Two-photon-excited luminescence in organic dye doped drops

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Two-photon-excited luminescence (TPEL) in dye doped drops was studied at different ratios of the excitation beam diameter to the drop diameter. Luminescence of millimeter-sized drops of rhodamine 6G in dibutyl phthalate was excited by the focused IR laser radiation (wavelength of 1064 nm, pulse duration of 10 ns, pulse energy of 10 mJ). The spectral, time, and power characteristics of luminescence in a drop show that as some pump threshold is achieved, the spontaneous TPEL becomes a stimulated TPEL. It is shown that the power threshold for occurrence of the stimulated TPEL in drops is an order of magnitude lower than in a continuous medium (in a cell).

The study of nonlinear optical effects occurring in spherical micro-cavities from ten micrometers to few millimeters in radius receives considerable attention in recent time. The interest to optical phenomena in such objects is motivated by their promises for creation of miniature laser sources and high-efficiency frequency converters of optical radiation.[1] The main distinguishing features of nonlinear optical effects in spherical particles and drops as compared with a continuous medium are the abnormally low energy threshold and the peaked structure of the secondary emission spectrum. These features are physically caused by the capability of spherical particles to concentrate the incident electromagnetic radiation in their volume and the resonance character of excitation in them of the internal optical field. The maximal intensity of the internal optical field in this case is near the particle surface.

The existing physical model of stimulated optical processes in a spherical particle is described thoroughly in Ref. 1. It is the following. The interaction of the incident radiation with the particle substance results in the secondary emission in it. A part of the secondary radiation leaves the particle sphere, while another part propagates near the particle surface at an angle close to the angle of total internal reflection. At a certain power of the incident radiation, the secondary radiation can experience amplification in the medium at the frequency coinciding with free resonance modes of the spherical particle.

This paper is devoted to the experimental study of two-photon-excited luminescence (TPEL) in millimeter-sized dye doped drops.

The TPEL intensity of organic molecules is proportional to the two-photon absorption cross sections ranging from 10^{-49} to 10^{-51} $cm^4 \cdot s/(phot \cdot mol)$ (Ref. 2) and, consequently, rather high intensity of the exciting radiation is needed to excite TPEL. In practice, such intensity can be obtained when using solutions of organic dyes in the liquid-drop state.

In our experiments, dye TPEL was excited by YAG:Nd laser pulses (wavelength of 1064 nm, pulse duration of 10 ns).

The pulse energy was measured by an IMO-2N meter of mean power and energy. The time characteristics of TPEL pulse were measured with an FK-40 photo-cell, FEU 18 ELU-FK photomultiplier tube, and S7-19 oscilloscope with the time resolution no less than 0.5 and 2 ns, respectively. Parasitic elastic scattering was blocked by optical filters and was not observed in the whole range of the exciting radiation power. The laser radiation was attenuated by the Glan polarization prism and neutral filters. The power density of the focused laser radiation P varied from 30 kW/cm^2 to 2 GW/cm^2. To obtain spectral characteristics of dye TPEL, we used a monochromator based on a DFS-452 spectrograph with the instrumental function having the spectral width of 10 Å. The TPEL spectra were recorded by a FEU-79 photomultiplier tube with optical filters on a photocathode to suppress possible parasitic illumination at the wavelength of the incident radiation.

The focused laser radiation was directed into a 1.5-mm drop of rhodamine 6G solution in dibutyl phthalate (DBP). The dye concentration was 10^{-3} mol/l. The drop was set at an end of a capillary in air. Dibutyl phthalate was selected as a solvent to prevent changes in the drop size due to evaporation during the experiment. The power, spectral, and time TPEL characteristics were studied at different positions of a beam with the cross section of 100 μm inside the drop.

The drop luminescence spectrum under IR pumping and the luminescence spectrum of the channel of a beam propagating in a 3 mm thick cell filled with the same dye are depicted in Fig. 1. The significant difference between the drop and cell TPEL spectra is a

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pronounced two-peak structure, i.e., appearance of a second peak on a dip of the TPEL line in the cell. For comparison, Fig. 2 depicts the luminescence spectrum of a drop of the rhodamine 6G solution in DBP at single-photon absorption.[3] It follows from the analysis of spectral, time, and power characteristics of radiation attributed to the second spectral peak in Fig. 2 (Ref. 3), that this radiation can be assigned to generation of the near-surface luminescence in the drop at whispering gallery modes.

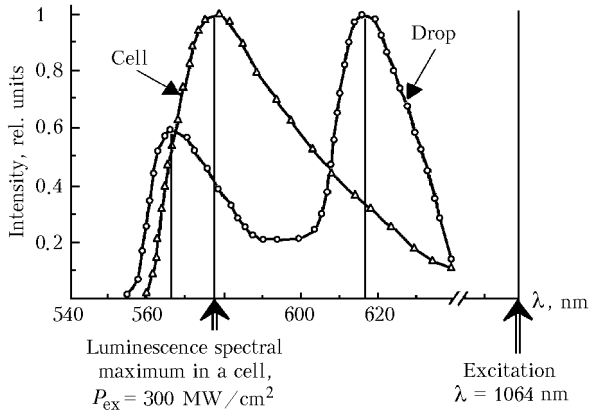

Fig. 1. Luminescence spectra of rhodamine 6G solution in dibutyl phthalate in drops and a cell under IR radiation excitation.

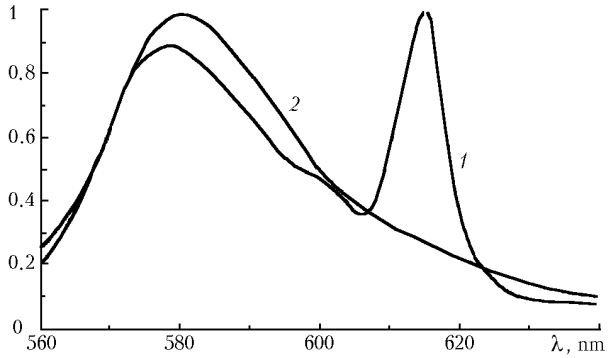

Fig. 2. Luminescence spectra of rhodamine 6G solution in dibutyl phthalate in drops (*1*) and a cell (*2*) under radiation excitation (λ = 532 nm, P_{ex} = 5 MW/cm^2).

Spectral localization of the generated radiation at the longwave wing of the luminescence spectrum of dye molecules is caused by re-absorption of luminescence radiation by dye molecules that prevails in the shortwave spectral region.[4,5] As known, the lasing spectrum in lasers is located in that part of the luminescence spectrum, where the lasing conditions are fulfilled, that is, gain exceeds loss due to emission and re-absorption. The change in the gain/loss ratio due to re-absorption leads to the shift of the lasing spectrum to the longwave region.

The dependence of the drop luminescence intensity at the wavelength of 618 nm on the pump power density is shown in Fig. 3.

It can be seen from Fig. 3 that at some threshold pump power density the square dependence characteristic of TPEL[6] changes for the linear one with following saturation. According to Refs. 7 and 8, this change can be connected with the transition from spontaneous TPEL to the stimulated one.

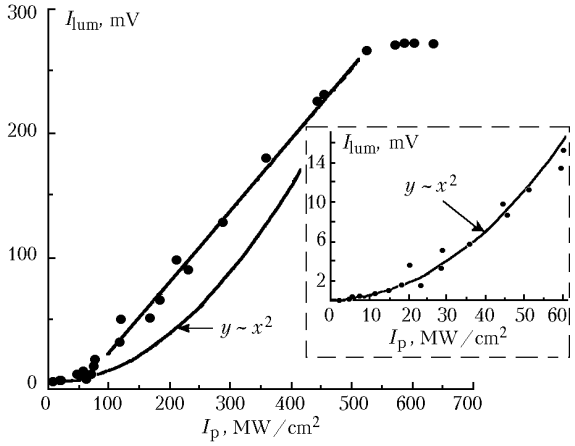

Fig. 3. Dependence of TPEL intensity on pump power density (λ = 1064 nm). Dots are for the experimental data.

The time profiles of TPEL signal recorded with FEU 18 ELU-FK (time resolution of 2 ns) are depicted in Fig. 4. Figure 4 shows the profiles of the pump laser pulse (*a*), the TPEL pulse at the pump power density lower than the threshold (*b*), the TPEL pulse at the pump power density higher than the threshold (*c*), and, for comparison, the pulse of spontaneous TPEL excited in a cell. It can be seen that if the pump intensity is higher than the threshold, the duration of the TPEL signal in drops does not exceed the duration of the pump pulse, what may be indicative of the stimulated character of luminescence.

Thus, the time characteristics of TPEL in drops, along with the energy and spectral characteristics, point to the stimulated character of drop luminescence under IR pumping.

The distribution of the internal optical field (according to our calculations[9]) in liquid cavities has to depend on the excitation geometry. Figure 5 depicts the calculated spatial structure of the internal optical field in a spherical particle at different position of the pump beam inside the sphere.

It turned out that as the beam moves from the sphere's center to the edge, the field structure changes considerably. At excitation of the drop edge, the most part of the pump energy is concentrated in the near-surface layer, what leads to excitation of high-Q whispering gallery modes.

Figure 6 shows the dependence of the luminescence intensity on the pump intensity along the drop diameter and into the near-surface region. It can be seen that the energy threshold for transition of the square dependence into the linear one when pumping into the near-surface region is almost twice as low as when pumping into the central region. (The beam radius is 100 μm, and the drop radius is 1.5 mm).

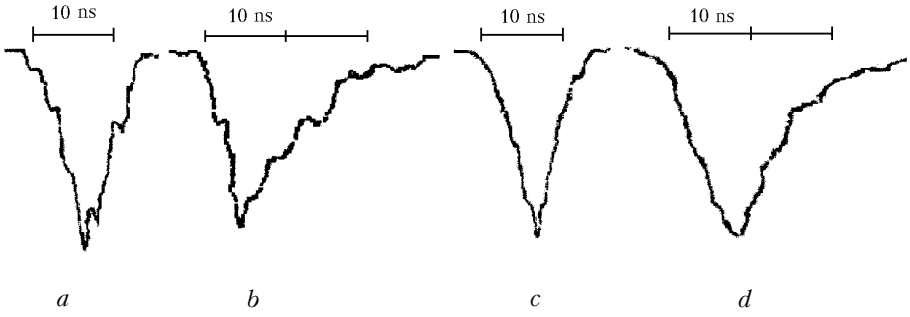

Fig. 4. Typical oscillograms of TPEL pulses in drops and a cell.

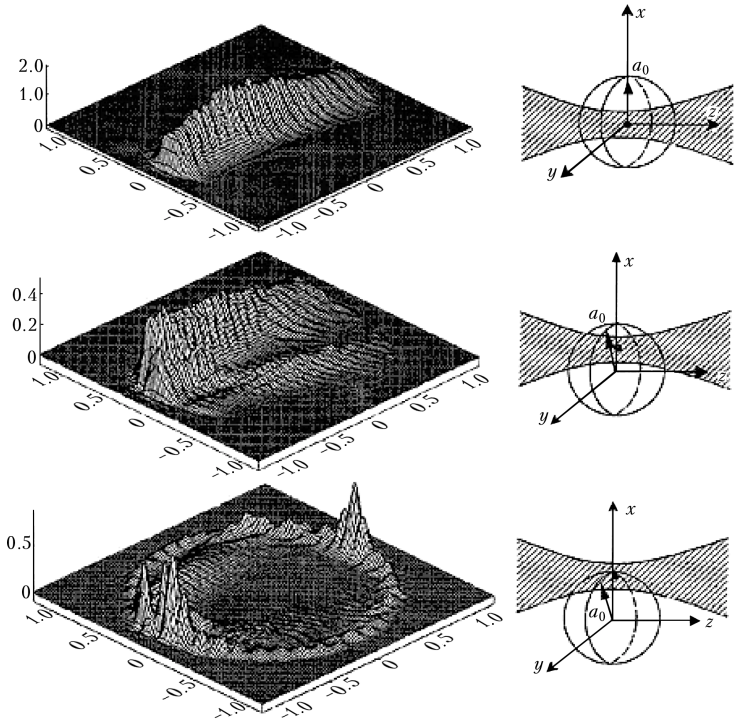

Fig. 5. Intensity distribution of the internal optical field at the drop cross section (a_0 is the drop radius, the radiation propagates from right to left).

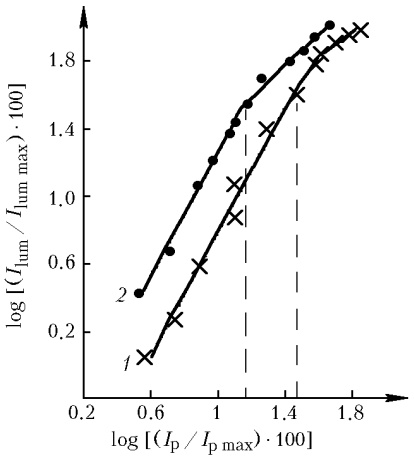

Fig. 6. TPEL intensity at different excitation geometry: pumping into the drop's center (*1*) and the edge (*2*); $I_{p\ max}$ and $I_{lum\ max}$ are the maximal values of pump and luminescence intensity.

The marked decrease of the threshold for appearance of the stimulated TPEL can be explained as follows. At pumping into the drop center, the decisive role in formation of lasing is played by the cavity, whose effective mirrors are segments of the spherical surface (absorption coefficient of 2–4%). At excitation into the edge, the decisive role passes to the cavity at whispering gallery modes. At such excitation, the loss for emission is minimal for rays propagating at the angles close to the angles of total internal reflection. As this takes place, stimulated amplification increases because of the increasing volume of the inverted medium due to localization of the pump energy of the drop's surface layer.

Thus, the study of energy, spectral, and time characteristics of TPEL in dye doped drops gave the results indicative of the stimulated character of luminescence, in which the threshold for appearance of

stimulated TPEL is determined by the geometry of drop excitation.

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