Stimulated Emission of Solutions of Cyanine Dyes

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Stimulated Emission of Solutions of Cyanine Dyes

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Many organic compounds possess intense luminescence, which makes them very attractive for use as active media in optical quantum generators. There have been comparatively many proposals for creating organic lasers, but until recently practical realization had been achieved only for a laser using solutions of organometallic compounds (chelates) ([1,2]). The difficulty of obtaining the generation effect in organic systems on allowed singlet-singlet transitions was connected mainly with the absence of excitation sources of very high power. After the creation of giant-pulse lasers such sources appeared, and recently the first reports were published on obtaining generation in solutions of organic dyes ([3–5]).

The aim of the present work was to obtain generation in solutions of cyanine dyes. The investigations were carried out on alcoholic solutions of 3,3′-diethylthiotricarbocyanine iodide.

Fig. 1 Fig. 2

Fig. 1. Absorption spectrum (a) and luminescence spectrum (b) of a solution of thiotricarbocyanine in ethyl alcohol

Fig. 2. Schematic of the setup for obtaining generation. *1, 6* —mirrors; *2* —phototropic shutter; *3* —ruby crystal; *4* —reflecting quartz plate; *5* —cuvette with the solution under study; *7* —diaphragm; *8* —rotating plate; *9, 10* —spectral filters; *11* —photomultiplier; *12* —oscilloscope; *13* —STE-1 spectrograph

The spectral characteristics of a solution of this substance, measured on an SF-4 spectrophotometer and on a UM-2 monochromator with a photoelectric attachment, are given in Fig. 1. In the region of ruby luminescence at $\lambda = 6943$ Å the absorption of a solution with concentration $3 \cdot 10^{-5}$ mol/l is 5 cm^{-1}. The pump source for exciting generation of the thiotricarbocyanine solution was a giant pulse of a ruby laser, obtained with a phototropic shutter. The pulse power was ~ 10 MW, so that $\sim 10^{17}$ quanta in 10^{-8} sec fell on 1 cm^2 of solution. This number of quanta is quite sufficient to transfer into the excited state practically all molecules contained in 1 cm^3 of solution.

The schematic of the setup for obtaining generation is given in Fig. 2. Spectral filters *9* and *10* were selected in such a way as to cut off the generation peak of

Figure 3

Figure 1: Figure 3

Figure 4

Figure 2: Figure 4

ruby and to isolate the wavelength region 7900-9000 Å. When the giant ruby pulse passed through cuvette *5*, filled with ethyl alcohol, a curve was observed on the oscilloscope that repeated the shape of the flash of the pump lamp. If, however, the cuvette was filled with the investigated

Fig. 3. Generation spectra of thiatricarbocyanine solutions. *a* –$C = 7.4 \cdot 10^{-5}$ mol/l; *b* –$C = 3.7 \cdot 10^{-5}$ mol/l; *c* –$C = 1.85 \cdot 10^{-5}$ mol/l; *d* –$C = 7.4 \cdot 10^{-6}$ mol/l. Cuvette length 1 cm

Fig. 4. Generation spectra of thiatricarbocyanine solutions with concentration $3.7 \cdot 10^{-5}$ mol/l. Cuvette length: *a* –4.5 cm; *b* –0.2 cm; *c* –1.5 cm; *d* –2 cm

solutions, a significant amplification of the signal was observed, and on the oscilloscope trace a pulse was recorded which repeated (within our time resolution) the giant pulse of ruby.

The spectrum of the resulting radiation is shown in Fig. 3. It is considerably narrower than the luminescence spectrum of thiatricarbocyanine; its width is of the order of 100 Å. The significant increase in intensity and narrowing of the spectrum indicate the stimulated character of the dye radiation.

We observed a strong dependence of the wavelength of the generation band on the concentration of the solution in a cuvette of constant length, analogous to ([5]). With increasing concentration, a regular shift of the generation toward longer wavelengths was observed (Fig. 3a-g). The observed shift can apparently be attributed to strong reabsorption of light along the length of the cuvette, since in the spectral region under investigation the luminescence and absorption spectra strongly overlap. This supposition is confirmed by experiments involving variation of the cuvette length. At constant solution concentration, an increase in the cuvette length also leads to a long-wavelength shift of the spectrum (Fig. 4). At a concentration of $2 \cdot 10^{-4}$ mole/liter we were able to obtain generation in cuvettes up to 1 mm long.

The observed spectra are characterized by a clearly manifested structure, which changed when the cuvettes and other experimental conditions were varied. In a number of cases a nearly periodic structure was obtained with a spacing between lines of the order of 3 cm^{-1}. The nature of this structure has not yet been sufficiently clarified. It may be connected with the presence of a complex resonator. If mirror 6 is removed, the structure becomes less distinct. Generation also occurs in this case, as evidenced by the narrowness of the observed emission spectrum. The occurrence of generation in a resonator formed only by

the walls of the cuvette, with reflection of 4%, shows that the gain coefficient in the organic system under consideration is very large, as should be expected for the case of an allowed transition.

The substance under investigation can also serve as a phototropic shutter for ruby. Placing a solution of thiatricarbocyanine in the ruby resonator caused the appearance of a short, powerful pulse, analogous to the action of the known solution of cryptocyanine. The difference from the action of a cryptocyanine solution is that, together with the giant pulse of the ruby laser, generation of the thiatricarbocyanine solution itself arises in the resonator. Apparently, during the initial period the filter is bleached, and then, simultaneously with the development of the giant ruby pulse, its absorption by thiatricarbocyanine occurs, leading to the onset of generation. In the experiment according to the scheme of Fig. 2, without elements 2 and 4, the width of the generation spectrum of the solution increased to 140 Å.

Luminescent dyes of the cyanine series, which absorb intensely in the red region of the spectrum, are very promising for use as powerful converters of ruby generation at 6943 Å into generation at other wavelengths. With the appropriate choice of mirrors (1—$r_{6943} = 1\%; 4$—$r_{6943} = 80\%; r_{8100} = 5\%; 6$—$r_{8100} = 44\%$) and with complete absorption by the thiatricarbocyanine solution of the ruby generation, we obtained conversion of radiation at $\lambda = 6943$ Å into radiation in the region 8110–8220 Å with an efficiency of 30%.

Obtaining generation in dyes makes it possible to convert generation frequencies very effectively over a wide range of frequencies.

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