Photoluminescence of singlet oxygen in solutions of fullerenes and suspensions of fulleroids

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(Submitted April 26, 2001)
Opticheskii Zhurnal 68, 76–79 (July 2001)

Molecular oxygen in the singlet state plays an important role in nature and technology. It participates in a number of photobiological processes, being an active product in photodynamic oxidation reactions of organic and biological compounds. In particular, for example, singlet oxygen exerts photodynamic action on genetic material, proteins, membranes, and the retina of the eyes, and singlet oxygen has carcinogenic properties. The activity of singlet oxygen can be used in photochemotherapy for directed action on tumor cells and viruses.

In laser engineering, chemically produced singlet oxygen is a chemical-energy accumulator for exciting iodine atoms and producing lasing in the oxygen–iodine laser.

There are a number of papers in which singlet oxygen was obtained by transmitting energy from the triplet states of photoexcited molecules of sensitizer dyes (for example, protoporphyrin, naphthacene, chlorophyll a, bacteriochlorophyll, etc.) to an oxygen molecule.

When a photoexcited sensitiser molecule in the triplet state interacts with oxygen molecules, excited singlet oxygen can be formed in two states, $S_2^+$ and $D_g$. It is well known that the singlet state $S_g O_2$ is 22.5 kcal/mol and the singlet state $S_g^+ O_2$ is 37.5 kcal/mol above the ground state of the oxygen molecule, $S_g O_2$. The $S_g^+ \rightarrow S_g^0$ transition corresponds to luminescence at 7621 Å, while the $D_g \rightarrow S_g^0$ transition corresponds to luminescence at 12687 Å. The lifetime in the $S_g^+$ state is 7.1 sec, and that in the $D_g$ state is 45 min. Active biochemical properties are mainly possessed by singlet oxygen in the $D_g$ state because of the long-lived excited state. The same state of singlet oxygen is of interest for forming excited iodine in oxygen–iodine lasers.

There are two reasons that it is difficult to observe singlet-oxygen photoluminescence in solutions when molecular oxygen that saturates the solution interacts with sensitiser dyes: the low probability of the radiative transition, and the short lifetime $\tau$ of the $D_g$ state, which is $10^{-5} - 10^{-6}$ sec in most organic solvents, such as benzene, toluene, etc. An exception is observed for the solvents CCl₄, CS₂, and CF₄ used in Ref. 4, where $\tau$ equaled about $10^{-3}$ sec, since this made it possible to record the luminescence of $S_g O_2$ at 12687 Å fairly reliably. No luminescence was observed in solutions at 7621 Å, presumably because of the rapid relaxation of the $S_g^+$ state (10⁻¹⁰ sec) to the $D_g$ state.

This paper presents the results of obtaining and studying the photoluminescence of singlet oxygen accompanying the photoexcitation of fullerenes in various solvents and of suspensions of fulleroids (nanotubules and astralenes).

The electron shell of the fullerenes is characterized by delocalized $\pi$-conjugated electrons, which determine the optical and nonlinear-optical properties of the fullerenes. The kinetic diagram of singlet-oxygen formation accompanying photoexcitation of fullerene is shown in Fig. 1. The pump light excites the fullerene molecule, bringing it from the $3F(S_0)$ ground state to the singlet state $1F(S_g)$, after which an intrasystem, nonradiative transition to the lower triplet metastable state $3F(T_1)$ occurs in about a nanosecond.

The lifetime of the triplet state in the absence of quenchants can be as much as $10^{-2}$ sec. However, in the presence of a quencher, one of which is oxygen, the lifetime is reduced to 330 ns. When a fullerene molecule in a triplet state interacts with oxygen, a singlet oxygen $O_2$ is formed in the reaction

$$3F + O_2 = 1O_2 + O_0.$$ (1)

This provides the prerequisites for it to be formed in the two electronically excited states $1\Sigma_g^+$ and $1\Delta_g$, since the energy of the triplet state of fullerene, $E_T = 37.5 \pm 4.5$ kcal/mole, virtually coincides with the energy position of the $1\Sigma_g^+$ state and is greater than that for $1\Delta_g$. Reference 9 gives several of the important reaction constants of the interaction of fullerene C₆₀ with molecular oxygen. However, because that paper discussed the oxygen luminescence in a solution of C₆₀ in benzene, where the lifetime of the $1\Sigma_g^+$ state is short and its deactivation is presumably accompanied by a transition to the $1\Delta_g$ state in a time of about $10^{-10}$ sec, Snelling observed the singlet oxygen luminescence only at 12687 Å. As a consequence, the quantum
yield and the other reaction constants determined in that paper are entirely ascribed to the resultant singlet oxygen \( \Phi_1(O_2) = 0.96 \pm 0.04 \) (\( \lambda = 532 \) nm) and \( \Phi_2(O_2) = 0.76 \pm 0.05 \) (\( \lambda = 355 \) nm). The formation constant of singlet oxygen in Eq. (1) is \( K_q(O_2) = 2 \times 10^9 \text{M}^{-1}\text{sec}^{-1} \). It is noteworthy that the quenching constant of singlet oxygen when it interacts with fullerene \( C_{60} \) is anomalously small, \( K_q(1O_2) = (5 \pm 2) \times 10^9 \text{M}^{-1}\text{sec}^{-1} \), which is apparently associated with the structural features of the fullerene molecule. It is important to note that the quenching constant of singlet oxygen \( K_q(1O_2) \) for the majority of sensitizer dyes (for example, chlorophyll a, pheophytin a, \( \beta \)-carotene) is several orders of magnitude greater than this value for fullerenes and is \( \approx 10^8 \cdots 10^9 \text{M}^{-1}\text{sec}^{-1} \). This fact is extremely important for the possibility of producing a large quantity of singlet oxygen by the photoexcitation of fullerenes by comparison with dyes. It is clear from this that fullerene molecules are more efficient for biochemical applications of the directed action of the active singlet oxygen molecule, for example in phototherapy (malignant tumors, viruses).

**EXPERIMENTAL RESULTS AND COMPARISON WITH THE RESULTS OF CALCULATIONS**

The photochemical kinetics of the interaction of fullerenes with the pump radiation and with oxygen were studied on samples consisting of an air-saturated solution of fullerene \( C_{60} \). Moreover, studies were carried out on suspensions of fulleroids—nanotubes and astralenes. After carrying out a preliminary cycle of experiments, \( \text{CCl}_4 \) was chosen as a solvent. According to Refs. 4–6, the lifetime of singlet oxygen is greater in this solvent than in other solvents. The \( C_{60} \) concentration in the test sample was \( 3.7 \times 10^{17} \text{cm}^{-3} \) (determined experimentally from absorption), and the oxygen concentration in the solution was \( 6 \times 10^{18} \text{cm}^{-3} \).

Optical excitation was produced by the second harmonic of a neodymium laser (\( \lambda = 532 \) nm, pulselwidth about 10 ns, energy density here \( E \approx 0.6 \text{J/cm}^2 \)) and an IFK-20 xenon lamp. The pulselwidth in these experiments was 200 \( \mu \text{s} \), and the energy of the radiation on the sample reached \( 14 \text{mJ} \) (power \( 5 \cdots 35 \text{W/cm}^2 \)). The chosen pump pulselwidth in this case simulated the continuous operating regime in the photochemical kinetics.

A germanium photodiode with an amplifier was used as a radiation detector to observe the photoluminescence. All the measurements were made in absolute units, taking into account the spatial characteristics of the pumping and the luminescence, and this allowed them to be compared with the results of computer modeling.

The singlet oxygen luminescence was recorded at 12687 and 7621 Å, using a spectrometer with a 600-line/mm diffraction grating.

Figure 2 shows the time dependences of the singlet-oxygen luminescence power at 12687 and 7621 Å and the total luminescence at both wavelengths together. As can be seen, the lifetime of singlet oxygen in the \( 1\Sigma^+ \) state is 2.2 ms, and that in the \( 1\Pi^+ \) state is 0.5 ms. The luminescence energy at 7621 Å is about 20% of the total luminescence energy of \( 1O_2 \).

The large contribution of the 7621-Å luminescence in our experiments by comparison with those of Refs. 2–6 and 9, where no luminescence was recorded at that wavelength, is apparently associated on one hand with the substantially lower quenching constant of fullerene by comparison with that of sensitizer dyes, \( 4 \cdots 6 \) and on the other hand with the use of the solvent \( \text{CCl}_4 \), which has a significantly lower quenching constant of singlet oxygen by comparison with such a solvent as benzene.

Figure 3a shows the results of a measurement of the luminescence power of singlet oxygen \( 1\Delta_g \text{O}_2 \) with laser excitation. The same figure shows the results of computer modelling, taking into account the kinetics of singlet-oxygen formation and its quenching, including quenching by fullerenes and solvents, homogeneous quenching during col-

![FIG. 2. Luminescence power of singlet oxygen vs time at \( \lambda = 1.26 \) (1), 0.76 (2), and 1.26 + 0.76 \( \mu \text{m} \) (3).](image)

![FIG. 3. (a) Kinetics of the luminescence power of singlet oxygen (laser excitation) for \( E_{in} = 0.78 \) (1), 6 (2), 29.8 (3), 67.3 mJ (4), 5—result of theoretical modelling. (b) Luminescence energy of singlet oxygen vs laser-excitation energy.](image)
Collisions in the bulk, relaxation at the walls of the sample cell, etc.

Note that the experimental and calculated results in Fig. 3 show satisfactory agreement and demonstrate an important result—that the energy of the luminescence pulse saturates as the energy of the laser excitation of the fullerene molecules increases. This saturation appears at fairly high excitation-energy densities because of the appearance of the inverse saturated-absorption effect of the pump photons in the triplet-state channel of the fullerenes and the limitation effect, which produces additional losses of the singlet-oxygen formation efficiency, since the absorbed energy does not go to increase the concentration of fullerene molecules in the triplet state.

The results of a measurement of the luminescence power of \( {_{1}\Delta g} \) \( \text{O}_2 \) as a function of the lamp-excitation time are shown in Fig. 4a (the beginning of the signal shows interference from the pump pulse). Figure 4b shows the results of a measurement of the luminescence energy as a function of the optical excitation energy. Comparing these results with the data obtained with laser pumping, it is possible to note a substantial increase of the singlet-oxygen yield, which is associated with the virtual absence of nonlinear optical processes in this case and with an overall increase of the luminescing volume.

It is of interest to obtain singlet oxygen from the interaction of fulleroids with the pump radiation and with oxygen.

Astralenes are newly synthesized fulleroid materials. Their important characteristic parameters are the mean size of the particles of 80–150 nm, the presence of pores 20–60 nm in diameter in the particles, high thermobarostability (\( \geq 3000 \text{ K/kbar} \)), and the presence on the end surfaces of the astralene particles of unsaturated carbon chemical bonds, which readily interact with laser radiation. It can apparently also be assumed that nanotubes and astralenes possess a cloud of delocalized \( \pi \)-conjugated electrons, whose interaction with optical radiation can cause excited triplet states to form according to a scheme analogous to the fullerenes. One proof of this is that we obtained singlet-oxygen luminescence at 12687 Å by laser-irradiating suspensions of nanotubes and astralenes in \( \text{CCl}_4 \). Although the singlet-oxygen lifetime in these suspensions is substantially less than in solutions of fullerenes (about 0.1 ms) and the luminescence energy is about an order of magnitude less, this result is of interest both for studying the interaction of oxygen with nanostructures and for detecting the presence of triplet excited states in the given structures. The latter circumstance is important for revealing the features and the mechanism of the observed optical limitation of laser radiation by fulleroid materials.

Fullerenes and fulleroid materials are thus effective producers of singlet oxygen.

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