# Generation of singlet oxygen in fullerene-containing media: 2. Fullerene-containing solutions*

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***Abstract.*** **The generation of singlet oxygen in fullerene solutions is studied by luminescence methods upon excitation by pulsed, repetitively pulsed, and continuous radiation sources. The concentration of singlet oxygen in solutions is measured in stationary and pulsed irradiation regimes. The rate constants of quenching of $O_2$ ($^1\Delta_g$) by fullerenes $C_{70}$ and $C_{60}$ in the $CCl_4$ solution are measured to be $(7.2 \pm 0.1) \times 10^7$ $L\ mol^{-1}\ s^{-1}$ and less than $6 \times 10^4\ L\ mol^{-1}\ s^{-1}$, respectively. The temperature and photolytic variations in the generation properties of the fullerene solution exposed to intense continuous radiation are studied by the methods of optical and EPR spectroscopy. Pulsed irradiation resulted in the production of singlet oxygen in suspensions of fullerene-like structures, in particular, astralenes. A liquid pulsed singlet-oxygen generator based on the fullerene solution in $CCl_4$ is developed and studied, in which the yield of $O_2$ ($^1\Delta_g$) to the gas phase at concentrations up to $5 \times 10^{16}\ cm^{-3}$ is obtained.**

***Keywords****: fullerene solution, singlet oxygen, luminescence, gas phase.*

## 1. Introduction

Along with the study of the production of singlet oxygen on fullerene-containing solid surfaces and its escape from the adsorbed state to the gas phase [1], of interest is also the efficiency of singlet-oxygen generation in liquid fullerene-containing media and the possibility of singlet-oxygen removal from solution to the gas phase. It was already shown earlier [2–6] that the use of fullerene photosensitisers in solutions leads to the intense luminescence of singlet oxygen at 762 and 1268 nm, which confirms the formation of the excited states $^1\Sigma_g^+$ and $^1\Delta_g$ of molecular

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oxygen in solutions. The quantum yield of $O_2$ ($^1\Delta_g$) in the benzene solution of $C_{60}$ excited at 532 nm was $\phi = 0.96$ [3].

We mainly used $CCl_4$ as a solvent in our previous experiments [4, 6, 7] because it provides the maximum lifetime of singlet oxygen [8]. The luminescence of singlet oxygen in fullerene solutions was studied both upon pulsed excitation [4, 6, 7] and excitation of fullerene solutions by a cw argon laser [5]. It was found in [7] that a singlet-oxygen quencher was produced upon pulsed broadband pumping and the $C_{70}$ concentration in solution was irreversibly partially decreased, while in [5] the complete irreversible decomposition of fullerenes was observed upon continuous irradiation of the solutions of $C_{60}$ and $C_{70}$ in tetrachloro-ethylene. At the same time, the authors of [5] found that the solution of these fullerenes in toluene and n-hexane remained unchanged for several hours of irradiation.

However, it is obvious that the data available in the literature are insufficient for solving the problem of removal of singlet oxygen produced in solution to the gas phase, which is the aim of our paper. A number of parameters of the singlet-oxygen generation by fullerenes in $CCl_4$ and other weakly quenching organic liquids still remain poorly studied. We will attempt to make up for this gap by continuing to study the influence of the irradiation regime on the luminescence, lifetime, and concentration of singlet oxygen in solutions and investigate the conditions for its efficient escape to the gas phase. In addition, we studied the suspensions of astralenes (fullerene-like multilayer polyhedral particles of size $\sim 100$ nm) as photosensitises of singlet oxygen. The properties of astralenes are described in [9, 10].

The long lifetime of singlet oxygen in $CCl_4$, which is four orders of magnitude larger than its lifetime in aqueous systems used in chemical generators of singlet oxygen, gives promise that a lower concentration of singlet oxygen produced in the $CCl_4$ solution can be compensated due to the long lifetime of oxygen, providing thereby the concentrations of $O_2$ ($^1\Delta_g$) coming to the gas phase, which are comparable with those obtained in chemical singlet-oxygen generators.

## 2. Experimental

The luminescence of singlet oxygen at 1268 nm was observed upon pulsed, repetitively pulsed, and continuous excitation by monochromatic or broadband radiation sources into the absorption band (450–650 nm) of the $C_{60}$ solution. Excitation was performed by the 532-nm, 10-ns second-harmonic pulses of a Nd:YAG laser, 100-μs pulses from an IFP-800 flashlamp, 510-nm and 578-nm

pulses from a Kulon-LT-10CU copper vapour laser with a pulse repetition rate of 15 kHz (the 510-nm/578-nm intensity ration was 3 : 2), and by continuous radiation from an OSRAM HQI-TS-1000 metal halogen lamp. Laser radiation was directed from above to a sample cell, while radiation from the lamp was directed from below, through the cell bottom. The luminescence of singlet oxygen was observed from the side at a right angle to the exciting beam. Radiation was focused by a lens to a photodetector (germanium photodiode) through an interference filter with the transmission band at 1270 nm with the FWHN 18.5 nm. In some cases, luminescence was detected by using an MDR-2 monochromator. The replacement of the interference filter by the monochromator reduced the luminescence intensity by an order of magnitude, and the detection system operated at the sensitivity threshold. However, because its was established that luminescence of the solution was observed only at $1270 \pm 20$ nm, we believe that emission detected in all cases is the luminescence of singlet oxygen.

The experimental setup with a flashlamp is described in detail in [7]. Exposure to continuous radiation was performed by using a similar illumination scheme with a two-lens condenser focusing radiation to a sample. The light flux density was varied from 1 to 8 W cm$^{-2}$. The system with the lamp mounted with its window looking upwards was cooled by a fan to avoid the convective heating of solution. The solution temperature during prolonged irradiation was controlled with a thermocouple.

The emission spectra of lamps used in experiments consist of a broad band covering the entire visible region. The spectra of exciting radiation were determined by the transmission band of optical filters used (continuous spectra in the region from 350 to 600 nm and from 300 to 850 nm for the xenon flashlamp and metal halogen lamp, respectively).

The purity of fullerene was determined by the manufacturer with a liquid chromatograph with an accuracy of $\sim 0.1\%$. The fullerene under study had a $\sim 99.9\%$ purity. Solutions were prepared from CCl$_4$ of high purity controlled by the manufacturer with a NMR spectrometer. The certified purity of perfluorohexane was $\sim 99.9\%$.

The concentration of C$_{60}$ in solutions was measured by its transmission spectra recorded with a JENWAY 6405 UV/VIS spectrometer. The transmission spectra were calibrated by the transmission spectrum of the reference solution prepared from components weighted on an electronic balance with an accuracy of 1 %.

The maximum concentration of C$_{60}$ achieved in the CCl$_4$ solution at room temperature is $2.68 \times 10^{17}$ cm$^{-3}$ (0.445 mmol L$^{-1}$ or 0.32 mg mL$^{-1}$) [11]. The concentration of oxygen dissolved in the same liquid can vary from $1.36 \times 10^{18}$ cm$^{-3}$ by saturating the liquid with air to $6 \times 10^{18}$ cm$^{-3}$ by saturating the liquid with oxygen at the atmospheric pressure [12]. The lifetime of singlet oxygen in CCl$_4$, on the contrary, somewhat decreases after saturation of the solution with oxygen: the luminescence lifetime of singlet oxygen varied from $\sim 30$ ms [13, 14] in the solvent saturated with air to 128 ms [8] in the solvent degassed by more than 99.5 %. Thus, here the quenching of singlet oxygen by oxygen in the ground state takes place, which has the rate constant equal to $1.4 \times 10^3$ L mol$^{-1}$ s$^{-1}$ [12].

The EPR spectra were recorded with a Jeol JM-ME-3x EPR spectrometer at a frequency of 9470 MHz. The $g$-factor and intensity were determined by using a Mn$^{2+}$ : MgO reference crystal and coal in the KCl powder with the spin concentration of $1.2 \times 10^{14}$ cm$^{-3}$, respectively.

## 3. Pulsed regime

Figure 1a shows the time sweeps of luminescence at 1268 nm obtained in the C$_{60}$ solution and the astralene suspension in CCl$_4$. The semi-logarithmic scale makes it possible to separate processes responsible for luminescence. One can see that the signal in the astralene suspension consists of two linear intervals with different decay rates. The faster process corresponds to luminescence of singlet oxygen on the surface of a solid sensitiser, which quenches luminescence, thereby reducing its decay time. The longer process corresponds to luminescence of singlet oxygen escaped to solution. The duration of this tail interval is determined by the rate of quenching of singlet oxygen by the solvent and substances dissolved in it. The luminescence duration is 14 ms for the astralene suspension and 25 ms for the C$_{60}$ solution.

Figure 1b presents the dependences of the luminescence energy, proportional to the amount of singlet oxygen produced in C$_{60}$ solutions in CCl$_4$, on the pump pulse energy density for solutions prepared from two different fullerene batches. As the pump pulse intensity is increased,
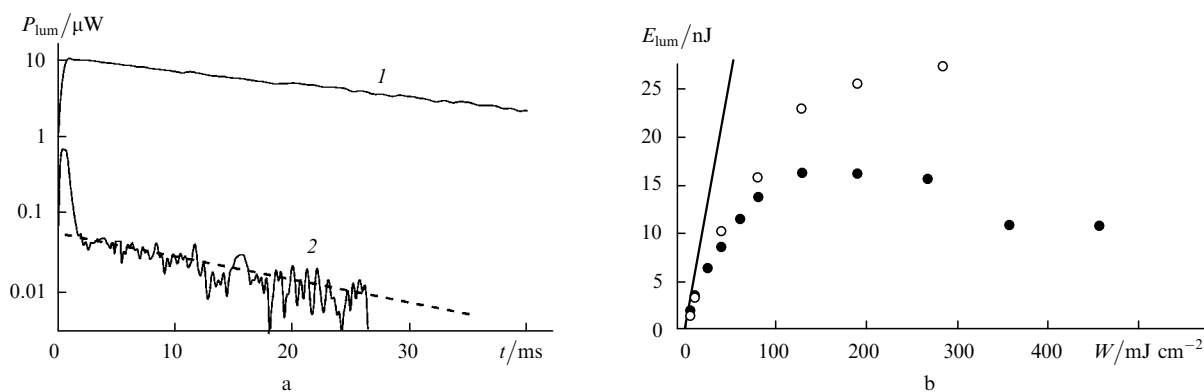


**Figure 1.** Luminescence pulses of singlet oxygen in the C$_{60}$ solution in CCl$_4$ upon flashlamp pumping with the radiation energy density $W = 10$ mJ cm$^{-2}$ (*1*) and in the astralene suspension in CCl$_4$ upon flashlamp pumping with $W = 190$ mJ cm$^{-2}$ (*2*) (a), and the luminescence energy of singlet oxygen in solutions prepared from two fullerene batches ($\circ$, $\bullet$) as a function of the pump energy density (b).

the luminescence energy first linearly increases (the straight line), then saturates at energy densities $W > 10$ mJ cm$^{-2}$, and begins to decrease at $W > 100$ mJ cm$^{-2}$. Such dependence is caused by two processes proceeding at high irradiation intensities: a decrease in the efficiency of excitation of the lower triplet state of fullerene due to inverse saturated absorption [15], which restricts the amount of produced singlet oxygen, and the formation of singlet-oxygen quenchers in the solution. The presence of the first process is confirmed by the characteristic dependence of the amplitude of luminescence pulses on the pump energy density, which saturates when a certain pump energy density $W$ is achieved. The production of quenchers in the solution is accompanied by a decrease in the luminescence pulse duration $\tau$, which is observed with increasing $W$ and the concentration $n_q$ of produced quenchers: $\tau = (kn_q)^{-1}$. The combined action of these two effects reduces the production of singlet oxygen observed in Fig. 1b. Thus, there exists the optimal pump energy density for each solution.

We also measured the dependence of the luminescence lifetime $\tau_{1/e}$ of singlet oxygen on the concentration of C$_{60}$ in solution. Figure 2 shows the dependence of the quenching rate of O$_2$($^1\Delta_g$) on the fullerene concentration. One can see that this dependence is linear within the measurement error and gives the quenching rate constant $k_X = (6 \pm 1) \times 10^4$ L mol$^{-1}$ s$^{-1}$. It is unlikely that fullerene C$_{60}$ itself is a quencher because the quenching rate varies randomly in solutions prepared from different batches of fullerene and solvent. The luminescence lifetime in different solutions varied from 10 to 30 ms. This suggests that luminescence is quenched by some uncontrollable impurity in these solutions. It is known [15] that fullerene C$_{60}$ can contain other fullerenes with close masses, which are simultaneously produced in an arc discharge, in particular, fullerene C$_{70}$. We studied in [7] the dependence of the quenching rate of singlet oxygen in the C$_{70}$ solution and estimated the quenching rate as $k_{C_{70}} = (7.2 \pm 0.1) \times 10$ L mol$^{-1}$ s$^{-1}$. To provide quenching illustrated in Fig. 2, the concentration of C$_{70}$ in solution should be 0.08 % of the C$_{60}$ concentration. Because the solubility of C$_{70}$ in CCl$_4$ [16] is comparable with the solubility of C$_{60}$ in CCl$_4$, the observed dependence can be explained by the presence of the C$_{70}$ impurity in the initial fullerene powder. We can conclude from this that the quenching of single oxygen by fullerene C$_{60}$ is not manifested for $t < 30$ ms. This gives the upper estimate of the
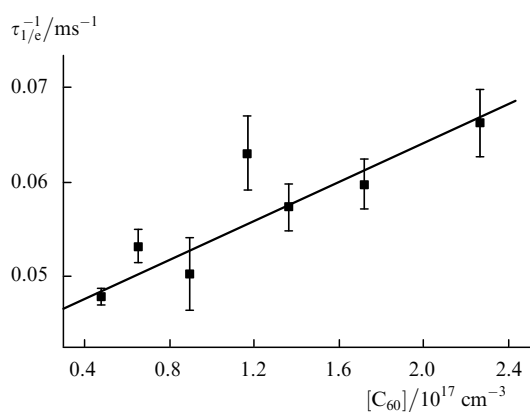
rate constant of quenching of singlet oxygen by fullerene C$_{60}$ ($k_{C_{60}} < 6 \times 10^4$ L mol$^{-1}$ s$^{-1}$), which is an order of magnitude lower than that presented in [3]. The use of the CCl$_4$ solvent instead of strongly quenching benzene [3] allows one to determine the rate constant $k_{C_{60}}$ more correctly. According to the above discussion, the difference between the curves for two fullerene batches in Fig. 1b can be explained by different concentrations of C$_{70}$ impurities.

By returning to Fig. 1a, we can compare luminescence pulses in the C$_{60}$ solution and astralene suspension [curves (1) and (2)] obtained upon pumping by the same flash-lamp. The integrated signals differ by a factor of 1000. The pump intensity in the case of astralene is 19 times larger at approximately the same (in mass) contents of fullerene in solution and astralene in suspension. Thus, the amount of singlet oxygen generated by fullerene C$_{60}$ in solution is four orders of magnitude larger than that generated by solid astralene of the same mass in the same medium. The maximum concentration of singlet oxygen produced in the pulsed regime in the fullerene C$_{60}$ solution in CCl$_4$ is estimated as $1.2 \times 10^{17}$ cm$^{-3}$.

## 4. Repetitively pulsed regime

The amount of singlet oxygen generated in solution can be accurately determined in the stationary irradiation regime, when the equilibrium concentration $\tau$ of singlet oxygen is established for the time $n_s$ in solution. Simple theoretical estimates show that the establishment process is described by the expression

$$n(t) = n_s \left[ 1 - \exp\left( -\frac{t}{\tau} \right) \right], \tag{1}$$

and the equilibrium concentration of singlet oxygen produced in the system is determined by the number $n_{hv}$ of exciting photons absorbed per unit time in the unit volume, the total quantum yield $\phi$ of singlet oxygen for the given photosensitiser, and the lifetime of singlet oxygen in the system:

$$n_s = n_{hv}\phi\tau. \tag{2}$$

The stationary regime is achieved when the production and quenching rates of singlet oxygen are equal. It is obvious that such a situation is possible not only upon continuous irradiation but also upon irradiation by a repetitively pulsed source, when the lifetime of singlet oxygen in the system under study is not shorter than the pulse repetition period. We used a laser with a pulse repetition period rate of 15 kHz corresponding to a repetition period of 70 μs, which is much shorter than the lifetime of singlet oxygen in CCl$_4$.

Figure 3 shows the time dependences of luminescence signals immediately after switching on radiation sources. Curve (3) illustrates the switching-on of laser radiation, the dot-and-dash straight line indicating the beginning of total-intensity irradiation. The development of luminescence in solution [curve (1)] begins before the achievement of the maximum pump intensity, which leads to the difference of curve (1) from dependence (1) at the initial stage of this curve. A weak decrease in the luminescence signal observed at large $t$ is explained by the instability of the photodetector current. Thus, the stationary signal corresponding to the
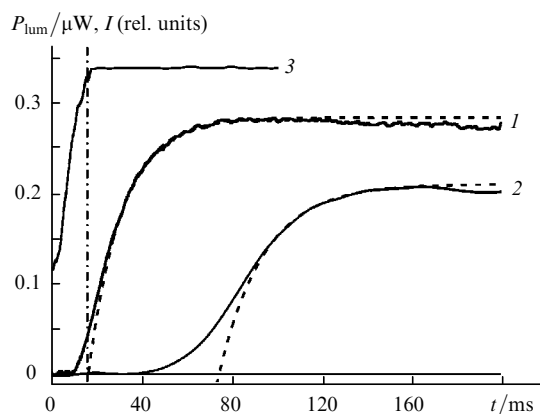


**Figure 2.** Dependence of the quenching rate of luminescence of singlet oxygen on the fullerene C$_{60}$ concentration in CCl$_4$.

$P_{lum}/\mu W$, $I$ (rel. units)

**Figure 3.** Time dependences of luminescence signals upon stationary irradiation: the establishment of emission in the $C_{60}$ solution in $CCl_4$ upon laser ( *1* ) and flashlamp ( *2* ) pumping. The dashed curves are approximations by expression (1), curve ( *3* ) is the pump laser intensity.

specified concentration of singlet oxygen is quite accurately determined by the theoretical approximation of the experimental dependence. This signal can be related to the concentration of singlet oxygen calculated from (2), where the number of absorbed pump photons upon the uniform illumination of the entire cross section of a cell is determined by the expression

$$n_{h\nu} = \frac{I}{h\nu L}\{1 - \exp[-D(\nu)]\}. \quad (3)$$

Here, $I$ is the radiation intensity at frequency $\nu$; $D(\nu)$ is the optical density of the solution; and $L$ is the height of a liquid column in the cell.

Knowing the concentration and optical density of the solution and measuring the luminescence lifetime of singlet oxygen in it upon pulsed excitation, we can calculate the stationary concentration $n_s$ with an accuracy of $\sim 10\%$. For the signal presented in Fig. 3 [curve ( *1* )], the concentration of singlet oxygen produced in the solution is $2.5 \times 10^{16}$ cm$^{-3}$.
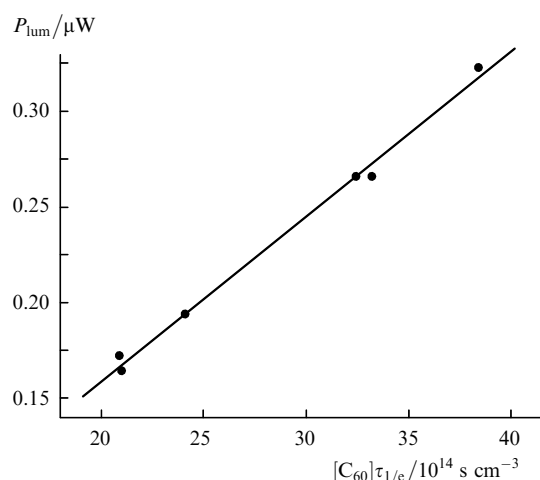
$P_{lum}/\mu W$

**Figure 4.** Dependence of the stationary luminescence power on the product of the fullerene $C_{60}$ concentration and the lifetime of singlet oxygen in solution.

We studied stationary luminescence in solutions with fullerene at different concentrations. Because the lifetime of singlet oxygen weakly depends on the concentration, the decay time of pulsed luminescence should be taken into account in the analysis of the results. Figure 4 presents the power of stationary luminescence of singlet oxygen in solutions with different fullerene concentrations as a function of the product of the fullerene concentration in solution and the decay time of pulsed luminescence. The linear dependence observed in Fig. 4 confirms the applicability of expressions (2) and (3): the expression in braces in (3) in the case of a weakly absorbing liquid layer is the optical density $D$, which is proportional to the solution concentration.

We also verified the dependence of the power of stationary luminescence of solution on the intensity of laser irradiation in the range of moderate intensities from 0.1 to 1 W cm$^{-2}$ and found that the reduction of the pump intensity by neutral filters leads to the proportional decrease in the luminescence signal.

## 5. Continuous regime

The results of our studies on pulsed irradiation of fullerene solutions have shown that it is preferable to use $C_{60}$ as the singlet-oxygen sensitiser because in this case the lifetime of $O_2(^1\Delta_g)$ in the $CCl_4$ solution can achieve $50-60$ ms. In addition, such a solution is more stable upon intense pulsed irradiation and can almost completely recover its temporal and spectral properties after the end of irradiation [7]. Based on these data, we believe that it is also necessary to test the stability of these solutions upon continuous irradiation.

It could be expected that upon excitation of fullerene solutions by continuous broadband radiation from a high-power lamp, the intensity of stationary luminescence should be higher than upon laser excitation. However, this was not observed in experiments. In the solution where singlet oxygen was produced at a concentration of $2.5 \times 10^{16}$ cm$^{-3}$ upon laser irradiation, this concentration was lower by 25% upon lamp irradiation [curve ( *2* ) in Fig. 3]. In this case, the stationary value was achieved slower due to the absence of a fast gate in the experimental scheme and, hence, the slower switching of the pump radiation.

The luminescence intensity was not proportional to the pump lamp intensity. As the pump power was changed from 1 to 8 W cm$^{-2}$, the luminescence signal was only doubled. Thus, the saturation of the concentration of the produced singlet oxygen was observed, similarly to that in the case of pulsed irradiation (Fig. 1b).

The production of quenchers is confirmed by the study of the influence of continuous lamp irradiation duration on the quenching time of pulsed luminescence in solution and also by investigations of the transmission spectra of the solution.

Figure 5a shows the change in the luminescence lifetime of singlet oxygen during exposure of the $C_{60}$ solution in $CCl_4$ to high-power continuous radiation. Note that the solution temperature was continuously controlled during irradiation, which allowed us to present the luminescence lifetime reduced to room temperature. Figure 5b illustrates the deformation of the absorption spectrum of the $C_{60}$ solution in $CCl_4$ after prolonged (180 min) exposing to continuous radiation. The results of measurements pre-
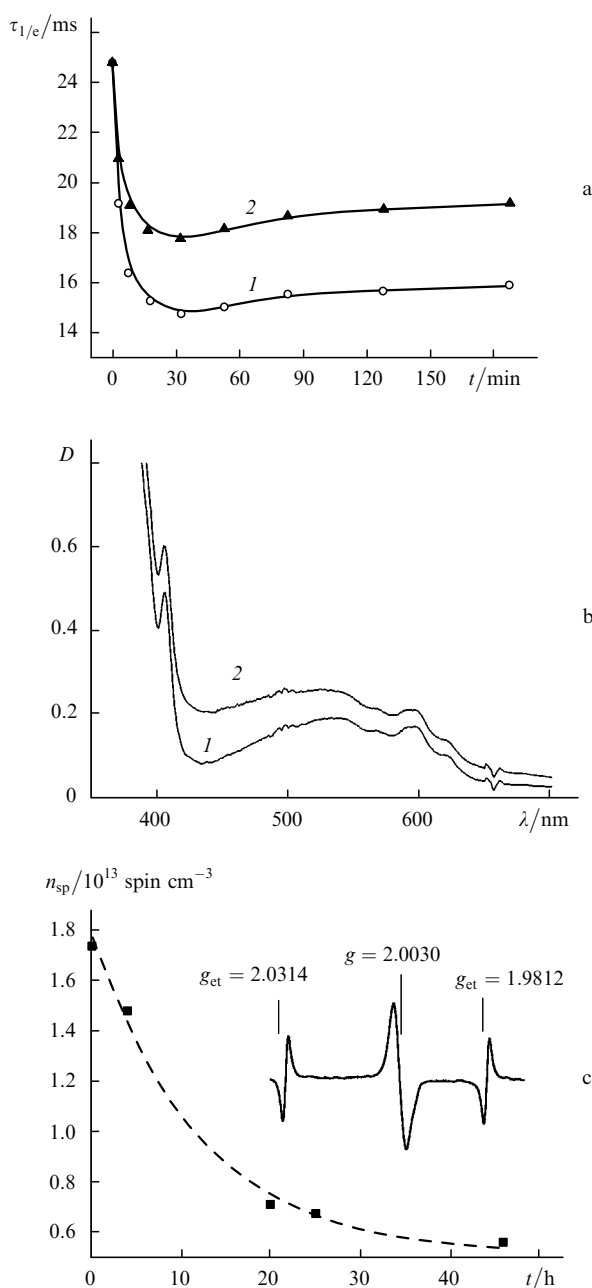
**Figure 5.** Lifetime $\tau_{1/e}$ of singlet oxygen in the fullerene $C_{60}$ solution in $CCl_4$ as a function of the irradiation time $t$: measured lifetimes ($1$) and reduced to room temperature ($2$) (a); absorption spectra of the fullerene solution before ($1$) and after ($2$) intense continuous irradiation for 180 min (b); time dependence of the intensity of the appeared resonance, which is proportional to the concentration $n_{sp}$ of spins of produced complexes, and the EPR spectrum of the solution after intense continuous irradiation for 30 min (c).

sented in Fig. 5 show that even upon such an intense continuous irradiation the luminescence lifetime did not change noticeably, as in the case of pulsed irradiation of the solution. Within 48 hours after irradiation, the lifetime of singlet oxygen recovered to its initial value, as in the case of pulsed irradiation [7]. This means that continuous irradiation leads to the production of the complexes of fullerene and oxygen, which act as efficient quenchers and decompose to initial components with time.

This is confirmed by the EPR spectra of the solution studied before intense irradiation and after it, which clearly

demonstrate the appearance of the EPR resonance after irradiation, which corresponds to these complexes and gradually decreases with time (Fig. 5c). Figure 5c shows the resonance appearing in the solution after irradiation and the decrease in its intensity with time. The $g$-factor determined from the spectrum of this resonance is $2.0030 \pm 0.0004$, which coincides with the $g$-factor value for the EPR resonance in solid fullerene films [17] and powders [18]. Because this resonance is usually assigned to the $C_{60}^{+}$ defects, we can conclude that the formation of the complex in our case is accompanied by the charge transfer, which is quite possible in the case of formation of dimers $C_{60} - O$ или $C_{60} - O_2$ [18].

At the same time, continuous irradiation of the solution resulted in the production of a precipitate unsolvable in $CCl_4$, which was deposited on the bottom of the vessel with solution. This effect was not observed upon pulsed irradiation of the solution. It could be assumed that this was a thermal effect because the solution temperature increased up to $50\,^{\circ}C$; however, this effect was not observed upon usual heating. At the same time, the absorption spectra show that the concentration of fullerene $C_{60}$ in the $CCl_4$ solution did not change considerably both upon continuous and pulsed irradiation, i.e. only an insignificant fraction of dissolved fullerene was involved in the precipitate formation. The resulting spectrum in Fig. 5b was a superposition of the absorption spectrum of the initial solution and the spectrum of scattering by the unsolvable suspension of the produced reaction products. The production of this suspension is probably related to the combined action of two factors: intense irradiation and accompanying heating of the solution.

# 6. Liquid singlet-oxygen generator based on the $C_{60}$ solution in $CCl_4$

To increase the luminescence intensity of singlet oxygen and realise its outcome to the gas phase, we designed a special cell with the $C_{60}$ solution in $CCl_4$ placed inside a coaxial pump flashlamp (Fig. 6). The cell output was connected to a vacuum system for the circulation of the produced singlet oxygen through a chamber simulating the oxygen – iodine laser cell. A cryogenic trap placed on the way to the laser chamber prevented the penetration of the solvent vapour to the active region of the laser cell. The supply of the molecular oxygen flow through a special Schott filter dissector to the lower part of the pumped fullerene solution region was provided. This flow fulfils two main functions: compensates for the oxygen consumption in the solution and provides a more efficient transport of singlet oxygen from the solution to the gas volume. This system is similar to some extent to the bubbling scheme of the singlet-oxygen generator used in a chemical oxygen – iodine laser (COIL) [19 – 21], only instead of the aqueous $H_2O_2 -$ KOH(NaOH) solution blown through with gaseous chlorine the fullerene solution in $CCl_4$ was used, which was irradiated by a pump source and blown with oxygen. A buffer gas could be blown simultaneously with oxygen.

The solution was irradiated by 500-µs pulses from a coaxial xenon flashlamp. The pumping conditions were identical to those described in [7], except that the lamp volume in our case was 9 times larger and the cross section through which the discharge current flowed was 28 times larger. As a result, the discharge current density in the
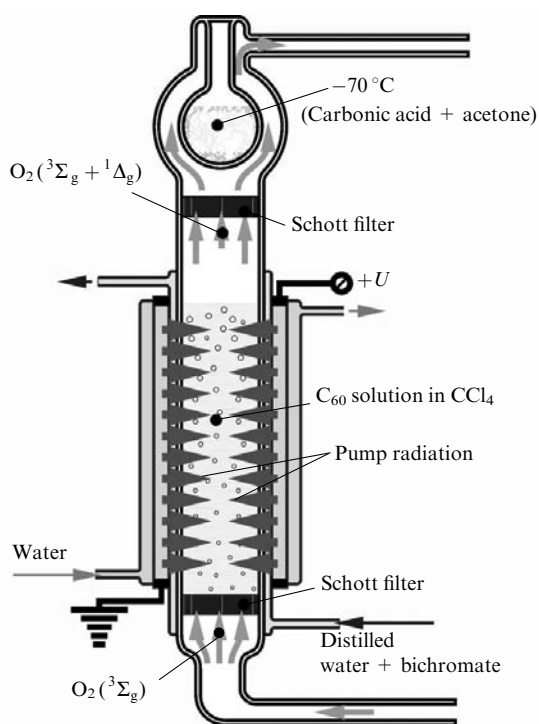
**Figure 6.** Scheme of the liquid singlet-oxygen generator.

flashlamp was considerably smaller and the brightness temperature was lower. At the same time, the coaxial design of the flashlamp provided much more efficient pumping than in [7].

The detection scheme provided the observation of luminescence at 1268 nm both from the solution volume and the gas phase at different distances from the liquid surface and irradiated region. In addition, we measured pump signals in the region from 500 to 800 nm, which gave the time interval of illumination from the pump source and allowed us to exclude it from analysis of luminescence of singlet oxygen at 1268 nm.

The preliminary results of studies performed by using this generator are illustrated in Fig. 7, which presents the luminescence signals of singlet oxygen at 1268 nm observed from the solution volume and the gas phase over it. Note

first of all that the lifetime of luminescence from the gas phase only slightly differ from that in the solution. However, the mechanisms of quenching of the excited state of oxygen in liquid and gas phases are probably different. This fact is not clear because it is unlikely that a quencher produced in the solution, which determines the lifetime of singlet oxygen in liquid, can escape to the gas phase. All this requires further detailed studies and interpretation. Note, however, that compared to the lifetime of singlet oxygen escaping to the gas phase from the irradiated solid surface, where it is efficiently quenched by products formed due to the interaction of light with the fullerene surface [1], the lifetime of singlet oxygen in the given case is considerably larger. Another characteristic feature illustrated in Fig. 8 is a rather fast decay of the luminescence intensity and, hence, of the concentration of singlet oxygen in the gas phase determining this intensity with distance from the solution surface. This is explained by the quenching of singlet oxygen with distance from the solution surface, although the luminescence lifetime remains the same within the entire gas-phase volume. The maximum luminescence intensity observed directly over the solution surface exceeds more than twice the luminescence signal from the solution volume adjacent to the liquid–phase interface, but is considerably lower than the luminescence intensity observed from the irradiated region.

Note also that the efficiency of oxygen escape to the gas phase strongly depends on the intensity of blowing gaseous
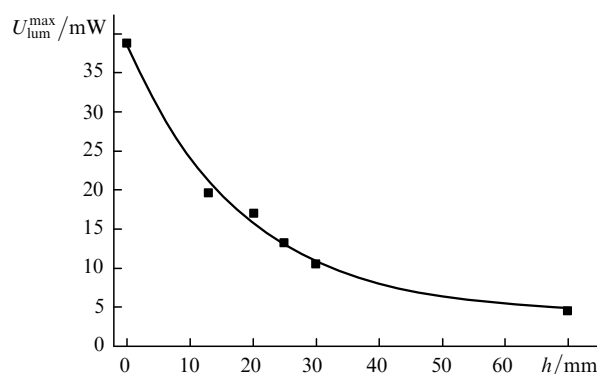


**Figure 8.** Dependence of the luminescence signal of singlet oxygen in the gas phase on the height $h$ over the liquid level.
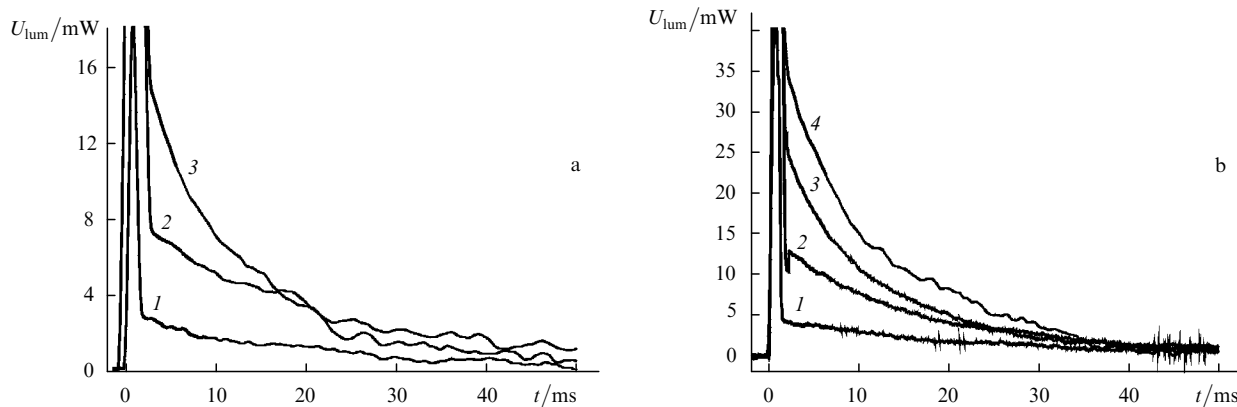


**Figure 7.** Luminescence signals of singlet oxygen in the solution (a) and gas phase over the solution (b) for volume pump energy densities 76 ( *1* ), 300 ( *2* ) and 680 mJ cm$^{-3}$ ( *3, 4* ). Curve ( *4* ) is obtained by blowing oxygen through the solution.

oxygen through the irradiated solution volume, increasing by $2-3$ times with increasing the blowing through intensity compared to the escape efficiency in the absence of blowing through (see Fig. 7). The blowing through intensity is determined by the oxygen pressure at the input to the liquid medium. This pressure (up to 1 atm) also determines the concentration of gaseous oxygen dissolved in $CCl_4$. If the solution is saturated with oxygen, the blowing of inert gas (neon) through it leads to almost the same increase in the luminescence signal as the blowing through by oxygen. This effect, however, takes place only until oxygen is stored in the solution. As oxygen is escaping from the solution, the luminescence signal decreases and can be recovered only after the repeated saturation of the solution by oxygen. This suggests that neon being purged through the solution acts as the carrier of the produced singlet oxygen. By entering into gas bubbles moving upwards through the irradiated fullerene solution, singlet oxygen is more efficiently carried out to the gas phase. It is obvious that the unexcited oxygen is also carried out to the gas phase over the irradiated solution. The ratio of the amounts of the excited and unexcited oxygen can be accurately measured with an EPR spectrometer. The results of such measurements will be presented elsewhere.

By estimating the luminescence intensity of singlet oxygen in the gas phase in absolute units, we can say that its maximum value found experimentally corresponds by the order of magnitude to the concentration of singlet oxygen in the gas phase equal to $\sim(5\pm3)\times10^{16}$ $cm^{-3}$. Note here that the design shown in Fig. 6 is far from optimal for obtaining the high output parameters of the generator. The main goal of these experiments was to confirm the efficient escape of singlet oxygen to the gas phase from the irradiated fullerene solution. This problem has been successfully solved, while the generator design will be optimised in the future studies.

## 7. Conclusions

We have studied the generation of singlet oxygen in liquid fullerene-containing media in different regimes of irradiation of solutions and suspensions, analysed the production and quenching of singlet oxygen by varying experimental conditions, and have shown that singlet oxygen can be efficiently carried out from solution to the gas phase. By continuing our earlier study [7] of the processes of singlet-oxygen quenching in the irradiated solution, these quenching mechanisms have been considered by using additionally EPR spectroscopy, which confirmed our assumption about the production of complexes of fullerene oxides in the solution, considerably restricting the lifetime of oxygen in the $^1\Delta_g$ state. The appearance and decomposition of these complexes have been also demonstrated by observing the gradual changing of the amplitude of the corresponding EPR resonance. The g-factor of the EPR resonance has been measured. The dependence of the luminescence lifetime of singlet oxygen on the $C_{60}$ concentration in solution has been found. This dependence can be explained by the presence of the fullerene $C_{70}$ impurity (0.1 %) in solution for which the rate constant of $O_2(^1\Delta_g)$ quenching is $(7.2\pm0.1)\times10^7$ L $mol^{-1}$ $s^{-1}$ [7]. According to this, the rate constant of quenching of the $O_2(^1\Delta_g)$ state by fullerene $C_{60}$ does not exceed $6\times10^4$ L $mol^{-1}$ $s^{-1}$, which is an order of magnitude lower than the value presented in [3].

The temperature and photolytic variations in the generation properties of the fullerene solution have been investigated upon intense irradiation. The studies have shown that there exists the optimal pump energy at which the maximum production of singlet oxygen is observed. This energy is determined by the inverse saturated absorption effect and processes of formation of quenchers in the solution.

The production of singlet oxygen in solution has been observed upon pulsed irradiation of astralene suspensions. It has been shown that fullerene $C_{60}$ in solution generates singlet oxygen in amounts four orders of magnitude larger than solid astralene of the same mass in the same medium.

The production of singlet oxygen was estimated quantitatively upon stationary and pulsed irradiation of solutions. It has been found that the concentration of singlet oxygen in the irradiated solution can achieve $2.5\times10^{16}$ $cm^{-3}$ in the stationary regime and $1.2\times10^{17}$ $cm^{-3}$ in the pulsed regime. It has been shown that the maximum luminescence intensity of singlet oxygen escaped from the solution corresponds to its concentration in the gas phase of $\sim(5\pm3)\times10^{16}$ $cm^{-3}$.

The concentrations of singlet oxygen in solutions obtained in experiments and first of all its concentration in the gas phase, which is comparable with concentrations measured at the initial stage of experiments with a chemical generator of singlet oxygen for a COIL [19–21], allow us to consider the results of our paper as quite optimistic for realisation of a liquid singlet-oxygen generator based on fullerene $C_{60}$ in $CCl_4$ for a fullerene–oxygen–iodine laser [22, 23].

## References

1. Belousova I.M., Belousov V.P., Danilov O.B., Ermakov A.V., Kiselev V.M., Kislyakov I.M., Sosnov E.N. *Kvantovaya Elektron.*, **38**, 280 (2008) [ *Quantum Electron.*, **38**, 280 (2008)].
2. Krasnovsky A.A. Jr. *Singletnyi molekulyarnyi kislorod i pervichnye mekhanizmy fotodinamicheskogo deistviya opticheskogo izlucheniya* (Singlet Molecular Oxygen and Primary Mechanisms of the Photodynamic Action of Optical Radiation) [Itogi nauki i tekhniki. Ser. 'Sovremennye problemy lazernoi fiziki'] (Advances of Science and Technology, Ser. 'Modern Problems of Laser Physics') (Moscow: VINITI, 1990) Vol. 3.
3. Arbogast J.W., Darmanyan A.O., Foote Ch.S., et al. *J. Phys. Chem.*, **95**, 11 (1991).
4. Belousov V.P., Belousova I.M., Grigor'ev V.A., Danilov O.B., Kris'ko A.V., Ponomarev A.N., Sosnov E.N. *Opt. Zh.*, **68**, 76 (2001).
5. Juha L., Ehrenberg B., Couris S., et al. *Chem. Phys. Lett.*, **335**, 539 (2001).
6. Danilov O.B., Belousova I.M., Mak A.A., Belousov V.P., Genishin A.S., Kiselev V.M., Kris'ko A.V., Ponomarev A.N, Sosnov E.N. *Opt. Spektrosk.*, **95**, 891 (2003).
7. Bagrov I.V., Belousova I.M., Danilov O.B., Kiselev V.M., Murav'eva T.D., Sosnov E.N. *Opt. Spektrosk.*, **102**, 58 (2007).
8. Schweitzer C., Schmidt R. *Chem. Rev.*, **103**, 1685 (2003).
9. Ponomarev A.N., Nikitin V.A. RF Patent No. 200 020 001 248 87/12(026 430) dated 21.09.00.
10. Belousov V.P., Belousova I.M., Ermakov A.V., Kiselev V.M., Sosnov E.N. *Zh. Fiz. Khim.*, **81**, 1847 (2007).
11. Ruoff R.S., Tse D.S., Malhotra R., Lorents D.C. *J. Phys. Chem.*, **97**, 3379 (1993).

12. Razumovsky S.D. *Kislorod – elementarnye formy i svoistva* (Oxygen: Elementary Forms and Properties) (Moscow: Khimiya, 1979).
13. Jenny T.A., Turro N.J. *Tetrahedron Lett.*, **23**, 2923 (1982).
14. Krasnovsky A.A. Jr., Egorov S.Yu., Nasarova O.V., Yartsev E.I., Ponomarev G.V. *Stud. Biophys.*, **124**, 123 (1988).
15. Belousov V.P., Belousova I.M., Budtov V.P., Danilov V.V., Danilov O.B., Kalintsev A.G., Mak A.A. *Opt. Zh.*, **64**, 3 (1997).
16. Sidorov L.N., Yurovskaya M.A., Borshchevskii A.Ya., Trushkov I.V., Ioffe I.N. *Fullereny: Uchebnoe posobie* (Fullerenes: Educational Manual) (Moscow: Ekzamen, 2005).
17. Shames A.I., Katz E.A., Goren S.D., Faiman D., Shtutina S. *Mat. Sci. Eng. B*, **45**, 134 (1997).
18. Leporini D., Andreozzi L., Callegari C., Fuso F. *Phys. Lett. A*, **189**, 322 (1994).
19. McDermott W.E., Pchelkin N.R., Benard D.J., Bousek R.R. *Appl. Phys. Lett.*, **32**, 469 (1978).
20. Benard D.J., McDermott W.E., Pchelkin N.R., Bousek R.R. *Appl. Phys. Lett.*, **34**, 40 (1979).
21. Yuryshev N.N. *Kvantovaya Elektron.*, **23**, 583 (1996) [*Quantum Electron.*, **26**, 567 (1996)].
22. Belousova I.M., Danilov O.B., Mak A.A. RF Patent no. 218 1224 (2002).
23. Belousov V.P., Belousova I.M., Grenishin A.S., Danilov O.B., Kiselev V.M., Kris'ko A.V., Mak A.A., Murav'eva T.D., Sosnov E.N. *Opt. Spektrosk.*, **95**, 888 (2003).