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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 196 (2008) 210–218
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Luminescence and photochemical studies of singlet oxygen photonics

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Available online 25 December 2007

Abstract

This paper starts from the short historical account presenting seminal contributions of A.N. Terenin to studies of the dye triplet states and photonics of singlet oxygen. Then, three the most successful projects of author's group dealing with singlet oxygen photonics are discussed. The most attention was devoted to discovery of photosensitized phosphorescence of singlet oxygen in the solution-phase and to its kinetic features in organic solvents and aqueous solutions after short laser pulses. The second project dealt with photosensitized luminescence, which accompanies summation of energy of two singlet oxygen molecules, and was shown to be emitted by singlet oxygen dimols $(^1O_2)_2$ or dye molecules, which accumulate energy from two $^1O_2$ molecules. The third project dealt with photochemical investigation of the oxygen absorption bands corresponding to the triplet–singlet transitions in oxygen molecules dissolved in organic solvents and water saturated with air at normal atmospheric pressure. The results of these projects have been shown to work for theoretical and applied problems of spectroscopy, photochemistry, photobiology and photomedicine.

Keywords: Singlet oxygen; Phosphorescence; Delayed fluorescence; Phthalocyanine; Naphthalocyanines; Bacteriochlorins; Oxygen dimols; Oxygen spectroscopy

1. Introduction

Singlet molecular oxygen ($^1O_2$) is known to be efficiently produced upon illumination of pigments and dyes in aerobic conditions. Singlet oxygen is highly reactive and causes oxygenation of many chemically and biologically important compounds. Therefore, $^1O_2$ is involved in numerous photodynamic reactions in chemical and biological systems and in particular, in photodynamic elimination of cancer tumors and other phenomena important for photomedicine (see reviews [1–3]). These conceptions, which are universally adopted in current scientific literature, have been proved as a result of long dramatic discussion, which lasted during more than 64 years (1900–1964). A.N. Terenin actively participated in this discussion and was the author of seminal contributions, which are described in the short historical introduction given below.

Honor of the discovery of singlet oxygen belongs to R. Mulliken. In 1928, he applied the molecular orbital theory to the oxygen molecule. He concluded that O_2 is triplet in the ground state and has two relatively low-lying singlet states. The electronic transition from the ground to one of these singlet states corresponded to the well-known Fraunhofer line at 762 nm caused by the absorption spectrum of oxygen in the Earth atmosphere. Mulliken claimed that another singlet level should have lower energy and predicted the existence of additional oxygen absorption band at about 1500 nm, which was not known at that time [4,5]. In 1933–1934, the predicted band was observed at ~1270 nm in the absorption spectra of liquid oxygen and the Earth atmosphere [6,7]. Analysis of the absorption spectra of liquid oxygen revealed also the absorption bands of oxygen dimols $(O_2)_2$ [6]. Later, the dimol absorption bands were also found in gaseous oxygen and in oxygen solutions at high pressure (about 130 atm) [8,9]. According to the modern terminology, the ground state of molecular oxygen is denoted by spectroscopic symbols $^3\Sigma_g^-$, and the singlet states by symbols $^1\Sigma_g^+$ and $^1\Delta_g$ (Fig. 1).

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doi:10.1016/j.jphotochem.2007.12.015

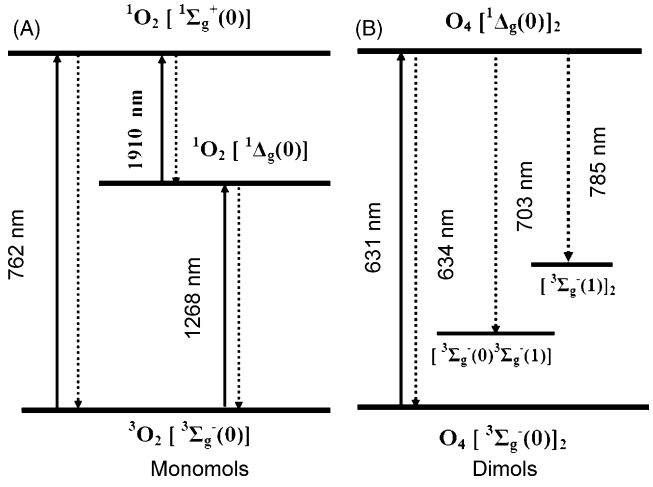

Fig. 1. Diagram of electronic transitions between the ground and the lowest excited singlet states of monomeric (A) and dimeric (B) molecules of oxygen. Solid lines show transitions caused by light absorption, dashed line correspond to radiative transitions. The wavelengths correspond to the maxima of the absorption and luminescence spectra in the gas phase. Numbers in brackets indicate vibrational sublevels.

In 1931, soon after the first Mulliken's papers, Kautsky proposed that photodynamic reactions are caused by reactive singlet states of oxygen ($^1O_2$), which are formed as a result of energy transfer from excited molecules of photosensitizers (Sens*) to O_2 [10–12]. To prove this idea, he performed a well-known experiment, during which he observed photosensitized oxygenation of substrate molecules when the substrate and photosensitizer molecules were absorbed on different silica gel grains. This experiment showed that the intermediate responsible for photooxygenation was gaseous oxygen [11].

Kautsky noticed also that oxygen quenched fluorescence and delayed fluorescence of dyes absorbed by silica gel. Quenching of delayed fluorescence by oxygen was much more efficient. Kautsky proposed that singlet oxygen can be generated by both fluorescent and metastable states of dyes [12]. It is worth noting, that nature of the dye metastable state was not clear at that time. In 1933–1935, Jablonski reported his famous diagram, where he claimed that dye molecules possess both the short-lived fluorescence state and long-lived metastable state [13]. Kautsky's ideas were too innovative for researchers at that time and were not supported. However, they stimulated very active discussion. The first alternative explanation of Kautsky's experiments was proposed by Weis [14] and Franck and Livingston [15]. They suggested that photooxygenation proceeded due to formation of free radicals $^{\bullet}O_2^-$ and $HO_2^{\bullet}$, which appear in the reaction between excited photosensitizer molecules and oxygen.

Terenin joined this discussion in 1943, when he claimed that the fluorescence state of dyes is singlet and the metastable state is triplet [16,17]. One year later, Lewis and Kasha independently came to the same conclusion [18]. Terenin also claimed that two mechanisms of $^1O_2$ generation by photoexcited dye molecules are allowed by the principle of the constancy of the total spin of the system (the Wigner rule) [16,17]:

$$^1\text{Sens} * (\uparrow\downarrow) + {}^3O_2(\uparrow\uparrow) \rightarrow {}^3\text{Sens} * (\uparrow\uparrow) + {}^1O_2(\uparrow\downarrow) \quad (1)$$

$$^3\text{Sens} * (\uparrow\uparrow) + {}^3O_2(\downarrow\downarrow) \rightarrow {}^1\text{Sens} * (\uparrow\downarrow) + {}^1O_2(\uparrow\downarrow) \quad (2)$$

where ^{1}Sens, ^{1}Sens* and ^{3}Sens* are photosensitizer molecules in the ground, singlet and triplet states. The first mechanism is possible for relatively small group of photosensitizers whose energy gaps between ^{1}Sens* and ^{3}Sens* is more than energies of the singlet states of oxygen. The second mechanism is possible for much more abundant group of photosensitizers whose triplet levels are higher than the singlet levels of oxygen. Terenin stressed that the triplet states of dyes should be much more efficient than the singlet states in promotion of photodynamic oxygenation reactions because the lifetime of ^{3}Sens* is 10^3 to 10^7 times longer than the lifetimes of ^{1}Sens*. In 1952, Terenin and Ermolaev discovered triplet-triplet energy transfer between dye molecules [19]. According to Dexter, this process is a result of exchange energy transfer [20]. Singlet oxygen formation was proposed to be a result of the same energy transfer between triplet dye and oxygen molecules where oxygen molecules are energy acceptors [21,22].

Terenin's mechanisms provided comprehensive explanation of Kautsky's data obtained in the heterogeneous systems. However, Terenin suggested in his first papers that biradical complex of triplet dye molecules with oxygen (moloxide) should be more reactive and play more important role in photodynamic reactions in homogeneous solutions [16,17]. Similar ideas were supported by most photochemists at that time ([23] and refs. therein).

In 1964, Foote and Wexler [24,25] and then Corey and Taylor [26] proved that the singlet $^1\Delta_g$ state of oxygen, is the primary reactive intermediate in the Type II photodynamic processes in the solution-phase. Their work was stimulated by the chemiluminescence studies of several groups. These groups observed that $^1O_2$ luminescence appeared in the dark without photosensitizers under the electrodeless microwave discharge in the gas stream or in bubbles of oxygen released in the chemical reaction of H_2O_2 with Cl_2 or ClO^- ([27–29] and refs. therein). Foote and Wexler [24,25] and Corey and Taylor [26] discovered that $^1O_2$ formed in these luminescence systems reacted chemically in the darkness with certain substrates of the photodynamic reactions. The reaction products were identical to those, which were formed photochemically.

It became clear after these experiments and subsequent papers of many researchers that Terenin's mechanisms of singlet oxygen production are valid also in liquid solutions and biological systems. Therefore, early Terenin's papers laid down the basics, on which current concepts of photodynamic action and photonics of singlet oxygen are built. Terenin's papers and his personality strongly influenced also my work. Below, the lecture of this author at the memorial Terenin meeting at St. Petersburg is presented. It summarizes three the most successful projects of my group, which dealt with photonics of singlet oxygen.

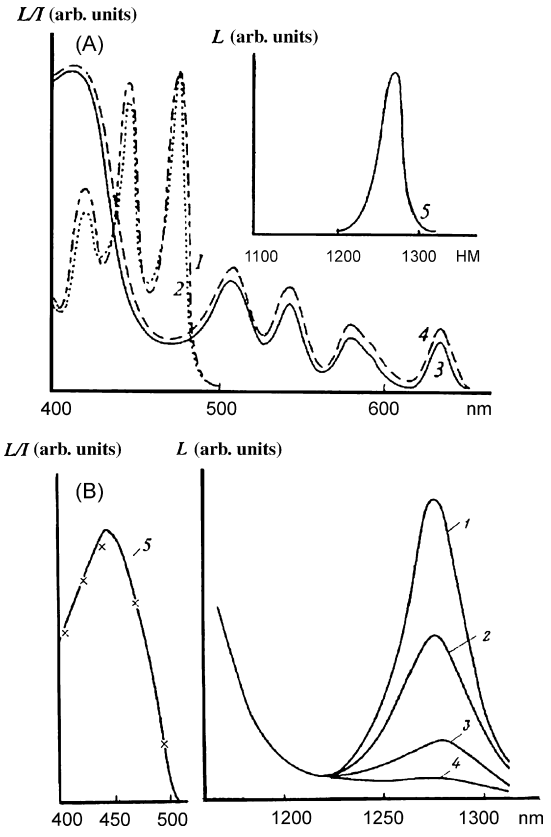

Fig. 2. The results of the first measurements of photosensitized phosphorescence of singlet oxygen in the solution-phase: (A) absorption spectra of naphthacene and protoporphyrin IX d.m.e. in air-saturated carbon tetrachloride (1 and 3). Excitation (2 and 4) and emission (5) spectra of singlet oxygen phosphorescence in the same solutions as measured at the set-up with the mechanical phosphoroscope [30] and (B) emission spectra of oxygen phosphorescence in D_2O (1) and in D_2O containing 5% (2) and 50% (3) H_2O and in H_2O (4). Left part: the absorption spectrum of riboflavin in D_2O (solid line) and excitation spectrum of oxygen phosphorescence (×). *L* is the phosphorescence intensity and *I* is the intensity of excitation [36].

2. Photosensitized phosphorescence of singlet oxygen

The photosensitized phosphorescence of $^1O_2$ ($^1\Delta_g$, 1270 nm) in air-saturated solutions of pigments was discovered by this author in 1976 [30]. The results of the first phosphorescence measurement in an organic solvent are shown in Fig. 2A. Phosphorescence was observed using a mechanical phosphoroscope, cooled S-1 photomultipliers and continuous light sources (xenon lamps) in air-saturated carbon tetrachloride due to energy transfer from triplet molecules of protoporphyrin or tetracene to oxygen. During 1977–1979, we found this phosphorescence also in solutions of many photodynamically active pigments including porphyrins, chlorophylls, bacteriochlorophylls, pheophytins and retinals. The solvents were CCl_4, CS_2 and Freon 113 where the singlet oxygen lifetime was shown to be very high, ≥20 ms. It was demonstrated that phosphorescence measurements can be easily used for determination of the $^1O_2$ lifetimes, quantum yields of $^1O_2$ production and the rate constants of $^1O_2$ quenching by different compounds ([30–34] and refs. therein). Later, the steady-state measurements of photosensitized $^1O_2$ phosphorescence were performed in organic solvents whose molecules contained hydrogen atoms, deuterium oxide and water [35–39]. The results of the first phosphorescence measurement in D_2O and D_2O–H_2O mixtures are shown in Fig. 2B [36]. In parallel, the technique for time-resolved phosphorescence detection after short pulses of lasers or flash lamps was developed in the Minsk Institute of Physics [40–42]. Phosphorescence was measured through the interference filter with the transmission maximum at 1270 nm. Detectors were cooled S-1 photomultipliers or germanium photodiodes. The phosphorescence kinetic traces were registered by storage oscilloscopes. In 1982–1983, time-resolved set-ups with germanium photodetectors and computer systems of signal averaging over a few laser pulses appeared in the USA ([43–45] and refs. therein). The power of excitation pulses in these papers varied from 3 to 400 mJ. This technique allowed microsecond time-resolution and reliable detection of the decays of photosensitized $^1O_2$ phosphorescence after laser shots in organic solvents and deuterium oxide. The use of this equipment for investigation of singlet oxygen in aqueous pigment solutions and biological materials was not quite successful (see [46] for the detailed review of the data obtained before 1998).

In 1983, we found more efficient technical solutions and markedly raised the sensitivity of time-resolved measurements by using for phosphorescence excitation pulsed nitrogen lasers with short pulse duration (10–20 ns) and high pulse repetition rates. Phosphorescence was measured by cooled S-1 photomultipliers using time-resolved photon counting and signal accumulation from unlimited number of laser pulses [47]. These measurements allowed us to greatly improve the signal-to-noise ratio. As a result, we got an opportunity to use low intensity laser pulses for phosphorescence excitation (10–20 μJ) and to measure phosphorescence through a monochromator that allowed simultaneous control of the phosphorescence spectra and kinetic traces. The time resolution of the first set-up of this type was limited by the dwell time (5 μs) of our multichannel analyzer. However, reliable phosphorescence decays after laser shots were obtained in organic solvents, deuterium oxide and water ([47–49] and refs. therein).

In 1988, we achieved nanosecond resolution owing to application of copper-vapor lasers with 10–12 kHz pulse repetition rates, 20 ns pulse duration and phosphorescence detection using time-correlated single photon counting [50–52]. Later, we additionally improved this equipment by using better laser generators and electronic registration systems [3,46,53,54]. Fig. 3 shows the functional layout of the laser set-up, which presently works in our laboratory. Since 1997, Hamamatsu Photonics Company started to manufacture similar set-ups using novel photomultipliers with the InP/InGaAs and InP/InGaAsP photocathods, which are highly sensitive in infrared [55]. Such set-ups are the most efficient because they combine high sensitivity and high (nanosecond) time resolution, therefore they are presently employed in many laboratories.

The use of the nanosecond set-ups allows detailed analysis of the phosphorescence kinetic curves after short laser shots in air-saturated water and organic solvents [3,46,50–54]. Fig. 4 shows that these curves comprise two phases: rise and decay, with a peak in between, and can be approximated by the following

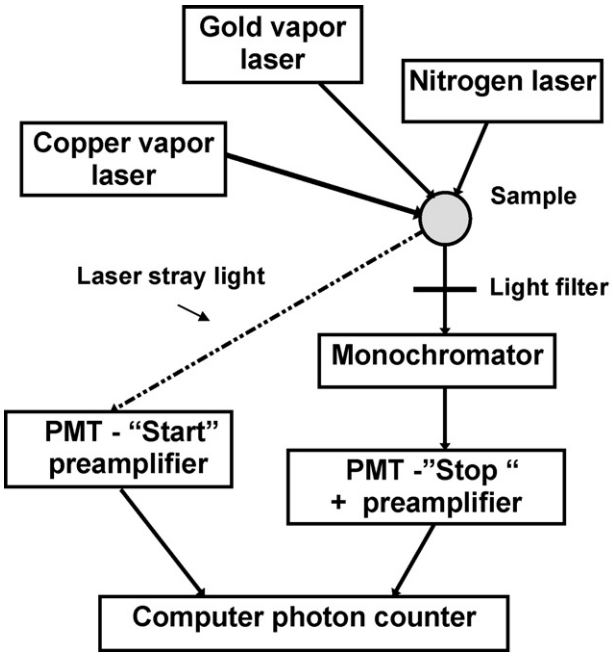

Fig. 3. Functional layout of the laser phosphorescence spectrometer with nanosecond resolution [3].

two-exponential equation:

$$L(t) = L_0 \left[\exp\left(-\frac{t}{\tau_{decay}}\right) - \exp\left(-\frac{t}{\tau_{rise}}\right) \right] \quad (3)$$

where $L(t)$ is the phosphorescence intensity in Einstein's per second, L_0 the pre-exponential factor and τ_{decay} and τ_{rise} are time-constants of the decay and rise phases.

Similar equation can be obtained from the kinetic analysis based on Terenin's mechanism (2), i.e. $^1O_2$ production by energy transfer to oxygen from triplet photosensitizer molecules:

$$L(t) = \frac{k_{et} k_{rad} [^3\text{Sens}^*]_0 [O_2]}{(1/\tau_T - 1/\tau_\Delta)} \left[\exp\left(\frac{-t}{\tau_\Delta}\right) - \exp\left(\frac{-t}{\tau_T}\right) \right] \quad (4)$$

where k_{et} is the rate constant of $^1O_2$ generation as a result of energy transfer from ^{3}Sens* to oxygen, k_{rad} the rate constant of $^1O_2$ radiative deactivation, $[^3\text{Sens}^*]_0$ the concentration of triplet photosensitizer molecules just after the laser pulse, $[O_2]$ is the concentration of oxygen, τ_T is the lifetime of ^{3}Sens* in oxygen-containing solutions ($1/\tau_T = k_q[O_2] + k_T$, where k_q is the rate constant of overall deactivation ^{3}Sens* by oxygen, including energy transfer and quenching, and k_T is the rate constant of spontaneous ^{3}Sens* deactivation), τ_Δ is the $^1O_2$ lifetime. Analysis of Eq. (4) shows that the physical sense of τ_{rise} and τ_{decay} in Eq. (3) depends on the relative magnitudes of τ_T and τ_Δ. If $\tau_\Delta > \tau_T$, $\tau_{rise} = \tau_T$, and $\tau_{decay} = \tau_\Delta$. Hence, the phosphorescence rise time corresponds to the lifetime of the photosensitizer triplet state and the decay time corresponds to the singlet oxygen lifetime. If $\tau_\Delta < \tau_T$, the pre-exponential factor in Eq. (4) changes its sign, therefore $\tau_{rise} = \tau_\Delta$, and $\tau_{decay} = \tau_T$. Hence, the phosphorescence rise time corresponds to the singlet oxygen lifetime and the decay time corresponds to the lifetime of the photosensitizer triplet states. We proposed a term "kinetic inversion" to denote this phenomenon [3,53,54].

Experiments have shown that Eq. (4) correctly describes the phosphorescence kinetic traces. We observed that in air-saturated porphyrin solutions the phosphorescence rise time in organic solvents and water coincided with the lifetime of the porphyrin triplet state in the same solutions and the decay time was equal to the lifetimes of singlet oxygen (Table 1) [3,53,54]. If oxygen concentration in aqueous porphyrin solutions was changed from 0.2 to 15 atm., the decay time did not change within the accuracy of our measurements. At the same time, the rise time decreased with the increase of the oxygen concentration and was always equal to the lifetime of the porphyrin triplet state (Table 2) [50,51]. Recently, Dedic et al. have shown that when the oxygen concentration was reduced and became about 3 times less than in air-saturated solution, τ_{decay} increased up to 5–5.5 μs [56]. The values of τ_{rise} and τ_T were not reported. However, it is easy to calculate that τ_T should be equal to 5–6 μs that resembles τ_{decay} in this experiment. In my opinion, we see in this case the "kinetic inversion" mentioned above. Indeed, in this experiment, τ_T was more than τ_Δ therefore, the phosphorescence decay time was equal to τ_T.

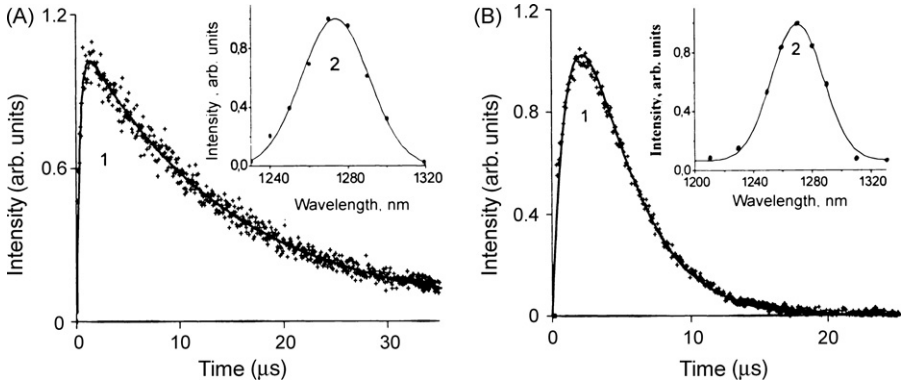

Fig. 4. (A) Kinetic curve (1) and spectrum (2) of $^1O_2$ phosphorescence in air-saturated ethanolic solution tetra(*p*-sulfophenyl) porphyrin (15 μM) after the laser pulse. The kinetic curve was obtained as a result of averaging the signal from 2.4×10^6 laser pulses and (B) kinetic curve (1) and spectrum (2) of $^1O_2$ phosphorescence in air-saturated solutions of tetra(*p*-sulfophenyl) porphyrin (15 μM, pH 5.8) in water (1) after the laser pulses. The curve was obtained as a result of averaging the signal from 1.2×10^7 laser pulses. Dots show experimental data, the solid lines are computer approximations according to Eq. (3). The spectra correspond to the overall phosphorescence intensity in the interval 1–45 μs after the laser pulse [3,54].

Table 1
Kinetic parameters of singlet oxygen phosphorescence in air-saturated solutions of tetraphenylporphyrin (benzene) and its tetra(*p*-sulfophenyl)porphin (TPPS) (other solvents)

Solvents	τ_{decay} (μs) (±5%)	τ_{rise} (μs) (±10%)	τ_T (μs)[a] (±10%)	τ_Δ[b] (μs)
Benzene	30	0.40	0.35	30
Methanol	10	0.40	0.40	10
Ethanol +4% water	13.5	0.40	0.40	10–15
Water	3.2	2.0	2.0	3–4

[a] Obtained by the flash-photolysis method.
[b] Literature data [40–45].

It should be noted here that if τ_Δ is equal toτ_T ($\tau_T \rightarrow \tau_\Delta$), Eq. (4) does not work. It is transformed into the formula:

$$L(t) = k_{et}k_{rad}[^3\text{Sens}^*]_0[O_2]t \exp\left(\frac{-t}{\tau}\right) \quad (5)$$

This causes problems, when one approximates experimental data using Eq. (4). We noticed that if the standard programs "Origin" or "Grafit" were used and the ratios τ_Δ/τ_T were 10–100, computers calculated parameters τ_T and τ_Δ with high precision and the obtained numbers were reproduced very well in different experiments. If the difference between these parameters was small, like in water or especially, in aqueous solutions of $^1O_2$ quenchers, the fitting parameters were reproduced markedly worse and were much more sensitive to the level of the noise and technical properties of the equipment. Probably due to this reason, the fitting parameters reported by different groups for aqueous porphyrin solutions saturated with air do not quite coincide. The reported decay times varies from 3.1 to 3.9 μs and the rise times from 1.7 to 2.2 μs [50–58].

With a goal of mimicking the "kinetic inversion", we studied quenching of $^1O_2$ phosphorescence in air-saturated aqueous solutions of tetra(*p*-sulfophenyl)porphin (TPPS) by sodium azide [3,53,54]. We observed that addition of sodium azide decreased the overall phosphorescence intensity according to the Stern–Volmer equation with the quenching rate constant $(4 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$. However, the phosphorescence decay

Table 2
The rise and decay times of $^1O_2$ phosphorescence after the laser pulses in aqueous solutions of TPPS (20 μM) at different oxygen concentrations in solutions

Oxygen pressure (atm.)	τ_{decay} (μs) (±6%)	τ_{rise} (μs) (±10%)	τ_T (μs)
0.07[d]	5	–	5.7
0.2[b]	3.2	2.0	2.0
1.0[c]	3.2	0.45	0.4
4[a]	3.08	0.11	0.1
6[a]	3.11	0.08	0.07
8[a]	3.11	0.06	0.05
10[a]	3.08	0.04	0.04
15[a]	3.06	0.03	0.024

τ_T for the oxygen concentrations corresponding to 0.2 and 1 atm. were measured by this author using the flash photolysis method, for other oxygen pressures, τ_T was calculated using the equation: $\tau_T = 1/k_q[O_2]$, where k_q is the rate constant of quenching the triplet TPPS by oxygen.
[a] From Refs. [50,51].
[b] From Ref. [54].
[c] New measurements.
[d] From Ref. [56].

Table 3
The rise and decay times of $^1O_2$ phosphorescence after the laser pulses in air-saturated aqueous solutions of TPPS (15 μM) containing sodium azide [54]

Sodium azide (mM)	τ_{decay} (μs)	τ_{rise} (μs)
0	3.2 ± 0.2	2.0 ± 0.2
3	1.9 ± 0.2	1.3 ± 0.4
6	1.9 ± 0.2	0.8 ± 0.3
9	1.8 ± 0.2	0.6 ± 0.2
12	1.9 ± 0.2	<0.4

time changed from 3.15 ± 0.2 μs in pure water to about 1.9 μs after addition of 3 mM azide. Further increase of azide concentration caused strong reduction of the phosphorescence intensity but did not change τ_{decay}, which was apparently equal to the lifetime of the TPPS triplet state (Table 3). Simultaneously, the rise time decreased to several hundred nanoseconds that corresponded to the $^1O_2$ lifetimes calculated from the Stern–Volmer equation. Hence, sodium azide did not quench the TPPS triplet state, and strongly decreased τ_Δ, which became less than τ_T. This caused the "kinetics inversion", i.e. in the presence of the high azide concentration, the rise time of the phosphorescence kinetic curve reflected the $^1O_2$ lifetime (τ_Δ). The decay time reflected the lifetime of the triplet porphyrins caused by the rate of interaction of triplet porphyrin molecules with oxygen (τ_T). Similar inversion occurred in detergent-containing solutions in the presence of sodium azide [54].

The inversion phenomenon is especially important when one studies $^1O_2$ phosphorescence in living cells and tissues, because the lifetimes of the pigment triplet states in biological systems are longer than in solutions (usually about 10 μs), and the lifetime of singlet oxygen (10–200 ns) is much shorter than the lifetime of the photosensitizer triplet state ([46,59] and refs. therein). Registration of the kinetic traces in dye-loaded living cells is a technically difficult problem. A few years ago, we managed to measure the kinetic curves of flash-induced $^1O_2$ phosphorescence in suspensions of porphyrin-loaded yeast cells and blood plasma in buffer solutions [50,51,53]. More recently, Neidre et al. [57] and Baier et al. [58] reported time-resolved phosphorescence measurements in stained skin tissues and suspensions of cancer cells. In my opinion, the reported data indicate that in stained blood plasma, rat liver and suspensions of cancer cells [53,57,58] the "kinetic inversion" occurred and the phosphorescence decays were determined by the triplet state of photosensitizer molecules. Analysis of recent papers of several groups shows that the "kinetic inversion" is usually

not taken into account. Apparently, this can result in wrong interpretation of the data.

Thus, at present, measurements of photosensitized $^1O_2$ phosphorescence are widely used for photochemistry and photobiology research. Recently, clear correlation was found between photodynamic elimination of cancer cells and the singlet oxygen phosphorescence intensities. As a result, two new directions of biomedical phosphorescence research appeared: phosphorescence imaging and phosphorescence dosimetry [50,51,57,58,60–65].

3. Photosensitized luminescence of oxygen dimols $(O_2)_2$

Photosensitized luminescence of singlet oxygen dimols was actually observed for the first time in our experiments with porphyrin solutions using the set-up with a mechanical phosphoroscope. It was found that $^1O_2$ phosphorescence photosensitized by dimethyl ester of protoporphyrin IX (PP) in air-saturated CCl_4 was accompanied by much less intensive delayed light emission in the visible region with the maximum at 700 nm, which coincided with one of the emission bands of dimols. The intensity of this light emission was proportional to the square of the intensity of exciting light. Upon illumination, the luminescence intensity slowly increased and a new peak at about 760 nm appeared [30,32]. Further studies of porphyrin solutions have shown that the maximum at 703 nm dominated also in the spectrum of delayed luminescence of solutions of tetraphenylporphin (TPP), pheophytin *a* (PN) and pheophorbide *a*. In TPP solutions, this light emission was about 100 times weaker than in solutions of other porphyrins. The 635 nm band of singlet oxygen dimols was not observed in the delayed luminescence spectra of porphyrin solutions. However, weak shoulders were observed in the spectral region of the pigment fluorescence maxima (640, 650 and 680 nm in solutions of PP, TPP and PN, respectively) [32,66–68].

Photosensitized delayed luminescence with typical bands of dimol emission was found when we studied solutions of 2,3,7,8-dibenzopyrene-1,6-quinone and Pd-tetraphenylporphyrin, the concentrations of which corresponded to 3–8 and 30–100 μM, respectively. These dyes are practically non-fluorescent (the fluorescence yield is known to be <0.1%) and the energies of their fluorescent levels are much higher that the energy levels of singlet oxygen dimols. The delayed luminescence spectra in solutions of these dyes in CCl_4 and C_6F_6 showed three bands, the major, at 703 nm and two weaker bands, at 635 and 770–780 nm [67–69] (Fig. 5). These bands coincided with the spectral maxima of light emission by singlet oxygen dimols $(^1O_2)_2$ (Fig. 1) [28,29]. The band at 703 nm always dominated in the spectra of delayed luminescence. Relative intensities of other bands markedly depended on the time of storage of the solutions at room temperature and the presence of dye crystals, which appeared during storage of filtered solutions of dibenzopyrenequinone. The intensities of all luminescence bands were proportional to the square of the intensity of exciting light. The lifetime was equal to the half of the $^1O_2$ phosphorescence lifetime [66–68].

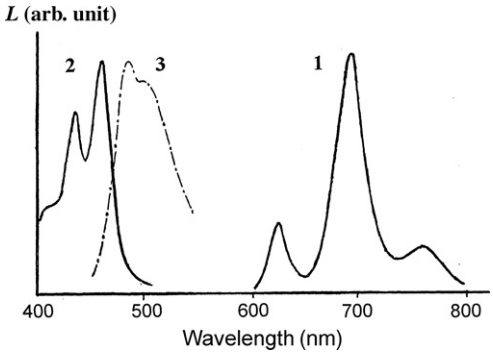

Fig. 5. The spectrum of photosensitized luminescence of dimols $(^1O_2)_2$ in air-saturated solutions of 2,3,7,8-dibenzopyrene-1,6-quinone (3 μM) in carbon tetrachloride (1) and normalized absorption (2) and fluorescence (3) spectra of the same solution (see [67,68] for details).

In light of these data, we proposed that the delayed luminescence of porphyrin and dibenzopyrenequinone solutions appeared as a result of interaction of two singlet oxygen molecules with dye molecules or products of their oxygenation. Dimols $(^1O_2)_2$ are the major emitters of this light emission. In certain cases, the delayed luminescence was probably generated on the surface of dye crystals. Tetraphenylporphin was proposed to have an ability to partially suppress the dimol light emission.

Chou et al. supported our observation of photosensitized luminescence of singlet oxygen dimols [70,71]. They studied air-saturated solutions of another non-fluorescent dye-phenalenon in CCl_4, C_6F_6 and C_6D_6 upon excitation by argon-ion laser (350 nm). As a result, delayed luminescence was observed with three spectral maxima at 634, 703 and 765 nm. The bands at 634 and 703 nm corresponded to singlet oxygen dimols, the band at 765 nm was proposed to appear due to direct energy transfer to oxygen from triplet phenalenon. The intensities of the dimol bands did not change in solutions of 2′-acetonaphtone, 1-acetonaphthone and if singlet oxygen was produced by photolysis of 1,4-dimethylnaphthalene endoperoxide. The lifetime of the dimol luminescence was always two times less than the lifetime of 1273 nm phosphorescence of singlet oxygen and the intensity of dimol emission was proportional to the square of the phosphorescence intensity when laser power was changed.

Thus, the data of Chou et al. resembled our data. However, in Chou's measurements, the intensity of the 634 nm band was higher than the intensity of the 703 nm band. The authors proposed that the delayed luminescence they observed corresponded to free singlet oxygen dimols, which are not bound to photosensitizer molecules [70,71]. It is also worth noting that the power density of excitation radiation in Chou's papers was much higher than in our experiments. Recently, Kazakov and Schmidt reported time-resolved measurement of dimol luminescence upon powerful pulse laser excitation of photosentizers in a few solvents [72]. The kinetic parameters of this luminescence resembled those reported in our papers [66–68] and by Chou et al. [70,71].

In aerobic solutions of dyes (phthalocyanines, naphthalocyanines and bacteriochlorines) whose fluorescence is strong and the fluorescence maxima are at $\lambda \geq 700$ nm, we observed

Table 4
Values of A_{1270} and ε_{1270} calculated from the rates of DPIBF (43 ± 3 μM) photobleaching in the pigment-free air-saturated solvents upon irradiation by the array of the diode GaAlAs lasers (50 mW) [89]

	CCl_4	$CHCl_3$	Freon 113	C_6F_6	C_6H_6	Toluene	Acetone	Ethanol
A_{1270} (arb. units)	1[a]	0.88	1.1	1.7	0.92	0.93	0.53	0.50
ε_{1270} (arb. units)	1[a]	0.95	0.55	1.0	1.25	1.35	0.60	0.80
$\varepsilon_{1270}/k_{rad}$ (arb. units)	1	0.95	0.90	1.1	0.9	0.95	1.1	1.6

k_{rad} is the rate constant of the radiative deactivation of singlet oxygen.
[a] In CCl_4, $A_{1270} = 7.2 \times 10^{-6}$ and $\varepsilon_{1270} = 0.003\ M^{-1}\ cm^{-1}$ [87].

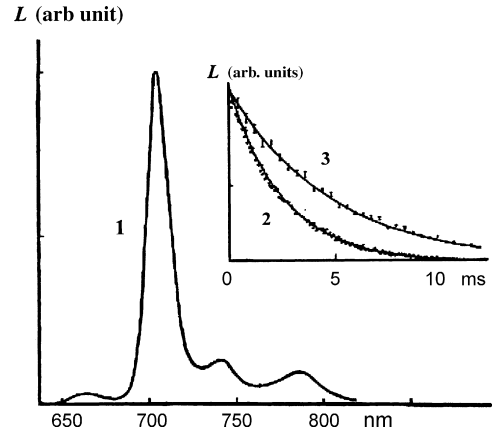

Fig. 6. Spectrum of singlet-oxygen-sensitized delayed fluorescence of tetra(4-*tert*-butyl) phthalocynine in hexafluorobenzene (1). The decays of phthalocynine delayed fluorescence (2) and $^1O_2$ phosphorescence (3) after nanosecond shots of nitrogen laser in the same solution. The phthalocyanine concentration was 0.5 μM. Curves 2 and 3 were obtained by summation of the signal from 10^3 and 10^5 laser pulses, respectively. The spectrum was recorded using steady-state regime of measurements. The monochromator slits corresponded to the wavelength interval equal to 5 nm.

dye delayed fluorescence whose lifetime was exactly two times smaller than the $^1O_2$ lifetime in the same solution (Fig. 6) [66–68]. To denote this light emission, a term singlet-oxygen sensitized delayed fluorescence (SOSDF) was proposed [73]. SOSDF was found in phthalocyanine solutions in CCl_4, C_6F_6, C_6D_6, chloroform, benzene, acetone and D_2O. The SOSDF intensity was higher than the intensity of dimol luminescence by several orders of magnitude. The intensity of SOSDF depended quadratically on the intensity of exciting light and linearly on the dye concentrations [66–68,74–76]. This showed that light was emitted due to interaction of two $^1O_2$ molecules and one dye molecule. Moreover, we discovered that under rather low-intensity laser excitation, the intensity of SOSDF in solutions of certain phthalocyanines and naphthacocyanines was much stronger than that of infrared $^1O_2$ phosphorescence at 1270 nm [77,78]. Detailed analysis, which was performed in solutions of tetra (4-*tert*-butyl) phthalocynine in deuterated benzene, indicated that the quantum yield of SOSDF reached ≥10% if the phthalocyanine concentrations exceeded 2 μM [77]. It was also found that phthalocyanine SOSDF is quenched by many biologically important compounds. The quenching obeys the Stern–Volmer equation therefore, analysis of SOSDF quenching can be used for measurement of the rate constants of the reactions of singlet oxygen with different molecules [72]. In addition, SOSDF was detected upon thermal decomposition of endoperoxides in solutions containing both phthalocyanine and endoperoxides [79].

Thus, during this project we discovered two novel luminescence phenomena: photosensitized luminescence of singlet oxygen dimols and singlet-oxygen-sensitized delayed fluorescence of phthalocyanines, naphthalocyanines and bacteriochlorins. SOSDF accompanied accumulation of energy of two $^1O_2$ molecules by one molecule of dyes. It was also found that the SOSDF intensity under pulse laser excitation in solutions of phthalocyanines and naphthalocyanines was much higher than the intensity of infrared $^1O_2$ phosphorescence. In addition, SOSDF is emitted in the dark red region, which is more convenient for luminescence measurement than infrared. Hence, detection of phthalocyanine delayed fluorescence can be used as a sensitive luminescence tool for investigation of singlet oxygen in different systems. The mechanistic aspects of the studied phenomena will not be discussed in this paper. One can refer to papers [3,71,80,81], where different points of view are presented.

4. Activation of oxygen by direct laser excitation

In the previous sections, we dealt with pigment-photosensitized singlet oxygen production. As shown in classic papers of Evans's and Matheson's groups, at high oxygen pressure (about 100–130 atm.) singlet oxygen can also be produced without pigments due to direct excitation of oxygen molecules by radiation of powerful lamps or lasers [8,82–84]. Though conditions of these experiments were very far from normal for biological systems, an idea was advanced that direct oxygen excitation might be involved in biological effects of laser radiation ([85] and refs. therein). With a goal of mimicking effects of low energy laser irradiation, a few years ago we started systematic analysis of the efficiency of $^1O_2$ formation upon direct laser excitation of oxygen molecules in organic solvents and water saturated by air at normal atmospheric pressure. We found that laser irradiation at 765 (500–750 mW) and 1270 nm (30–150 mW) causes readily observed photooxygenation of the $^1O_2$ traps tetracene or 1,3-diphenylisobenzofuran (DPIBF) in air-saturated solvents [86–90]. The action spectra of photooxygenation measured in carbon tetrachloride within the 1220–1290 and 740–790 nm range showed two narrow bands with the maxima at 1273 and 765 nm (Fig. 7). The obtained data provided unambiguous evidence that photooxygenation occurred due to direct laser excitation of dissolved

oxygen:

$$O_2[^3\Sigma_g^-(v=0)] + h\nu_{765} \rightarrow {}^1O_2[^1\textstyle\sum_g^+(v=0)] \rightarrow {}^1O_2[^1\Delta_g(v=0)]$$

$$O_2[^3\Sigma_g^-(v=0)] + h\nu_{1270} \rightarrow {}^1O_2[^1\Delta_g(v=0)]$$

$$^1O_2(^1\Delta_g) + \text{Trap} \rightarrow \text{oxygenation}$$

Using this mechanistic scheme and experimentally measured photooxygenation rates, we obtained that in CCl_4 saturated with air at normal atmospheric pressure, the optical density (A) and molar absorption coefficient (ε) of molecular oxygen at 1273 nm are equal to 7.2×10^{-6} (in the 10 mm cell) and $\approx 0.003\ M^{-1}\ cm^{-1}$, respectively [87]. At 765 nm, these parameters are 3.5 times smaller [90]. Table 4 shows A_{1270} and ε_{1270} estimated by the mentioned photochemical method in several organic solvents. The data indicate that the values of ε_{1270} reasonably correlate with the values of k_{rad}, which were measured by the phosphorescence method ([89] and refs. therein). The values of A_{1270} and ε_{1270} were also estimated in water and deuterium oxide. However, in these experiments detergents were used to solubilize DPIBF therefore, the aqueous solutions contained the hydrophobic micellar pseudophase. The data indicate that in 0.1 M SDS solutions the micellar pseudophase, which takes less than 3% of total volume, doubles the oxygen absorbance of the overall solution [90]. This probably happens because in hydrophobic micelles, the solubility of oxygen and the $^1O_2$ radiative rate constant are markedly higher than in water [91–93].

Thus, the results of this project indicate that direct excitation of oxygen molecules by infrared laser radiation causes readily observed oxygenation of singlet oxygen traps under normal conditions. These oxygenation reactions allow researchers to investigate the absorption bands of molecular oxygen in solutions at atmospheric pressure. The most efficient oxygen excitation was shown to occur in hydrophobic structures. However, even in these structures the absorbance of oxygen and the rates of $^1O_2$ generation caused by direct oxygen photoexcitation is very low. In the paper [88], we compared the rates of tetracene photooxygenation in CCl_4 under direct oxygen excitation by 1267 nm laser radiation and under protoporhyrin-photosensitized $^1O_2$ production. It was shown that the quantum efficiency (the ratio of the reaction rate to the intensity of exciting light in photons per second) is about 10^4 to 10^5 times (depending on the porphyrin concentration) higher in the porphyrin-photosensitized reaction. Owing to respiration, the concentration of free oxygen in living cells is known to be 100–1000 times less than in air-saturated CCl_4. Therefore, it is difficult to imagine that direct excitation of free oxygen dissolved in living structures causes strong destructive consequences. However, it is not excluded that IR radiation can influence bound oxygen molecules whose concentration is much more in biological systems.

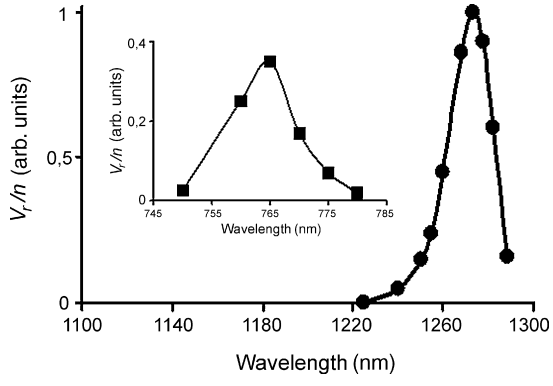

Fig. 7. Action spectra of tetracene photobleaching in carbon tetrachloride upon irradiation by cw wavelength tunable lasers. V_r is the rate of tetracene photobleaching, n is the number of photons of laser radiation [87,90].

5. Conclusion

Thus, this paper shortly summarizes results of three research projects of author's group dealing with singlet oxygen photonics. All projects are directly connected with basic ideas presented in seminal Terenin's works. One project resulted in discovery of the solution-phase photosensitized phosphorescence of singlet oxygen, which is presently used worldwide as the most reliable method for investigation of singlet oxygen and photosensitized oxygenation reactions. The major attention was devoted to nanosecond time-resolved measurements of this phosphorescence in aqueous solutions and to the phenomenon of the "kinetic inversion", which is especially important for understanding the results of phosphorescence studies of singlet oxygen in biological systems. The second project dealt with photosensitized luminescence, which accompanies summation of energy of two singlet oxygen molecules. This luminescence was shown to belong to singlet oxygen dimols ($^1O_2)_2$ or dye molecules, which accumulate energy from two $^1O_2$ molecules. The third project was devoted to photochemical investigation of the oxygen absorption bands corresponding to the triplet–singlet transitions in oxygen molecules dissolved in organic solvents and water saturated with air at normal atmospheric pressure. It has been shown that the luminescence and photochemical phenomena studied in our work provide unique information about photonics of singlet oxygen, which is important for photochemical, photobiological and biomedical research.

References

[1] C.S. Foote, E.L. Clennan, in: C.S. Foote, J.S. Valentine, A. Greenberg, J.F. Liebman (Eds.), Active Oxygen in Chemistry, Black Academic Professionals, London, 1995, pp. 105–140.
[2] M.J. Ochsner, Photochem. Photobiol. B: Biol. 39 (1997) 1–18.
[3] A.A. Krasnovsky Jr., Biofizika 49 (2004) 305–321.
[4] R.S. Mulliken, Nature 122 (1928) 505.
[5] R.S. Mulliken, Phys. Rev. 32 (1928) 880–887.
[6] J.M. Ellis, H.O. Kneser, Z. Physik. B 86 (1933) 583–591.
[7] G. Herzberg, Nature 133 (1934) 759.
[8] D.F. Evans, Chem. Commun. (1969) 367–368.
[9] I.B.C. Matheson, J. Lee, Chem. Phys. Lett. 8 (1971) 173–176.
[10] H. Kautsky, H. de Bruin, Naturwiss 19 (1931) 1043.
[11] H. Kautsky, H. de Bruin, R. Neuwirth, W. Baumeister, Chem. Ber. 66 (1933) 1588–1600.

[12] H. Kautsky, Trans. Faraday Soc. 35 (1939) 216–219.
[13] A. Jablonski, Z. Physik 94 (1935) 38–46.
[14] J. Weiss, Naturwiss 34 (1935) 610.
[15] J. Franck, R. Livingston, J. Chem. Phys. 9 (1941) 184–190.
[16] A.N. Terenin, Acta Phisicochim. (USSR) 18 (1943) 210–241.
[17] A.N. Terenin, Zh. Phys. Khimii 17 (1944) 1–12.
[18] G.N. Lewis, M. Kasha, J. Am. Chem. Soc. 66 (1944) 2100–2116.
[19] A.N. Terenin, V.L. Ermolaev, Dokl. AN SSSR 85 (1952) 547–550.
[20] D.L. Dexter, J. Chem. Phys. 21 (1953) 836–850.
[21] A.N. Terenin, Photonics of Dye Molecules, Nauka Publication, Leningrad, 1967.
[22] V.L. Ermolaev, E.N. Bodunov, E.V. Sveshnikova, T.A. Shakhverdov, Non Radiative Energy Transfer of Electronic Excitation, Nauka, Leningrad, 1977.
[23] G.O. Schenck, Ann. NY Acad. Sci. 171 (1970) 67–77.
[24] C.S. Foote, S. Wexler, J. Am. Chem. Soc. 86 (1964) 3879–3880.
[25] C.S. Foote, S. Wexler, J. Am. Chem. Soc. 86 (1964) 3880–3881.
[26] E.J. Corey, W.C. Taylor, J. Am. Chem. Soc. 86 (1964) 3881–3882.
[27] A.U. Khan, M. Kasha, J. Chem. Phys. 39 (1963) 2105–2106.
[28] S.J. Arnold, E.A. Ogryzlo, H. Witzke, J. Chem. Phys. 40 (1964) 1769–1770.
[29] A.U. Khan, M. Kasha, J. Am. Chem. Soc. 92 (1970) 3293–3300.
[30] A.A. Krasnovsky Jr., Biofizika 21 (1976) 748–749.
[31] A.A. Krasnovsky Jr., Biofizika 22 (1977) 927–928.
[32] A.A. Krasnovsky Jr., Photochem. Photobiol. 29 (1979) 29–36.
[33] A.A. Krasnovsky Jr., V.E. Kagan, FEBS Lett. 108 (1979) 152–154.
[34] E.A. Venediktov, A.A. Krasnovsky Jr., Bull Higher Schools Ser. Chem., Chem. Technol. 22 (1979) 395–398.
[35] I.M. Byteva, G.P. Gurinovich, S.P. Izbavitilev, Zh. Prikl. Spektr. (J. Appl. Spectr., Minsk) 29 (1978) 156–158.
[36] A.A. Krasnovsky Jr., Biofizika 24 (1979) 747–748.
[37] A.U. Khan, M. Kasha, Proc. Natl. Acad. Sci. 76 (1979) 6047–6049.
[38] A.A. Krasnovsky Jr., Z. Prikl. Spektr. (J. Appl. Spectr., Minsk) 32 (1980) 852–856.
[39] A.A. Krasnovsky Jr., Chem. Phys. Lett. 81 (1981) 443–445.
[40] K.I. Salokhiddinov, I.M. Byteva, B.M. Dzhagarov, Opt. Spektr. 47 (1979) 881–886.
[41] I.M. Byteva, G.P. Gurinovich, J. Lumin. 21 (1979) 17–20.
[42] K.I. Salokhiddinov, B.M. Dzhagarov, I.M. Byteva, G.P. Gurinovich, Chem. Phys. Lett. 76 (1980) 85–87.
[43] P.R. Ogilby, C.S. Foote, J. Am. Chem. Soc. 105 (1983) 3423–3430.
[44] J.R. Hurst, G.B. Schuster, J. Am. Chem. Soc. 105 (1983) 5756–5760.
[45] M.A.J. Rodgers, J. Am. Chem. Soc. 105 (1983) 6201–6205.
[46] A.A. Krasnovsky Jr., Membr. Cell Biol. 12 (1998) 660–665.
[47] S.Yu. Egorov, A.A. Krasnovsky Jr., Biofizika 28 (1983) 497–498.
[48] A.A. Krasnovsky Jr., S.Yu. Egorov, O.V. Nasarova, E.I. Yartsev, G.V. Ponomarev, Stud. biophys. 124 (1988) 123–142.
[49] S.Yu. Egorov, A.A. Krasnovsky Jr., Proc. SPIE 1403 (1990) 611–621.
[50] S.Yu. Egorov, S.V. Zinukov, V.F. Kamalov, N.I. Koroteev, A.A. Krasnovsky Jr., B.N. Toleutaev, Optika Spektrosc. 65 (1988) 899–903.
[51] S.Yu. Egorov, V.F. Kamalov, N.I. Koroteev, A.A. Krasnovsky Jr., B.N. Toleutaev, S.V. Zinukov, Chem. Phys. Lett. 163 (1989) 421–424.
[52] S.V. Zinukov, V.F. Kamalov, N.I. Koroteev, A.A. Krasnovsky Jr., Opt. Spektrosc. 70 (1991) 790–794.
[53] D.N. Butorina, A.A. Krasnovsky Jr., M.E. Bashtanov, S.Yu. Egorov, A.V. Priezzhev, Proc. SPIE 4241 (2001) 317–323.
[54] D.N. Butorina, A.A. Krasnovsky Jr., A.V. Priezzhev, Biofizika 48 (2003) 201–209.
[55] O. Shimizu, J. Watanabe, K. Imakubo, J. Phys. Soc., Japan 66 (1997) 268–269.
[56] R. Dedic, M. Korinek, A. Molnar, A. Svoboda, J. Hala, J. Lumin. 119/120 (2006) 209–213.
[57] M. Neidre, M.S. Patterson, B.C. Wilson, Photochem. Photobiol. 75 (2002) 382–391.
[58] A. Baier, M. Maier, R. Engl, M. Landthaler, W. Baumler, J. Phys. Chem. B 109 (2005) 3041–3046.
[59] J. Moan, K. Berg, Photochem. Photobiol. 53 (1991) 549–554.
[60] S. Lee, L. Zhu, A. Minhaj, M.F. Hinds, A.A. Ferrante, D.H. Vu, D. Rosen, S.J. Davis, T. Hasan, Proc. SPIE 5689 (2005) 90–96.
[61] T. Hirano, E. Kohno, M. Nishiwaki, J. Jpn. Soc. Las. Surg. Med. 22 (2002) 99–108.
[62] M.T. Jarvi, M.J. Niedre, M.S. Patterson, B.C. Wilson, Photochem. Photobiol. 82 (2006) 1198–1210.
[63] I. Zeber, J.W. Snyder, L.K. Andersen, L. Poulsen, Z. Gao, J. Lamber, U. Kristiansen, P.R. Ogilby, Photochem. Photobiol. 79 (2004) 319–322.
[64] E. Skovsen, J.W. Snyder, P.R. Ogilby, Photochem. Photobiol. 82 (2006) 1187–1197.
[65] J. Yamamoto, S. Yamamoto, T. Hirano, S. Li, M. Koide, E. Kohno, M. Okada, C. Inenaga, T. Tokuyama, N. Yokota, S. Terakawa, H. Namba, Clin. Cancer Res. 12 (2006) 7132–7139.
[66] A.A. Krasnovsky Jr., K.V. Neverov, Biofizika 23 (1988) 884–885.
[67] A.A. Krasnovsky Jr., K.V. Neverov, Chem. Phys. Lett. 167 (1990) 591–597.
[68] K.V. Neverov, A.A. Krasnovsky Jr., Opt. Spektr. 71 (1991) 105–110.
[69] K.V. Neverov, A.A. Krasnovsky Jr., Chem. Phys. Lett. 189 (1992) 189–192.
[70] P.-T. Chou, G.-T. Wei, C.-H. Lin, C.-Y. Wei, C.-H. Chang, J. Am. Chem. Soc. 118 (1996) 3031–3032.
[71] P.-T. Chou, Y.-C. Chen, C.-Y. Wei, S.-J. Chen, H.-L. Lu, J. Phys. Chem. A 101 (1997) 8581–8586.
[72] D.V. Kazakov, R. Schmidt, J. Phys. Chem. A 111 (2007) 4274–4279.
[73] Y. Fu, A.A. Krasnovsky Jr., C.S. Foote, J. Phys. Chem. A 101 (1997) 2552–2554.
[74] A.A. Krasnovsky Jr., C.S. Foote, J. Am. Chem. Soc. 115 (1993) 6013–6016.
[75] M.E. Bashtanov, A.A. Krasnovsky Jr., Quant. Electron. 29 (1999) 163–167.
[76] A.A. Krasnovsky Jr., M.E. Bashtanov, N.N. Drozdova, O.A. Yuzakova, E.A. Luk'yanetz, Quant. Electron. 32 (2002) 83–86.
[77] A.A. Krasnovsky Jr., Y. Fu, M.E. Bashtanov, S. Murphy, C.S. Foote, Opt. Spektr. 83 (1997) 616–620.
[78] M.E. Bashtanov, A.A. Krasnovsky Jr., High Energ. Chem. 31 (1997) 338–343.
[79] Y. Fu, A.A. Krasnovsky Jr., C.S. Foote, J. Am. Chem. Soc. 115 (1993) 10282–10285.
[80] D.M. Baigel, A.A. Gorman, I. Hamblett, T.J. Hill, J. Photochem. Photobiol. B: Biol. 43 (1998) 229–231.
[81] S. Murphy, K. Kondo, C.S. Foote, J. Am. Chem. Soc. 121 (1999) 3751–3755.
[82] I.B.C. Matheson, J. Lee, Chem. Phys. Lett. 77 (1970) 475–476.
[83] D.F. Evans, J.N. Tucker, J. Chem. Soc. Faraday Trans. II 9 (1976) 1661–1666.
[84] I.B.C. Matheson, J. Lee, Photochem. Photobiol. 29 (1979) 879–881.
[85] S.D. Zakharov, A.V. Ivanov, Quant. Electron. 29 (1999) 1031–1053.
[86] A.A. Krasnovsky Jr., N.N. Drozdova, A.V. Ivanov, R.V. Ambartzumian, Biochem. Moscow 68 (2003) 963–966.
[87] A.A. Krasnovsky Jr., R.V. Ambartzumian, Chem. Phys. Lett. 400 (2004) 531–553.
[88] A.A. Krasnovsky Jr., N.N. Drozdova, Ya.V. Roumbal, A.V. Ivanov, R.V. Ambartzumian, Chin. Opt. Lett. 3S (2005) 1–4.
[89] A.A. Krasnovsky, Ya.V. Roumbal, A.V. Ivanov, R.V. Ambartzumian, Chem. Phys. Lett. 430 (2006) 260–264.
[90] A.A. Krasnovsky Jr., I.V. Kryukov, A.V. Sharkov, Proc. SPIE 6535 (2007) 65351Q1–65351Q5.
[91] A.A. Gorman, I. Hamblett, C. Lambert, A.L. Presscott, M.A.J. Rodgers, H.M. Spence, J. Am. Chem. Soc. 109 (1987) 3091–3097.
[92] L.A. Martinez, G.G. Martinez, B.B. Klopotek, J. Lang, A. Neuner, A.M. Braun, E. Oliveros, J. Photochem. Photobiol. B 58 (2000) 94–109.
[93] C. Schweitzer, R. Schmidt, Chem. Rev. 103 (2003) 1685–1757.