the threshold radiation dose for oxygen free samples (20 kJ cm^{-2}) at the intensity of 300 W cm^{-2}. The threshold for PP in the case of FS was 50- 60 kJ cm^{-2} at average radiation intensity 95 W cm^{-2} and the threshold increased approximately 3 times while intensity increased up to 130 W cm^{-2}.

Micro- Raman spectra of the irradiated areas revealed characteristic changes attributed to PP in the case of CW as well as in the case of FS. Raman lines were split after the irradiation. The intensities of *Hg*(1), *Hg*(4), *Ag*(1), *Ag*(2) decreased. and the intensity of *Hg*(3) increased. The most significant changes took place for tangential mode *Ag*(2) (wavenumber 1469 cm^{-1}). Its intensity fell considerably and its decrease was proportional to the spot darkening. The most significant changes conditioned by PP are observed in the vicinity of *Ag*(2) mode ; it is shown on figure 3. CW irradiation of the C_{60} films leads to the more significant differences of the Raman spectra from the spectrum of initial sample than FS irradiation (though the degree of spot darkering was the same in both cases). It is especially pronounced for the A_g(2) mode intensity. In addition the *Ag*(2) mode was more extended to the lower frequency in the case of CW. These changes were more noticeable at increased exposure time. There was no broadening of *Ag*(2) mode in the case of the FS even at the maximal exposure time of 780 min.

It is noteworthy that there was no PP observation after several hours long irradiation of the C_{60} films by femtosecond pulses of 790 nm wavelength at intensities varied in the wide range; it is so even at intensities close to the sample damage threshold during several hours irradiation. In these cases the film of 140 nm thickness absorbed about 25% of the radiation energy.

The experimental Raman spectra were fitted by Lorentz functions with the assumption that lines of pristine fullerene *Ag*(2) (1469 cm^{-1}) and *Hg*(7) (1425 cm^{-1}) are emitted simultaneously with lines of photoproducts: photopolymer C_{60} - line 1459 cm^{-1} and carbonyl $C_{60}O_2$ (fig. 3). The spectrum of the unexposed film (top of fig. 3) was fitted by only two lines: pristine C_{60} and the line of $C_{60}O_2$: photopolymer was supposed to be absent. The best fitting for the 1469 cm^{-1} line provides the FWHM value as 3.5 cm^{-1}, the position of $C_{60}O_2$ line at 1465 cm^{-1} and its FWHM of 10 cm^{-1}. These data are in a good agreement with data of the Ref. [1] and we used them for the fitting of the spectra of irradiated areas. The frequency (1459 cm $^{-1}$) of the polymer line and its FWHM (17 cm^{-1}) are taken from Ref.[6].

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MICRO-RAMAN SPECTRA OF C60 FILM

after CW and FS irradiation

(each spectrum was obtained for 15 min at 488 nm, 50 W/cm^2)

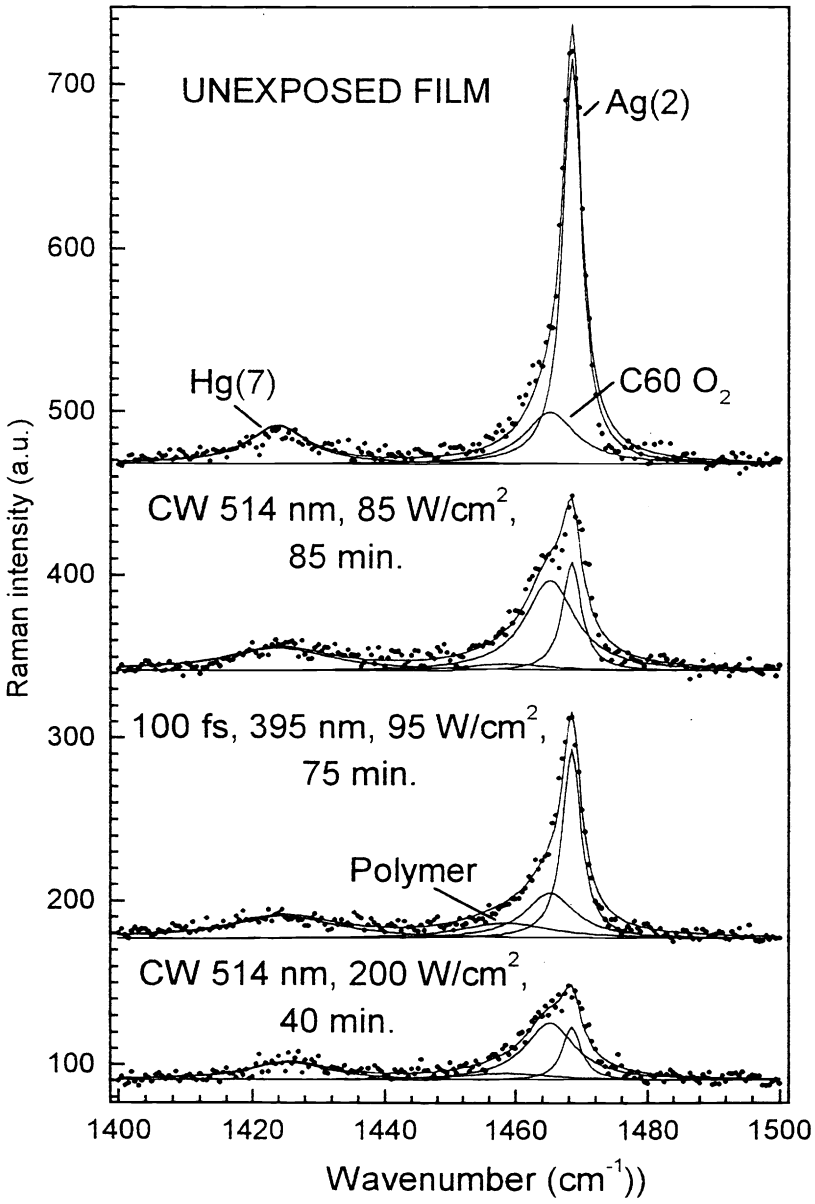


Fig.3

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As can be seen from fig.3 the intensity of photopolymer line does not exceed the noise level. This result must be attributed to the high broadening of the polymer line and to its very low cross section of absorption (it is three times lower than that of pristine C_{60}). Also a weak polymer line can be covered by a strong carbonyl line at 1465 cm^{-1}. Nevertheless, estimates of the fraction photopolymerized molecules can be made with the assumption that the loss in the number of molecules in initial state is equal to the number of new molecules giving lines for $C_{60}O_2$ and photopolymers. The results are: of 35% for CW 514 nm, 85 W cm^{-2},85 min; 50% for 100 fs, 395 nm, 95 W cm^{-2}, 75 min; and 60% for CW 514 nm, 200 W cm^{-2}, 40 min (fig. 3). These data are in agreement with observed photodarkening in all the cases. From spectra for CW irradiation (fig. 3) it can be seen that $C_{60}O_2$ line formation (1465 cm^{-1}) is more effective for longer exposure times even at less intensity. FS irradiation doesn't give rise of $C_{60}O_2$ line at all.

The measurement of absorbed energy which is sufficient for the observation of PP showed that PP process is much less effective in the case of FS than that in the case of CW. At average intensity of 100 Wcm^{-2} the threshold dose at CW irradiation (λ = 514 nm) was $2x10^6$ photons per molecule and that was 7 times more at FS irradiation (λ = 395 nm).

The fall of the efficiency was associated with the high peak power of the femtosecond pulses. Under our experimental condition the maximum concentration of molecules excited by pulsed irradiation was over five orders of magnitude higher than the concentration produced by CW irradiation at the same average power. The intermolecular relaxation (mainly by singlet-singlet annihilation) was then much faster than the transfer of molecules to the triplet states, which were the starting point for PP (fig. 1). Thus the suggestion[13,18] that the production of dimers and polymers is more effective at higher densities of excitied molecules seems to be not valid.

The difference in Raman spectra in the cases of FS and CW irradiations (fig.3) allowed us to draw conclusion about photoinduced uptake of oxygen in both cases. We connect the rise of the carbonyl line in the case of continuous radiation with photoinduced molecular oxygen diffusion from the ambient atmosphere to the bulk of the sample[1,7]. The absence of the carbonyl line rise in the case of FS means that photoinduced oxygen diffusion doesn't take place in this case. Physical mechanisms of that phenomenon are to be studied in more detail.

Oxygen uptake at CW irradiation results in C_{60} triplets quenching and subsequent carbonyl production in the bulk of the sample. At FS irradiation this reaction is blocked. It means that for this case the PP conditions in sufficiently thick C_{60} films (of the order of several tens of nm) are the same as in oxygen free and oxygen contained films. The process, resulted in shortening of relaxation time[13] at characteristic irradiation dose of approximately 1 kJ cm^{-2} at 463 nm can't be attributed to PP, because the threshold dose measured at present experiments is more of some tens times. Our experiments have also shown that different timescales of excitation of C_{60} molecules lead to different photochemical processes and this provides a tool to affect them.

3. ACKNOWLEDGMENTS

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