

Influence of overlapping between the fluorescence spectra of dye molecules and the spectrum of plasmon absorption of silver nanoparticles on the luminescence of laser dyes in ethyl alcohol

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In the present work, the influence of the degree of overlapping between the plasmon absorption spectrum of silver nanoparticles and the luminescence spectra of P6Zh, phenalemine 160, and oxazine 17 on their luminescence was studied. With the addition of Ag NPs to the ethanol solution, the absorption of dyes depends on the concentration of Ag nanoparticles. The overlapping integrals between the plasmon absorption spectrum of Ag NPs and the absorption spectra of the studied dyes were 24.2 for P6J, 52 for phenalemine 160 and 38.5 for oxazine 17, respectively. The optical density in the maximum increased 1.6-fold for P6Zh, 1.4-fold – for phenalemine 160 and 1.2-fold – for oxazine 17. It was established that for P6Zh the fluorescence intensity reaches its maximum value at a concentration of $C = 2 \times 10^{-6}$ mol/l, for phenalemine 160 – at $C = 5 \times 10^{-6}$ mol/l, and for oxazine 17 at $C = 10^{-5}$ mol/l. The intensity of fluorescence of P6Zh increased 1.4 times, phenalemine 160 – 1.2 times, and for oksazine 17 – 1.1 times. The generation threshold for P6Zh showed, on average, a tenfold decrease, for phenalemine 160 – it was a 1.4-fold decrease, and for oxazine 17 – a 1.2-fold decrease. The luminescence kinetics of solutions in ethanol in the presence of silver NPs decreased by $\tau \approx 1$ ns for P6Zh, $\tau \approx 0.4$ ns for phenalemine 160 and $\tau \approx 0.1$ ns for oxazine 17.

Keywords: absorption spectrum, luminescence spectra, fluorescence, nanoparticles.

Introduction

In recent years, optical properties of materials, reinforced by a metallic surface, have been extensively studied. This interest is caused both by the problem of understanding their mechanisms, and by a wide possibility of using surface reinforcement processes in various scientific and practical applications [1]. From the practical point of view, interest in the plasmon effect is associated with the possibility of creating highly sensitive luminescent sensors [2], optoelectronic devices [3, 4], nanolasers [5] and other devices. One of the promising modern directions of laser physics is creation and study of composite media formed by laser-active molecules and metallic nanoclusters [6]. There is evidence that the addition of low-frequency metals to the active medium of dye lasers leads to a decrease in the lasing threshold [7, 8].

The effect of growing local field surrounding the metal nanostructures strongly depends on the excitation wavelength [9]. In addition, an increase or decrease in fluorescence intensity depends on the degree of overlapping plasmon absorption spectra of nanoparticles and emission spectra of phosphor molecules. However, so far very few papers were published on this problem [10-12].

Experimental technique

Ag nanoparticles were obtained by ablating a silver target with the second harmonic of a solid-state Nd laser: a YAG laser of the SOLAR LQ 215 laser ($\lambda_{gen} = 532$ nm, $E_{emp} = 90$ mJ, $\tau = 10$ ns). The concentration of Ag nanoparticles was determined by changing the mass of the target before and after ablation, and it amounted to 3.5×10^{-3} mol/l for 10 minutes of ablation. The average dimensions of Ag nanoparticles were determined by the method of dynamic light scattering by the Zetasizer Nano ZS submicron particle size analyzer. The measurements showed that the average nanoparticle size in the studied medium is 85 nm (Figure 1 (a)).

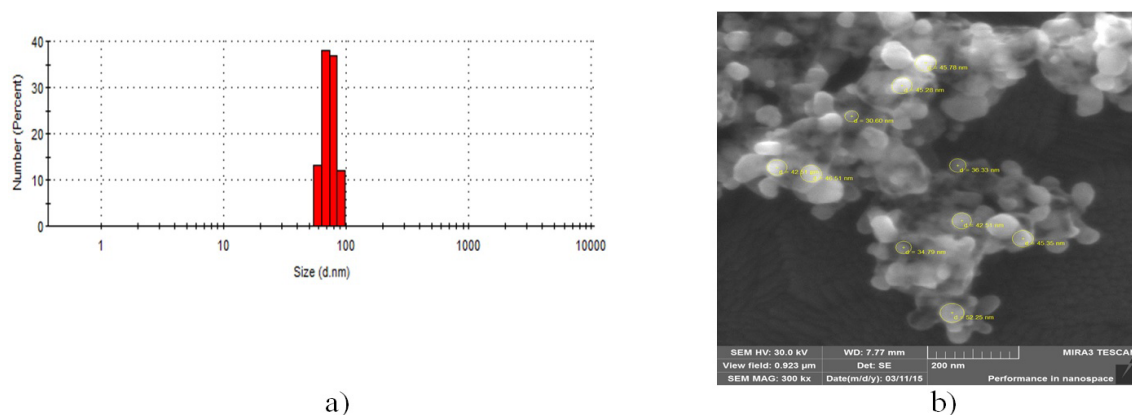


Figure 1. Distribution of silver NP sizes in ethanol (a) and microscopic images of silver nanoparticles (b).

The morphology of the surface of nanoparticles was studied using the Tescan Mira 3MLU electron microscope. It was found that in the studied solvent the predominantly spherical shape of nanoparticles is observed (Figure 1 (b)).

In the work we used the dyes, which are widely used in laser technology and a class of compounds with a complex molecular structure. Structural formulas of dyes are presented in Figure 2.

The absorption spectra of the samples were recorded on a Cary 300 (Agilent) spectrophotometer, and the fluorescence spectra on a Cary Eclipse (Agilent) spectrofluorimeter.

Figure 3 shows the absorption spectra of the studied dyes in ethyl alcohol. Figure 3 shows that the absorption spectrum of P6Zh in ethanol at a concentration of 10^{-5} mol/l has a maximum absorption at a wavelength of 530 nm and a half-width $\Delta\lambda_{1/2}^{abs} = 32$ nm. The maximum of the absorption spectrum of phenylemine 160 at a concentration of 10^{-5} mol/l is located at 540 nm with a half-width $\Delta\lambda_{1/2}^{abs} = 57$ nm. Oxazine 17 in the ethanol solution has the absorption maximum at a wavelength of 560 nm and a half-width $\Delta\lambda_{1/2}^{abs} = 55$ nm.

The overlap integrals between the plasmon absorption spectrum of Ag NPs and the absorption spectra of the studied dyes were calculated. The overlap inte-

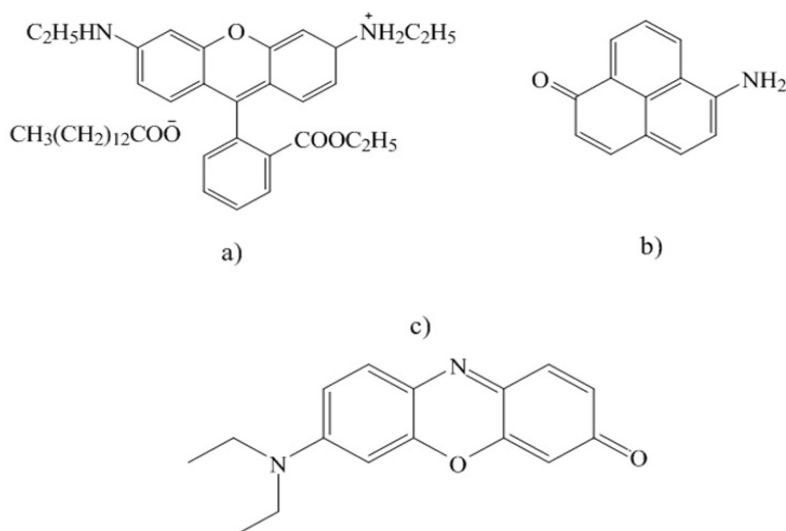


Figure 2. Structural formulas of P6Zh (a), Phenalamine 160 (b), Oxazine 17 perchlorate (c).

grals were 24.2 for P6Zh, 52 for phenalemine 160, and 38.5 for oxazine 17, respectively.

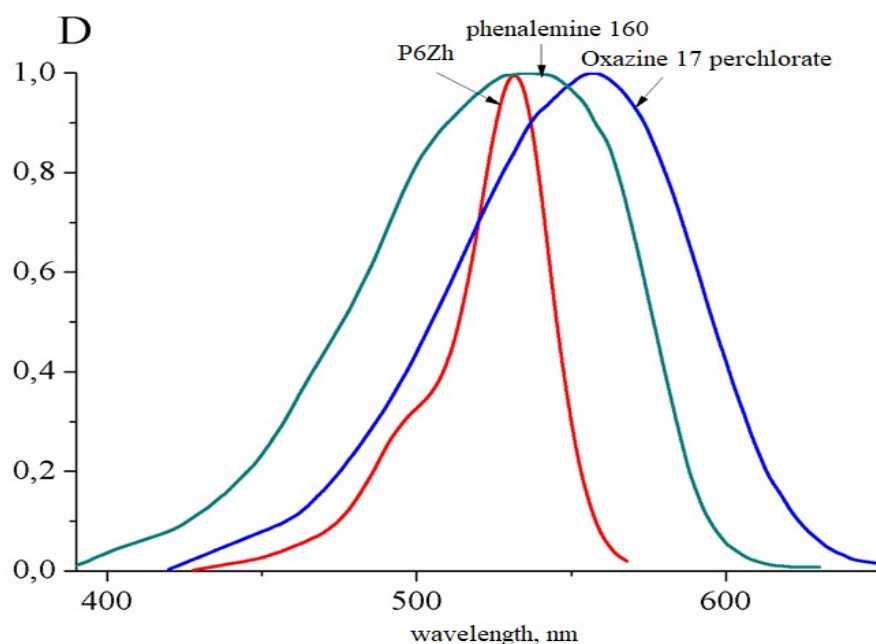


Figure 3. Relative location of the absorption spectra of the studied dyes in ethyl alcohol.

When Ag NPs are added to the ethanol solution of dyes, the absorption of dyes depends on the concentration of Ag nanoparticles. The dependence of the optical density in the maximum on the concentration of Ag nanoparticles showed that for all the studied dyes the fluorescence intensity reaches its maximum at different concentrations of Ag NPs (Table 1). Thus, for P6Zh, the optical density reaches a maximum value at a concentration $C = 2 \times 10^{-6}$ mol/l, for phenalemine 160 – at $C = 5 \times 10^{-6}$ mol/l, and for oxazine – at $C = 10^{-5}$ mol/l. The optical density in the maximum increased 1.6 times for P6Zh, 1.4 times for phenalemine 160, and 1.2 times for oxazine 17 (Table 1).

Table 1.

Characteristics of fluorescence bands of dyes in the presence of silver NPs in ethanol solutions

| Sample | Ph6Zh | | | Ph160 | | | O17 | | |
|--------------------|-------|----------------------------|----------------------------|-------|----------------------------|----------------------------|------|----------------------------|----------------------------|
| | D | λ_{max}^{abs} , nm | $\lambda_{1/2}^{abs}$, nm | D | λ_{max}^{abs} , nm | $\lambda_{1/2}^{abs}$, nm | D | λ_{max}^{abs} , nm | $\lambda_{1/2}^{abs}$, nm |
| 0 | 0.5 | 530 | 32 | 0.4 | 540 | 57 | 0.35 | 560 | 55 |
| 10^{-6} | 0.66 | 530 | 32 | 0.44 | 540 | 57 | 0.37 | 560 | 55 |
| 2×10^{-6} | 0.8 | 530 | 32 | 0.5 | 540 | 57 | 0.39 | 560 | 55 |
| 5×10^{-6} | 0.73 | 530 | 32 | 0.52 | 540 | 57 | 0.4 | 560 | 55 |
| 10^{-5} | 0.71 | 530 | 32 | 0.45 | 540 | 57 | 0.42 | 560 | 55 |
| 5×10^{-5} | 0.68 | 530 | 32 | 0.43 | 540 | 57 | 0.37 | 560 | 55 |
| 2×10^{-4} | 0.63 | 530 | 32 | 0.38 | 540 | 57 | 0.34 | 560 | 55 |

Fluorescence spectra of the studied dyes were recorded during excitation in the short-wave arm of absorption spectra (Figure 4). Photoexcitation of P6Zh, phenalamine 160, and oxazine 17 was carried out with excitation at a wavelength of 520 nm.

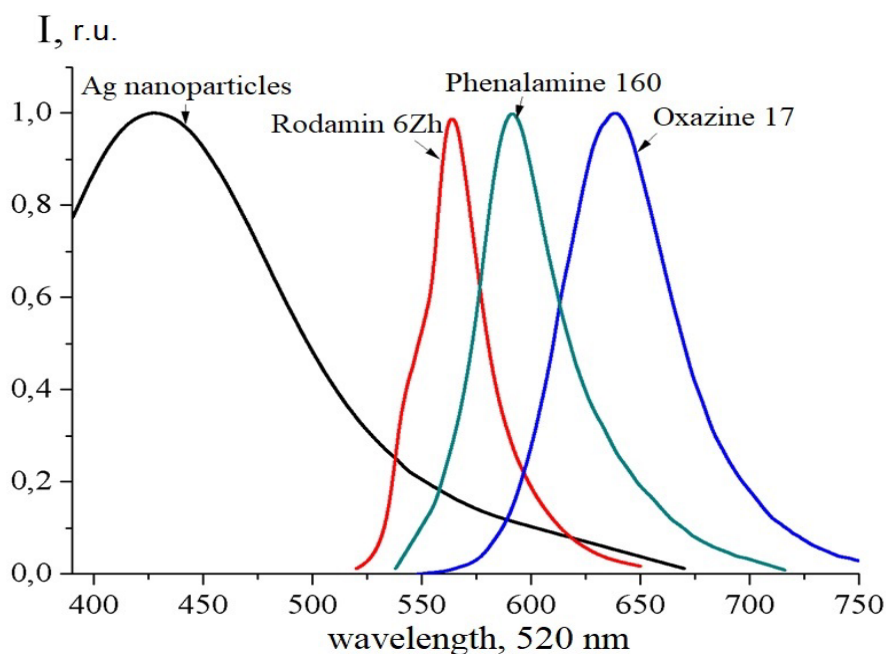


Figure 4. Relative location of the absorption spectrum of Ag Nps and the fluorescence spectra of the studied dyes.

When the alcohol solution of P6Zh with a concentration of 10^{-5} mol/l is excited, spontaneous fluorescence is observed with a maximum at 562 nm and a half-width of 34 nm. When the alcohol solution of phenalamine 160 with a concentration of 10^{-5} mol/l is excited, spontaneous fluorescence is observed with a maximum at 592 nm and a half-width of the band 43 nm. When the alcohol solution of Oxazine 17, $C = 10^{-5}$ mol/l, is excited, spontaneous fluorescence is observed with a maximum at 638 nm and a half-width of 52 nm.

The spectrum of plasmon absorption of a colloidal solution of Ag NPs is plotted on the same graph. It can be seen from Figure 4 that the fluorescence spectra of the studied dyes well overlap with the plasmon absorption spectrum of Ag

NPs, which indicates the fulfillment of plasmon resonance conditions. The overlap integrals were calculated between the plasmon absorption spectrum of Ag NPs and the fluorescence spectra of the studied dyes. The overlap integrals were 14.3 for P6Zh, 11.5 – for phenalemine 160 and 6.47 – for Oksazina 17, respectively.

Strong scattering properties of nanoparticles can lead to the realization of a random laser in the medium. Therefore, the dependences of the spectra and intensities of scattered light on the concentration of nanoparticles in ethanol were measured. The scattering spectra of silver NP in alcohol (Figure 5) form a broad band whose maximum, depending on the concentration of nanoparticles, changes its position on the wavelength scale.

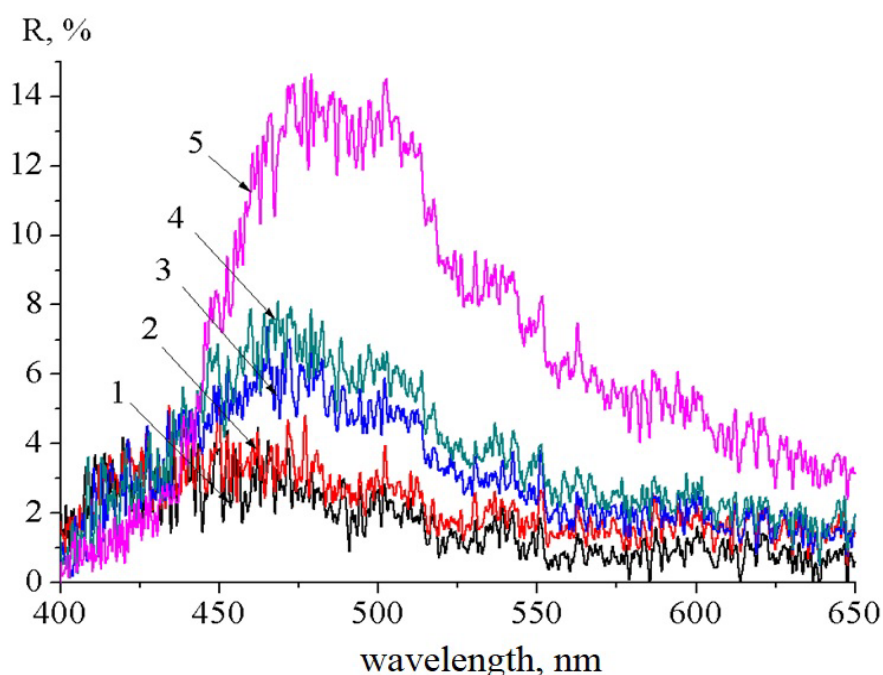


Figure 5. Spectra of scattering of silver nanoparticles in alcohol. Concentrations of nanoparticles, mol/l: 1 – 2×10^{-6} ; 2 – 10^{-5} ; 3 – 5×10^{-5} ; 4 – 10^{-4} ; 5 – 6×10^{-4} .

At low concentrations of nanoparticles in the solution, the intensity of the scattered light is small and, on average amounts to 3%. However, as the concentration of NPs increases, the scattered light makes about 14%. The change in the position of the maximum with an increase in the concentration of NPs in the solution is associated with the process of agglomeration of NPs in the solution. Table 2 shows the characteristics of the scattering spectra of nanoparticles as a function of concentration.

Table 2.

Characteristics of the scattering spectra of silver nanoparticles in alcohol

| C_{Ag} , mol/l | R_{max} , % | λ_{max} , nm | $\Delta\lambda_{1/2}^{scat}$, nm |
|--------------------------|---------------|----------------------|-----------------------------------|
| 2×10^{-6} mol/l | 5 | 462 | 28 |
| 10^{-5} mol/l | 5.2 | 464 | 28 |
| 5×10^{-5} mol/l | 7.5 | 471 | 93 |
| 10^{-4} mol/l | 8.3 | 473 | 90 |
| 6×10^{-4} mol/l | 14.8 | 486 | 98 |

The intensity of the scattered light was measured at a wavelength of 530 nm and at an angle of 90° with respect to the feeding beam. Figure 6 shows the dependence of the intensity of the scattered light with a solution of silver NPs on the concentration of nanoparticles. It is seen that at concentrations of NPs higher than 2×10^{-5} mol/l an almost linear increase in scattered light is observed.

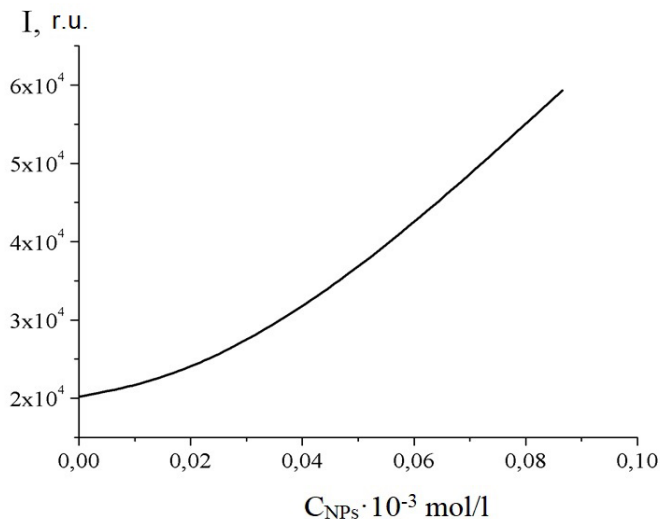


Figure 6. Influence of concentration of silver NPs in ethyl alcohol on the intensity of scattered light.

To study the influence of plasmon resonance on the emissivity of the studied dyes experimentally, it is necessary to choose such experimental conditions that would prevent multiple scattering. For this purpose, the dependences of the luminescence intensity of the dye solutions on the Ag NPs concentration were constructed. The concentration of nanoparticles in the solution ranged from 10^{-6} mol/l to 5×10^{-4} mol/l. When Ag NPs are added to the ethanol solution of the dyes, the fluorescence intensity of the dyes depends on the Ag NPs concentration (Figure 7).

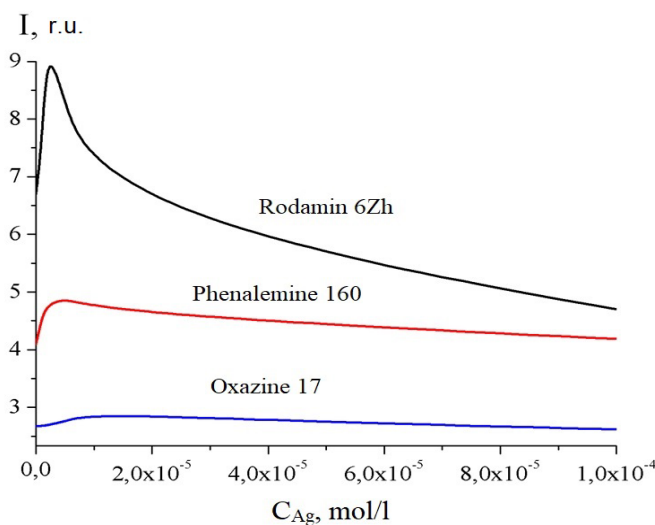


Figure 7. Dependence of fluorescence intensity at the maximum on the concentration of Ag NPs.

The dependence of the fluorescence intensity at the maximum on the Ag NPs concentration showed that for all the studied dyes the fluorescence intensity reaches the maximum at different Ag NPs concentrations. Thus, for P6Zh,

the fluorescence intensity reaches its maximum at a concentration of $C = 2 \times 10^{-6}$ mol/l, for phenalemine 160 – at $C = 5 \times 10^{-6}$ mol/l, and for oxazine 17 – at $C = 10^{-5}$ mol/l (Table 3).

The lifetimes of the excited state of the dye molecules were measured using a pulsed spectrofluorimeter with a picosecond resolution with registration in time-correlated photon counting (Becker & Hikl, Germany). The studied samples were excited using a pulsed semiconductor laser with the generation wavelength $\lambda_{gen} = 488$ nm with a pulse duration at half-height $\tau = 40$ ps. The values of the lifetimes of the studied dyes in the presence of silver nanoparticles in solution are given in Table 3.

Table 3.

Characteristics of the fluorescence spectra of dyes in the presence of silver NPs in alcohol

| Sample | Ph6Zh | | | | Ph160 | | | | O17 | | | |
|--------------------|-------------------------|-----------------------------|-----------------------------------|-------------|-------------------------|-----------------------------|-----------------------------------|-------------|-------------------------|-----------------------------|-----------------------------------|-------------|
| $C_{Ag},$ mol/l | $I_{max}^{fl},$ o.e. | $\lambda_{max}^{fl},$ nm | $\Delta\lambda_{1/2}^{fl},$ nm | τ_{fl} | $I_{max}^{fl},$ o.e. | $\lambda_{max}^{fl},$ nm | $\Delta\lambda_{1/2}^{fl},$ nm | τ_{fl} | $I_{max}^{fl},$ o.e. | $\lambda_{max}^{fl},$ nm | $\Delta\lambda_{1/2}^{fl},$ nm | τ_{fl} |
| 0 | 6.7 | 562 | 34 | 6.3 | 4.1 | 592 | 43 | 5.4 | 2.67 | 638 | 52 | 5 |
| 10^{-6} | 7.6 | 562 | 34 | 6.3 | 4.56 | 592 | 43 | 5.4 | 2.68 | 638 | 52 | 5 |
| 2×10^{-6} | 9.4 | 562 | 34 | 6.3 | 4.78 | 592 | 43 | 5.4 | 2.69 | 638 | 52 | 5 |
| 5×10^{-6} | 8.2 | 562 | 34 | 6.3 | 4.9 | 592 | 43 | 5.4 | 2.76 | 638 | 52 | 5 |
| 10^{-5} | 7 | 562 | 34 | 6 | 4.72 | 592 | 43 | 5.3 | 2.9 | 638 | 52 | 5 |
| 5×10^{-5} | 5.4 | 562 | 34 | 4.3 | 4.4 | 592 | 43 | 4.5 | 2.73 | 638 | 52 | 4.7 |
| 2×10^{-4} | 3 | 562 | 34 | 3.2 | 3.7 | 592 | 43 | 4 | 2.62 | 638 | 52 | 4.3 |

According to [2, 16], more intensive fluorescence of molecules near metal nanoparticles is caused by an increase in the rate of excitation of fluorescence due to localized plasmon resonance. When molecules are located near a metal surface or contact with it, nonradiative energy is transferred from molecules to nanoparticles, which leads to a decrease in the probability of radiative decay of excited molecules. At low concentrations of Ag nanoparticles, when nanoparticles and dye molecules are rather far apart, the observed increase in fluorescence is associated with plasmon resonance of silver nanoparticles. At high concentrations of Ag nanoparticles, the nonradiative deactivation of the excited fluorescent state dominates because of the decrease in the distance between fluorophores and nanoparticles.

The intensity of fluorescence in solutions with silver nanoparticles can increase due to additional absorption by the dye molecules of exciting radiation scattered by silver nanoparticles. However, the experiments showed that at high concentrations of silver nanoparticles, the fluorescence intensity of dyes decreases, indicating that at high concentrations of nanoparticles, the nonradiative decay channel of the excited molecules is apparently the main channel, as with increasing intensity of the scattered light the fluorescence intensity of the dyes also had to increase.

In addition, the fluorescence intensity of the studied dyes unequally increases with increasing concentration of silver nanoparticles. Thus, the intensity of fluorescence of P6Zh increased 1.4 times, phenalemine 160 – 1.2 times, and for oxazine 17 – 1.1 times. This indicates that, depending on the degree of overlapping

between the absorption spectrum of Ag NPs and fluorescence, the fluorescence intensities of the studied dyes increase not uniformly.

Spectral and energy characteristics of the stimulated luminescence in the solutions were measured by excitation of the samples with a second Nd harmonic: YAG laser (1) (SOLAR LQ 215, $\lambda_{gen} = 532$ nm, $E_{emp} = 90$ mJ, $\tau = 10$ ns) in the transverse variant. When measuring the laser generation characteristics, an optical resonator was used, which was formed by a blind mirror (6) and the front face of the cuvette with the dye solution (7). The pump radiation passing the diaphragm (3) with the help of cylindrical lenses (4, 5) was focused on the side face of the cuvette in the strip with an area of 0.07 cm^2 . Radiation was generated in a narrow near-wall region from the side of the inlet wall of the cuvette. The pump power density was varied by neutral filters (2) and was $0.005\text{--}0.2\text{ MW/cm}^2$. The luminescence signal by means of the collecting lens (8) was focused on the optical fiber input of the AvaSpec-2048 spectrometer (9). The relative error in determining spectral characteristics was 3 %.

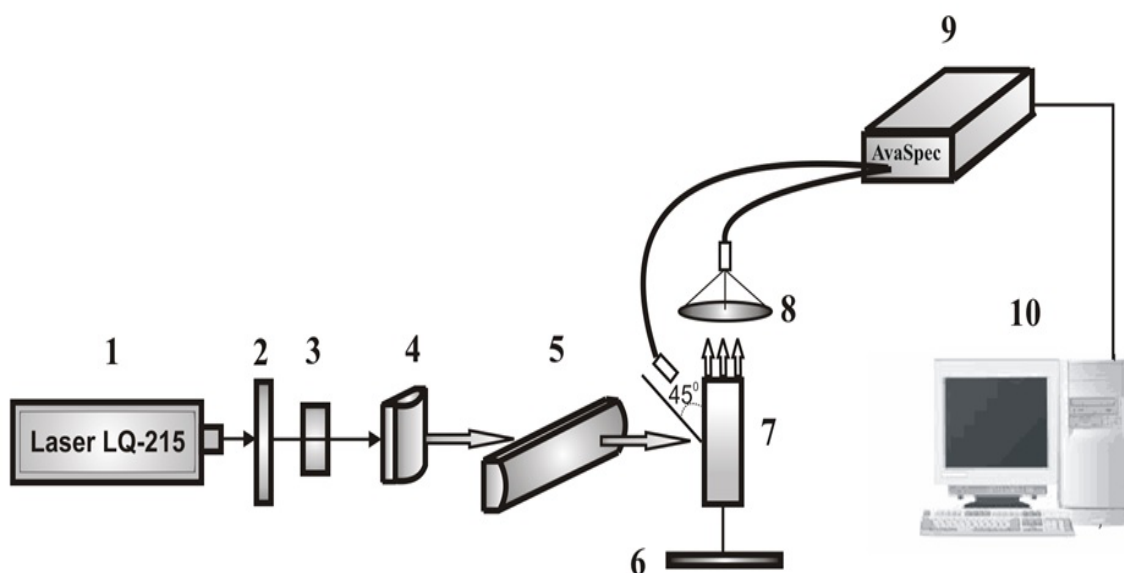


Figure 8. Scheme of the experimental setup for studying generation characteristics of molecular systems. 1 is laser LQ 215; 2 are neutral filters; 3 is a diaphragm; 4, 5 are cylindrical lenses; 6 is a blind mirror; 7 is a test sample; 8 is a collecting lens; 9 is a spectrometer AvaSpec-2048; 10 is a computer.

To study generation characteristics, alcohol solutions of dyes with concentrations $C = 10^{-3}$ mol/l were used. Such concentrations of silver nanoparticles were chosen that the maximum values of the fluorescence intensity were observed.

When the P6Zh solution in the resonator in the transverse variant is subjected to the laser excitation (SOLAR LQ 215), with the pump power density exceeding the threshold value in the long-wavelength band of the dye fluorescence, a band of stimulated emission at a wavelength equal to $\lambda_{gen} = 569$ nm appears.

A further increase in the pump power leads to an increase in the radiation intensity and narrowing of the lasing band. When silver nanoparticles are added to the solution, at a concentration of $C = 2 \times 10^{-6}$ mol/l, it causes narrowing of the generation band and a 10-fold decrease in the threshold for the onset of the stimulated emission (Figure 9).

When the phenalemine 160 solution in alcohol is excited by the laser LQ 215 at a pump power density exceeding the threshold value, a band of stimulated

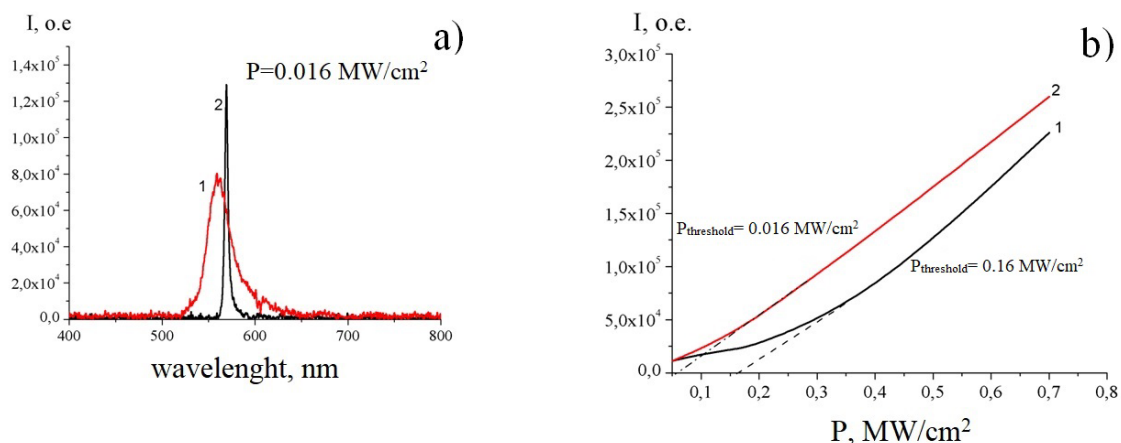


Figure 9. The generation spectrum (a) and the dependence of the radiation intensity in the maximum (b) for P6Zh in ethanol. 1- a dye solution; 2- a dye solution with Ag NPs.

emission at a wavelength of $\lambda_{gen} = 604$ nm appears.

When Ag NPs at a concentration of $C = 5 \times 10^{-6}$ mol/l are added to the solution of the phenalamine 160, the lasing band narrows and the threshold of stimulated emission is reduced 1.5 times (Figure 10).

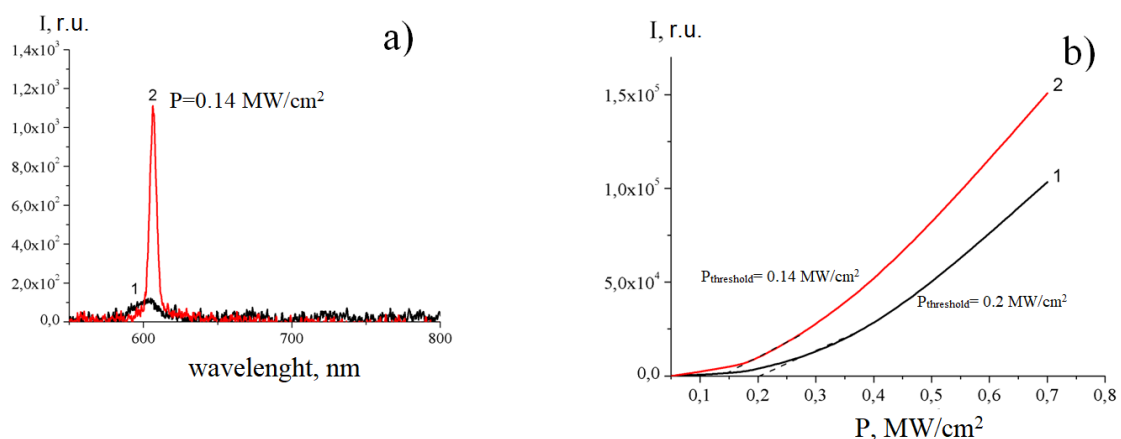


Figure 10. The generation spectrum (a) and the dependence of the radiation intensity in the maximum (b) for phenalamine 160 in ethanol. 1 - dye solution; 2 - dye solution with Ag Nps.

When oxazine 17 in ethanol is excited by a laser with a pump power density exceeding the threshold value, the spectrum of stimulated emission with a maximum at the wavelength $\lambda_{gen} = 695$ nm is observed. As the power density of the pump source increases, an increase in the radiation intensity and a narrowing of the lasing band are observed. Similarly, as in the other two cases, the addition of Ag NPs with a concentration $C = 10^{-5}$ mol/l to the dye solution leads to a narrowing of the generation band and a 1.2-fold decrease in the stimulated emission threshold (Figure 11).

It should be noted that the maxima of the generation spectra are shifted to the long-wavelength side relative to the maximum of the spectrum of the spontaneous fluorescence of the dyes. From the stimulated emission spectra, the dependences of the half-widths of the emission band ($\Delta\lambda_{1/2}$) and the luminescence intensity of solutions on the pump power density were obtained.

From the experimental data it was established that in the presence of Ag NPs the threshold of generation of laser radiation is substantially reduced in compar-

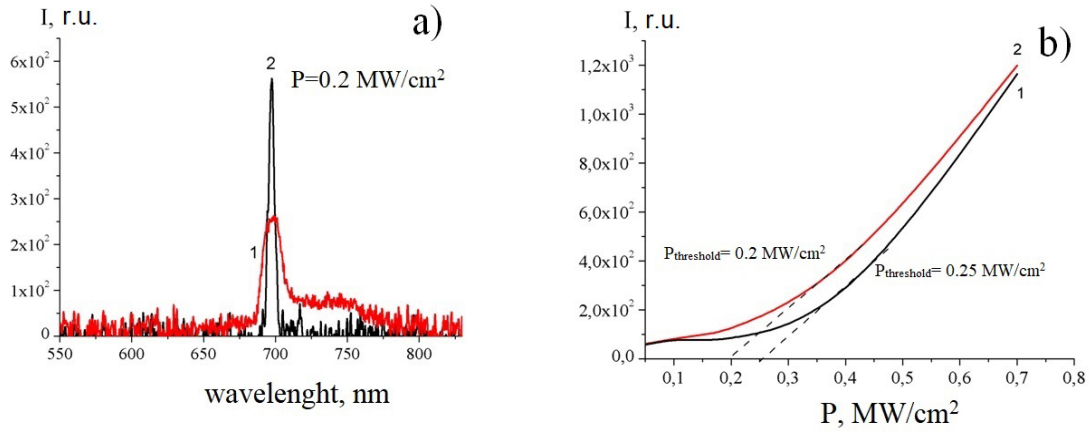


Figure 11. The generation spectrum (a) and the dependence of the radiation intensity in the maximum (b) for oxazine 17 in ethanol. 1 - dye solution; 2 - dye solution with Ag NPs.

ison with pure dye solutions. However, for selected dyes, the values of reduction of the lasing thresholds differ substantially depending on the degree of overlapping between the absorption spectrum of Ag NPs and the fluorescence of dyes. The time characteristics of the emission pulses of the solutions were measured using a picosecond receiver DET025A (Thorlabs) and an oscilloscope DSO-X-3102A (Agilent Technologies). The width of the time function of the measuring system at half-maximum was 0.1 ns.

Figure 12 shows the kinetics of luminescence of solutions in ethanol. The duration of the generation pulse is $\tau \approx 10$ ns for P6Zh, $\tau \approx 8$ ns for phenalemin 160 and $\tau \approx 8$ ns for oxazine 17 (Figure 12, curves 1).

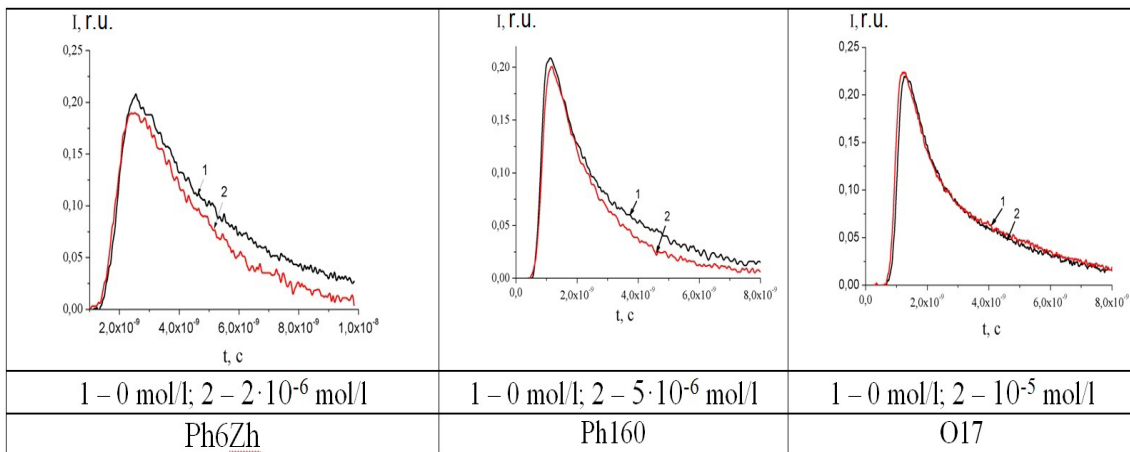


Figure 12. Kinetics of luminescence of dye solutions in ethanol in the presence of Ag NPs.

Concentrations of silver nanoparticles in the solution varied from 2×10^{-6} mol/l to 5×10^{-5} mol/l. It was found that the degree of overlapping between the plasmon absorption spectrum of Ag NPs and the luminescence spectra of the studied dyes has a strong influence on the kinetics of stimulated luminescence. Thus, with the addition of Ag nanoparticles with $C_{Ag} = 2 \times 10^{-6}$ mol/l to the P6Zh solution, the duration of the generation pulse is reduced $\tau_{gen} \approx 9$ ns (Figure 12, curve 2).

When Ag nanoparticles with $C_{Ag} = 5 \times 10^{-6}$ mol/l are added to the phenalamine 160 solution, the duration of the generation pulse is reduced to a

value of $\tau_{gen} \approx 7.6$ ns (Figure 12, curve 2). In the presence of Ag nanoparticles with of $C_{Ag} = 10^{-5}$ mol/l in the solution of oxazine 17, a decrease in the generation pulse duration is observed to $\tau_{gen} \approx 7.9$ ns (Figure 12, curve 2). The characteristics of dyes in the presence of Ag nanoparticles are shown in Table 4.

Table 4.

Generation characteristics of dyes in the presence of Ag nanoparticles

| Parameter | Ph6Zh | Ph6Zh+C _{Ag} = 2×10 ⁻⁶ mol/l | Ph160 | Ph160+C _{Ag} = 5×10 ⁻⁶ mol/l | O17 | O17+C _{Ag} = 10 ⁻⁵ mol/l |
|----------------------------------|-------|---|-------|---|------|---|
| <i>P</i> , MW/cm ² | 0,16 | 0,016 | 0,2 | 0,14 | 0,25 | 0,2 |
| λ_{max}^{gen} , nm | 562 | 569 | 604 | 604 | 695 | 695 |
| $\Delta\lambda_{1/2}$, nm | 40 | 9 | 25 | 6 | 30 | 10 |
| τ_{gen} , hc | 10 | 9 | 8 | 7,6 | 8 | 7,9 |

Conclusion

In the process of investigations it was established that the degree of overlapping between the plasmon absorption spectrum of silver nanoparticles and the luminescence spectra of the studied dyes leads to different degrees of influence of laser dyes on the luminescence. For all the dyes studied, the fluorescence intensity reached its maximum at different concentrations of Ag nanoparticles. The addition of Ag nanoparticles to the dye solution leads to a decrease in the threshold of stimulated emission. Thus, the generation threshold for P6Zh decreased, on average, 10 times, for phenalamine 160 – 1.5 times, and for oxazine 17 – 1.2 times. The luminescence kinetics of solutions in ethanol in the presence of silver nanoparticles reduced by $\tau \approx 1$ ns for P6Zh, $\tau \approx 0.4$ ns for phenalemine 160 and $\tau \approx 0.1$ ns for oxazine 17.

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