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CONDENSED-MATTER SPECTROSCOPY

The Influence of Silver Nanoparticles on the Stimulated Luminescence of Rhodamine 6G Solutions

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Abstract—The influence of silver nanoparticles on the spontaneous and stimulated luminescence of rhodamine 6G molecules in aqueous solutions is studied. It is found that the laser photoexcitation of the dye solution gives rise to spontaneous fluorescence, which, with increasing pump power, transforms into stimulated laser radiation and superluminescence. Addition of silver nanoparticles to rhodamine 6G solutions enhances all types of luminescence and lowers the generation threshold for both types of the stimulated emission. The dependences of the laser radiation and superluminescence intensities on the concentration of silver nanoparticles correlate with the data on the spontaneous fluorescence.

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INTRODUCTION

At present, extensive studies are being carried out on the excitation of localized plasmon resonance of metal nanoparticles (NPs) [1, 2]. The best-known optical manifestation of localized plasmon resonance of metal NPs is the surface-enhanced Raman scattering [3]. Luminophore molecules placed near the surface of metal NPs also experience the action of local electromagnetic fields. In this case, the fluorescence of luminophore molecules is either enhanced or quenched, depending on the distance between them and metal NPs [4, 5]. At small distances and in the case of direct contact of NPs with fluorophore molecules, fluorescence is quenched due to the dominance of nonradiative energy transfer from fluorescent molecules to NPs.

From a practical point of view, interest in the plasmon effect is related to the possibility of creating highly sensitive luminescent sensors [6], optoelectronic devices [7], nanolasers [8], efficient photovoltaic cells [9], etc. One promising area of development of laser physics is the creation and study of composite materials with laser-active molecules and metal nanoclusters [10]. There is evidence that the addition of metal NPs into the active media of dye lasers lowers the lasing threshold [11–13].

In the present work, we study the influence of silver NPs on the properties of laser radiation and superluminescence of rhodamine 6G in aqueous solutions.

EXPERIMENTAL TECHNIQUE

Silver NPs were obtained by citrate reduction of $AgNO_3$ in aqueous solution [14]. The colloidal solutions of silver NPs were prepared using deionized water obtained by multistage filtration with an Aqua-Max 360 Basic water purifier. The specific resistance of water was 18.2 MΩ/cm.

The size of silver NPs in colloidal solutions was determined by dynamic light scattering using a Zetasizer Nano ZS (Malvern) submicron particle size analyzer. The average size of silver particles was 85 nm. The size dispersion of silver particles was minimal, from 5 to 10 nm.

The absorption and fluorescence spectra of the samples under study were measured on a Solar CM2203 spectrometer. The absorption spectra of silver NPs were measured in a quartz cell 10 mm thick with respect to the cell with deionized water. To measure the dependence of the dye absorption spectra on the concentration of silver NPs, the reference cell was filled with aqueous solutions of silver NPs with corresponding concentrations.

The spectral and energy characteristics of the stimulated luminescence of rhodamine 6G (R6G) solutions were measured upon transverse excitation of the samples by the second harmonic of a Nd:YAG laser (*1*) (SOLAR LQ 215, $\lambda_{las} = 532$ nm, $E_{pulse} = 90$ mJ, and $\tau = 10$ ns) (Fig. 1).

To measure the lasing characteristics, we used an optical cavity formed by highly reflecting mirror *6* and the front face of cell *7* with the dye solution. The pump radiation passes through diaphragm *3* and is focused by cylindrical lenses *4* and *5* on the lateral surface of the cell into a strip with an area of 0.07 cm^2. Lasing arises in a narrow region near the entrance wall of the cell.

The pump power density was varied from 0.005 to 0.2 MW/cm^2 using neutral filters *2*. The luminescence

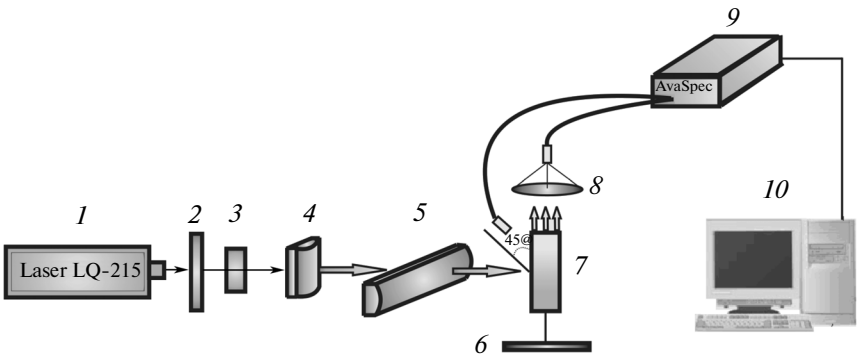

Fig. 1. Scheme of the experimental setup for investigation of the lasing characteristics of molecular systems: (*1*) LQ 215 laser, (*2*) neutral filters, (*3*) diaphragm, (*4*, *5*) cylindrical lenses, (*6*) highly reflecting mirror, (*7*) sample under study, (*8*) converging lens, (*9*) AvaSpec-2048 spectrometer, and (*10*) computer.

signal was focused by converging lens *8* on the entrance of the optical fiber of AvaSpec-2048 spectrometer *9*. The relative measurement error of the spectral characteristics was 3%.

The superluminescence of R6G dye was measured in the reflection geometry. In this case, the receiving end of the optical fiber was placed at an angle of 45° to the entrance wall of the cell (Fig. 1).

RESULTS AND DISCUSSION

The absorption spectrum of silver NPs in water (Fig. 2, curve *1*) has the shape of a broad band with a maximum at 428 nm, which is well overlapped with the R6G absorption and fluorescence spectra (Fig. 2, curves *2*, *3*), indicating that the plasmon resonance conditions are implemented. An increase in the concentration of silver NPs from 10^{-6} to 10^{-3} mol/L leads to an increase in the optical density in the absorption peak of silver NPs from 0.03 to 2.2.

In a pure aqueous solution, the R6G absorption band at a concentration of 10^{-5} mol/L has a maximum at the wavelength $\lambda_{max} = 531$ nm and half-width $\Delta\lambda_{1/2}^{abs} = 32$ nm. With increasing dye concentration, the absorption band broadens due to aggregation. With addition of silver NPs to the dye solution, the absorption ability of the dye solution slightly decreases. In particular, with the addition of 10^{-3} mol/L of silver NPs to the colored solution, the optical density in the R6G absorption band decreases by a factor of 1.2. At the same time, the absorption-band position and half-width do not change. A decrease in the R6G optical density in the presence of Ag NPs was also observed in [15].

Photoexcitation of the dye aqueous solution with a concentration of 10^{-5} mol/L gives rise to spontaneous fluorescence of R6G with the spectral maximum being at 564 nm and a band half-width of 34 nm. The dye fluorescence intensity depends on the concentration of Ag NPs added to its aqueous solution (Table 1). The dye-emission intensity increases with the NP concentration up to $C_{Ag} = 10^{-4}$ mol/L, while further increase in C_{Ag} leads to the fluorescence quenching. The position of the band maximum and the band half-width do not change.

Our measurements of the fluorescence kinetic characteristics by time-correlated photon counting under excitation by a diode laser ($\lambda_{las} = 488$ nm, $\tau = 150$ ps) showed that the R6G fluorescence decays exponentially with $\tau_{fl} = 3.2$ ns. The fluorescence lifetime does not change with addition of silver NPs to the solution.

According to [2, 16], the enhancement of the fluorescence of molecules near metal NPs is caused by an increase in the fluorescence excitation rate due to localized plasmon resonance. At the same time, when molecules lie near a metal surface or are in contact with it, nonradiative energy transfer occurs from mol-

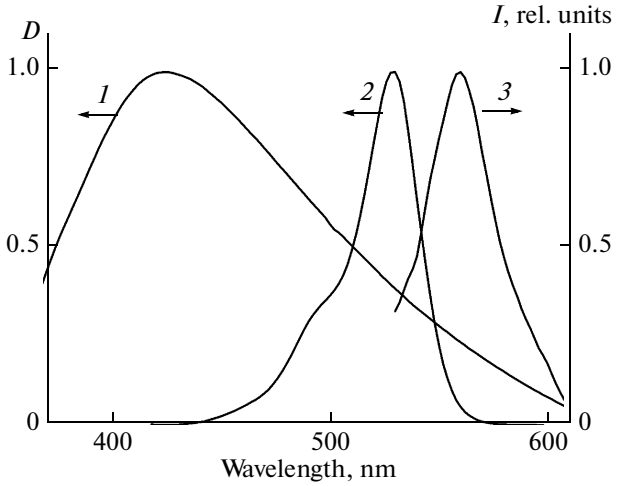

Fig. 2. Relative positions of the (*1*) Ag NPs absorption spectra, (*2*) R6G absorption spectra, and (*3*) R6G fluorescence spectra in aqueous solutions.

Table 1. Influence of silver NPs on the characteristics of R6G fluorescence

C_{Ag}, mol/L	I^{fl}_{max}, arb. units	λ^{fl}_{max}, nm	$\Delta\lambda^{fl}_{1/2}$, nm
0	2.43	564	34
10^{-6}	2.60	564	33
2×10^{-5}	2.66	564	34
5×10^{-5}	2.68	564	34
10^{-4}	2.73	564	34
3×10^{-4}	2.30	564	34
6×10^{-4}	2.16	564	34
10^{-3}	1.91	564	34

ecules to NPs, which decreases the probability of the radiative decay of excited molecules.

At low concentrations of Ag NPs, when NPs and dye molecules are sufficiently far from each other, the observed enhancement of R6G fluorescence is related to the plasmon resonance of silver NPs. At high concentrations of Ag NPs, due to a decrease in the distance between fluorophore molecules and NPs, nonradiative decay of the excited fluorescence state dominates.

The fluorescence intensity in solutions with silver NPs can also increase because the dye molecules can additionally absorb exciting radiation scattered by silver NPs. However, at high concentrations of NPs, a decisive part is obviously played by nonradiative decay of excited molecules.

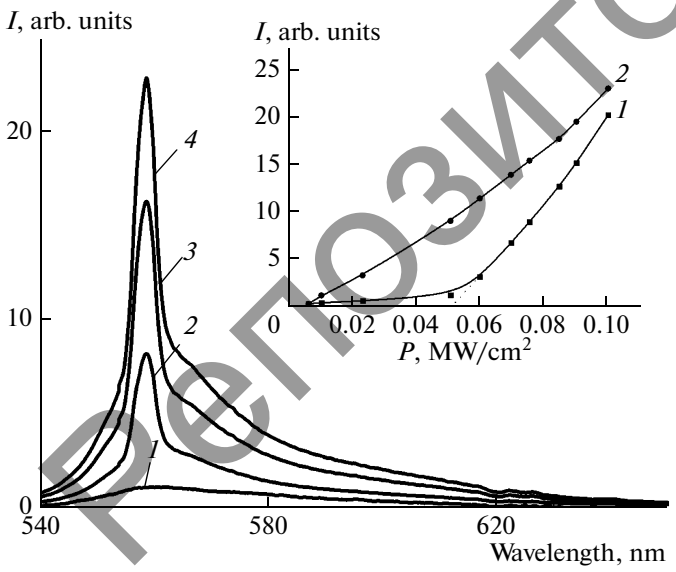

Fig. 3. Emission spectra of R6G aqueous solutions at pump power densities of (1) 0.01, (*2*) 0.03, (*3*) 0.04, and (*4*) 0.05 MW/cm^2. The inset shows the dependence of the emission intensity on the pump power for (*1*) pure dye solution and (*2*) R6G solution with 10^{-4} mol/L of Ag NPs.

To study the lasing characteristics, we used aqueous solutions of R6G with a concentration of 10^{-3} mol/L. Figure 3 shows the emission spectra of an R6G aqueous solution at different pump-power densities. At low pump-power densities, we observe spontaneous fluorescence (curve *1*) with the same spectral characteristics as in the case of stationary excitation (Fig. 2, curve *3*). With increasing pump power, the fluorescence-peak intensity increases simultaneously with narrowing of the spectrum (curves *2*, *3*). At the pump power $P = 0.05$ MW/cm^2, we observe lasing of the dye with the maximum at $\lambda^{las}_{max} = 559$ nm and band half-width $\Delta\lambda_{1/2} = 12.6$ nm (curve *4*).

With addition of silver NPs into the solution, the emission intensity increases and the lasing bandwidth narrows. Table 2 lists the R6G laser-radiation intensities and the band half-widths at different concentrations of Ag NPs. The laser-intensity maximum is observed at $C_{Ag} = 10^{-4}$ mol/L. At the maximum stimulated emission intensity, the laser line half-width almost halves. It should be noted that the laser-band maximum is shifted by 5 nm to shorter wavelengths with respect to the spontaneous fluorescence maximum.

As is seen from Tables 1 and 2, the dependence of the laser intensity on the concentration of silver NPs correlates with the data on the spontaneous fluorescence. This testifies that the stimulated emission originates from the spontaneous fluorescence.

It is known [17, 18] that a strongly scattering dispersive medium may exhibit a random laser effect. In our case, this phenomenon was absent because, in the opposite case, the random-laser efficiency would increase with increasing concentration of NPs, when the probability of stimulated emission scattering by NPs increases. Our results show that intensity I^{las}_{max} decreases at high concentrations of silver NPs.

In the course of experiments, we found the influence of silver NPs on the lasing threshold of R6G solutions. The inset in Fig. 3 presents the dependences of the laser-radiation intensity on the pump power, from which we determined the threshold values. These dependences show that the lasing threshold considerably decreases in the presence of NPs (approximately by a factor of 10) compared to the pure dye solution.

The measurements of the emission of R6G solutions in the reflection geometry from the side of the pump beam revealed superluminescence caused by amplification of spontaneous fluorescence [19, 20]. The shape of the superluminescence spectrum differs from the shape of both spontaneous fluorescence and laser spectra (Fig. 4). The maximum is shifted to shorter wavelengths with respect to the fluorescence spectrum and coincides with the laser-spectrum max-

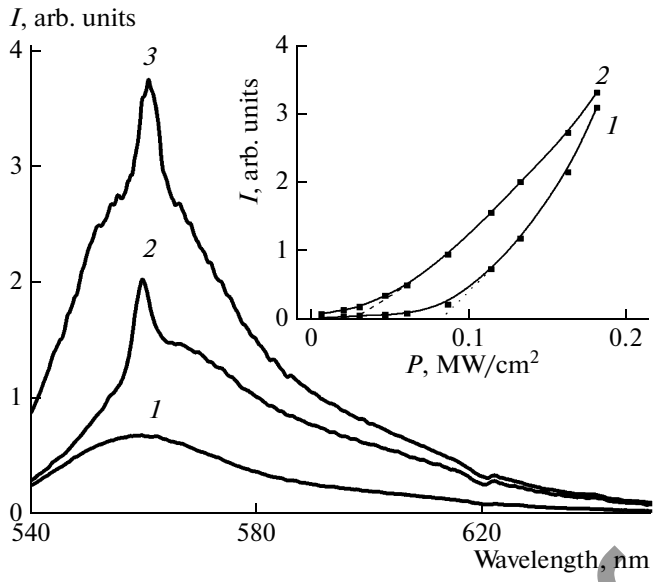

Fig. 4. Emission spectra of the R6G solution measured in the reflection geometry at pump powers of (*1*) 0.05, (*2*) 0.013, and (*3*) 0.17 MW/cm^2. The inset shows the dependence of the emission intensity on the pump power for (*1*) pure dye solution and (*2*) R6G solution with 10^{-4} mol/L of Ag NPs.

imum (Table 3). The short-wavelength shift of the maximum of the superluminescence spectrum of R6G in solutions was also observed in [10]. The half-width of the superluminescence spectrum is smaller than the half-width of the fluorescence spectrum, but larger than that of the laser radiation spectrum.

As is seen from Table 3, the superluminescence intensity increases with addition of Ag NPs to dye solutions up to concentration $C_{Ag} = 10^{-4}$ mol/L and then decreases. The half-width of the spectrum increases with increasing concentration of silver NPs.

From the experimental data obtained, we determined the effect of the presence of silver NPs on the pump threshold for superluminescence (see inset in Fig. 4). Similarly to the case of lasing, the presence of Ag NPs in the solution lowers the superluminescence threshold. The difference between the thresholds in the absence and presence of silver NPs for superluminescence is smaller than that in the case of lasing.

CONCLUSIONS

Thus, our investigations have shown that the dye fluorescence intensity increases with addition of silver NPs to the aqueous solution of R6G. The emission intensity maximum is observed at an NP concentration of 10^{-4} mol/L. Further increase in the amount of NPs leads to fluorescence quenching. The R6G fluorescence lifetime is 3.2 ns and does not change with addition of silver NPs.

Table 2. Influence of Ag NPs on the lasing properties of R6G in water

C_{Ag}, mol/L	I_{max}^{las}, arb. units	λ_{max}^{las}, nm	$\Delta\lambda_{1/2}$, nm
0	6.77	559	12.6
10^{-6}	6.80	559	10.8
2×10^{-5}	7.06	559	9.3
5×10^{-5}	7.13	559	8.4
10^{-4}	7.62	559	7.1
3×10^{-4}	6.48	559	16.7
6×10^{-4}	6.37	559	20.6
10^{-3}	5.32	559	21.9

Table 3. Influence of Ag NPs on the superluminescence characteristics of R6G in water

C_{Ag}, mol/L	$I_{max}^{superlum}$, arb. units	$\lambda_{max}^{superlum}$, nm	$\Delta\lambda_{1/2}$, nm
0	3.78	559	26.5
10^{-6}	3.98	559	27.3
2×10^{-5}	4.47	559	28.2
5×10^{-5}	4.54	559	29.5
10^{-4}	3.88	559	30.2
3×10^{-4}	3.85	559	31.2
6×10^{-4}	3.68	559	32.1
10^{-3}	3.60	559	32.5

The excitation of aqueous solutions with a dye concentration of 10^{-3} mol/L by the second harmonic of a Nd:YAG laser with the power $P = 0.05$ MW/cm^2 gives rise to lasing with the spectral maximum at a wavelength of 559 nm. With the addition of silver NPs to the dye solution, one observes an increase in the radiation intensity and narrowing of the laser band. The lasing threshold decreases approximately tenfold.

The measurements of the solution emission in the reflection geometry revealed superluminescence of R6G. The shape of the superluminescence spectrum differs from the shape of both the spontaneous fluorescence and laser spectra. The superluminescence maximum is shifted to shorter wavelengths with respect to the fluorescence spectrum and coincides with the laser spectrum maximum. The superluminescence band half-width is smaller than the half-width of the fluorescence band but larger than that of the laser band. The difference between the lasing thresholds in the absence and presence of silver NPs in solutions in the case of superluminescence is smaller than in the case of lasing. The dependences of the lasing and superluminescence intensities on the concentration of silver NPs correlate with data for spontaneous fluorescence. This indicates that both stimulated emission types originate from spontaneous fluorescence.

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