STATISTICAL PRECURSORS OF THE EFFECT OF STIMULATED FLUORESCENCE OF A POLYDISPERSE SYSTEM OF MICRON DROPLETS WITH A LASER DYE

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Received December 14, 1996

Based on the experimental data we propose a statistical model for description of stimulated fluorescence effect (lasing) of the ensemble of polydisperse micron droplets containing a laser dye. Various statistical criteria for identification of the stimulated fluorescence effect are considered in the frameworks of the model. The experimentally obtained statistical characteristics of the fluorescence of the rhodamine 6G solution in ethanol suspended into droplets of different size by the laser pulses of 0.53 μm *wavelength are presented in the paper.*

The stimulated fluorescence effect in an isolated droplet containing a laser dye is well-known as the "lasing" effect and is quite well studied in the experiments.[1–5] At the same time, the question of stimulated fluorescence of the ensemble of droplets of different size is only poorly studied,[5] though, in our opinion, it is of great scientific and practical interest.

In this paper we consider statistical characteristics of the stimulated fluorescence of a polydisperse system of droplets with the dye in order to obtain the criteria for identification of the lasing effect.

Droplet is a spherical resonator, the spectrum of natural modes of which is determined by the radiation wavelength, as well as by the size and complex refractive index of the particulate matter.[6] When illuminating a droplet containing a dye by a pumping radiation, the dye begins to fluoresce, and the generation (lasing) appears in the droplet at fulfilling the threshold conditions. The spectral pattern of lasing is the series of peaks corresponding to the excited natural modes of the spherical resonator.[1] As for the dye laser, the lasing spectrum is shifted to the longwave side relative to the maximum of the fluorescence spectrum of a liquid dye.[5] The increase of the pumping level results in the appearance of additional series of the spectral peaks, due to generation of the modes of higher orders.[4] Since the Q-factor of the big droplets is greater than that of small droplets, the generation conditions can be fulfilled and the lasing occurs in big droplets, while the small droplets fluoresce like liquid dye at the same pumping level.[5]

Thus, the spectral pattern of lasing of a polydisperse system of droplets should be the complex, irregular peak structure on the background of the spectral curve of the liquid dye fluorescence.

The mathematical model of the signal $y(\lambda)$ observed in a single experiment taking into account the above considered physical phenomena can be presented in the form

$$y(\lambda)=f(\lambda)+\sum_{i=1}^{M} C[\lambda_i-\Lambda(p)]\sum_{j=1}^{m_i} C_{ij}K(\lambda-\lambda_i-\Delta_{ij})+n(\lambda), \quad (1)$$

where $f(\lambda)$ is the determinate function describing the liquid dye fluorescence spectrum; $n(\lambda)$ is the equivalent noise of measurements; λ_i is the wavelength, in the vicinity of which one or few spectral peaks appear; M is the number of intervals, into which the wavelength range under investigation is divided; $\Lambda(p)$ is the wavelength, starting from which the stable generation is observed; p is the density of the pumping radiation power; $C(z) = \{1,\ z \ge 0,\ 0,\ z < 0\}$; j is the number of the peak in the ith zone in the vicinity of λ_i; m_i is the number of peaks in the ith zone; Δ_{ij} is the deviation of the jth peak position in the ith zone from λ_i; $K(\lambda - \lambda_i - \Delta_{ij})$ is the kernel function describing the spectral peaks $K(z)\ge 0$; $K(0)=1$, $K(z)=K(-z)$, $K(|z_1|)>K(|z_2|)$, $|z_1|<|z_2|$; $\sum_{j=1}^{m_i} C_{ij}K(\lambda - \lambda_i - \Delta_{ij})$ is the total value of the signals in the vicinity of λ_i; and C_{ij} is the amplitude of the jth peak in the ith zone.

We suppose that observations are carried out only on the wavelength set λ_i, $i = 1, \ldots, M$, and one can ignore overlapping of the peaks from neighbor zones. Under these assumptions, the signal (1) either contains the peak term or not, depending on whether or not λ_i exceeds the threshold $\Lambda(p)$.

The mathematical model of the signal observed in the ith zone has the form

$$y(\lambda_i)=\begin{cases} f(\lambda_i)+n(\lambda_i) & \text{at } \lambda_i<\Lambda(p), \\ f(\lambda_i)+\sum_{j=1}^{m_i} C_{ij}K(\Delta_{ij})+n(\lambda_i) & \text{at } \lambda_i\ge\Lambda(p). \end{cases} \quad (2)$$

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Let us designate as H_0^i the hypothesis that the signal is measured in the zone before the threshold, i.e. the upper row of the model (2) holds. Correspondingly, let H_1^i be the hypothesis on the signal measured in the zone after the threshold and having the structure described by the lower row of the model (2).

Since the value of the unknown threshold $\Lambda(p)$ is of particular interest, the problem of estimating it is reduced, in this case, to a successive examination of the hypotheses H_0^i and H_1^i, $i = 1, \ldots, M$ by the set of the experimental data. Then it is natural to take the value

$$\tilde{\Lambda}(p) = 1/2(\lambda_{i^*-1}, \lambda_{i^*}), \qquad (3)$$

where i^* is the minimum size of the zone where the hypothesis $H_1^{i^*}$ is accepted at the first time, as the estimate $\tilde{\Lambda}(p)$ of the threshold $\Lambda(p)$.

Let the series of N_i independent measurements of the signal $y = y(\lambda_i)$ be carried out at $\lambda = \lambda_i$. Let $\overline{y^i} = \{y_1(\lambda_i), \ldots, y_{N_i}(\lambda_i)\}$ be the observation record sheet or, simplifying the designations, let us write

$$\overline{y^i} = \{y_1, y_2, \ldots, y_{N_i}\}. \qquad (4)$$

It is known[7] that the optimum criterion for examination of our hypotheses in the meaning of the minimum error is the likelihood ratio. However, to calculate this ratio it is necessary to know the distribution densities $P(y/H_0^i)$ and $P(y/H_1^i)$ for the random value y in the ith zone under the condition of the zero and first hypothesis, respectively. Since the theoretical features of these distributions are absent, the synthesis of the discriminant criterion can be done using the information available.

Let us consider some variants of constructing of the criterion discriminating the hypotheses H_0^i and H_1^i. As is seen from the model of the signal observed (2), our hypotheses distinguish between the presence and absence of the sum of nonnegative random values $\sum_{j=1}^{m_i} C_{ij}K(\Delta_{ij})$. This structure difference should be revealed independently of the character of the distribution of the parameters included in this sum. In particular, the fact of the nonnegativeness of the terms results in the inequalities for first two moments of the signal $y(\lambda_i)$

$$M_1[y(\lambda_i)] \geq M_0[y(\lambda_i)] = f(\lambda_i), \qquad (5a)$$

$$D_1[y(\lambda_i)] \geq D_0[y(\lambda_i)]. \qquad (5b)$$

That means that the mean value and the variance of an independent signal are greater at the hypothesis H_1^i than at H_0^1.

Then we obtain two criteria (two statistics)

$$T_1(\overline{y}^i) = \frac{1}{N_i}\sum_{l=1}^{N_i} y_l,\; T_2(\overline{y}^i) = \frac{1}{N_i - 1}\sum_{l=1}^{N_i}[T_1(\overline{y}^i) - f(\lambda_i)]^2, \qquad (6)$$

each of them can be used for examination of the hypotheses by means of the solving rule of the form

$$T(\overline{y}^i)\begin{cases} \overset{H_1^i}{\geq} & d_i \\ \overset{H_0^i}{\leq} & d_i \end{cases}, \qquad (7)$$

where d_i is a constant.

It is expedient to consider such a combined criterion that simultaneously takes into account the difference in the mean values and the variances.

Such a criterion can be written as follows

$$T_3(\overline{y}^i) = T_3(\overline{y}^i) + [T_1(\overline{y}^i) - f(\lambda_i)]^2. \qquad (8)$$

The statistics T_3 mainly describes in the hypothesis H_0^i the variance of the measurement noise n, and in the hypothesis H_1^i it describes the variance created by the peaks, and the square of the difference in the mean values. So the criterion T_3 is more sensitive to the change between the hypotheses. It is necessary to additionally determine the threshold value d_i, with which the statistics is compared using the solving rule (7). Naturally, the threshold d_i should be selected according to the condition of the minimum of the probability of error in the decision. As in the optimum data processing, one can use here the asymptotic Gaussian property of the statistics T_1 and T_2, and calculate the optimum threshold d_i, however, one should estimate the parameters of the Gaussian distributions from the experimental data.

Let us consider one variant more of revealing the differences between the hypotheses H_0^i and H_1^i. We say about the structure of the distribution $P(y/H_1^i)$. Let us assume for simplicity that there is only one peak ($m_i = 1$ in Eq. (2)) of the width less than the width of the zone considered, in the ith zone. Two situations can occur under the conditions of a single experiment at the random nature of Δ_{ij}. Either the peak is not observed and the value

$$y(\lambda_i) = f((\lambda_i) + n(\lambda_i)),$$

is measured, as it occurs at the zero hypothesis, or a "false spike" occurs induced by an actual peak and the value

$$y(\lambda_i) = f(\lambda_i) + C_{i1}K(\Delta_{i1}) + n(\lambda_i).$$

is observed.

Such a character of observations can be interpreted in the statistical meaning by means of the mixture of two distributions, which can be presented in our case in the form

$$P(y/H_1^i) = (1 - \varepsilon)P(y/H_0^i) + \varepsilon H_1(y), \qquad (9)$$

where ε is the probability of obtaining the observation in a single measurement, related to the presence of the peak (or the fraction of such observations from that which can be obtained in the series of independent measurements); and $H_1(y)$ is the distribution density of observations with the presence of peaks.

Thus, if the number of peaks is comparatively small, one can approximate the observation distribution under the hypothesis H_1^i by the mixture (9). Then, in the case when the value of the peaks is great as compared with the variance of the measurement noise $n(\lambda_i)$, the mixture (9) can be separated at some λ, i.e. the carriers of the distribution $P(y/H_0^i)$ and $H_1(y)$ do not overlap. In our case, the fact of separation of the mixture (9) is a reliable criterion of the fact that this wavelength $\lambda \geq \Lambda(p)$ – the threshold value, i.e. the lasing occurs in our droplet medium in addition to the usual fluorescence.

Let us consider the results of our experiments. The laser radiation of the wavelength 0.53 μm and pulse duration 10 ns was focused on the stream of the rhodamine 6G suspended solution of the concentration $2\cdot10^{-4}$ mol/l. The droplet radii were distributed within the limits from 1 to 35 μm with the maximum near 5 μm. The power density of the pumping radiation varied from 0.05 MW/cm^2 and more. The spectral pattern of the droplet radiation was recorded at the width of the monochromator instrumentation function of 10 Å. The fluorescence signals were recorded with a PMT FEU–79 with individually selected divider of voltage for improving the temporal resolution up to 6 ns. The degree of suppression of the elastic scattering (at the wavelength of $\lambda = 0.53$ μm) by the optical filters and monochromator was no less than 10^{-7}.

The spectral curve of the fluorescence of the rhodamine 6G ethanol solution is shown in Figs. 1 and 2 by the dashed line (the curve is normalized to the fluorescence maximum).

The spectral distributions of the radiation of droplet cloud when exciting it by the pulses of the density $p_0 = 8$ MW/cm^2 (Fig. 1*b*) and $p = 0.2p_0$ (Fig. 1*a*) are shown in Figs. 1*a* and *b* by points. Each point is the mean value of 40 fluorescence signals. The mean values are normalized to the mean value at the wavelength corresponding to the liquid dye fluorescence. It is seen that the spectral pattern of the droplet fluorescence at $p = 0.2p_0$ practically coincides with the fluorescence curve of the liquid dye. The excess of the mean values of the droplet fluorescence signals over the corresponding mean values for he liquid dye is observed at $p = p_0$ in the longwave range.

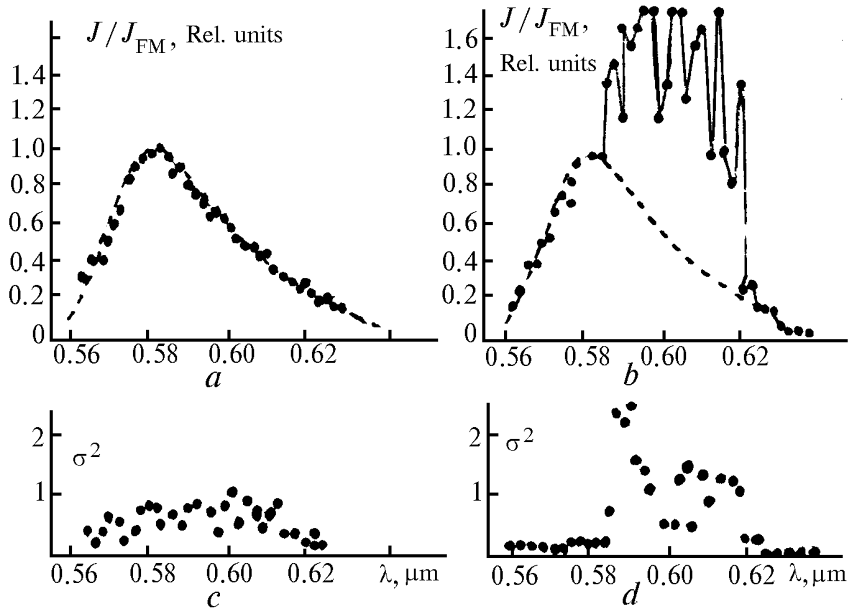

FIG. 1. Spectral dependence of the fluorescence intensity and the fluorescence signal variance of the stream of the micron droplets containing rhodamine 6G at different pumping power density p. The dashed line shows the dye solution fluorescence spectral characteristic normalized to the maximum value. The points are related to the dye solution in the form of the droplet stream (a) – droplet fluorescence at $p = 0.2\ p_0$; *b)* $p = p_0$; *c) droplet fluorescence signal variance at* $p = 0.2p_0$; *d) the same at* $p = p_0$).

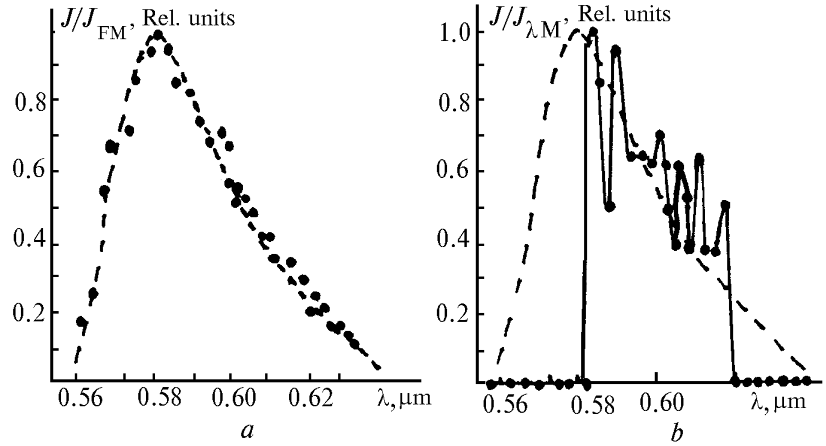

FIG. 2. Spectral dependence of the fluorescence for the signals of the zone A (a) and zone B (b). The signals are normalized to the maximum values.

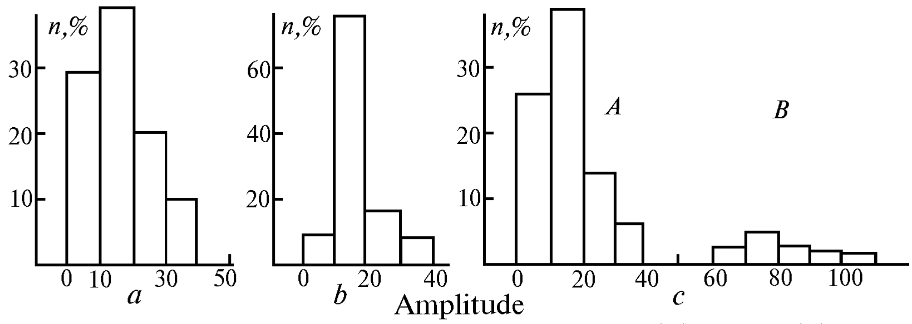

FIG. 3. Histograms of the droplet fluorescence signals of $p = 0.2p_0$ *(a),* $p = p_0$ *(c), and histogram of the elastic scattering signals of ethanol droplets (b).*

The spectral distributions of the variance of the droplet fluorescence signals are shown in Figs. 1*c* and *d* for the case $p = 0.2p_0$ (Fig. 1*c*) and $p = p_0$ (Fig. 1*d*). The sharp decrease of the variance is observed in the red spectral range starting from some value $\lambda = \Lambda$. The histograms of the droplet fluorescence signal amplitudes obtained at $\lambda < \Lambda$ and $\lambda > \Lambda$ are shown in Figs. 3*a* and *c*, respectively. The histograms are constructed for the sample bulk $N = 300$. The histogram of the elastic scattering signals of the ethanol droplets at $\lambda = 0.53$ μm is shown in Fig. 3*b* for a comparison. The signals are well separated into two groups at $p = p_0$. The group *A* is the group of weak signals, and *B* is the group of strong signals (Fig. 3*c*). One can suppose that the histogram in Fig. 3*c* describes the separation of the mixture (9), i.e. the signals of the group *A* are related to the fluorescence of nongenerating droplets ($P(y/H_0^i)$ in the mixture (9)), and the signals of the group *B* are related to the lasing ($H_1(y)$) ones. Indeed, the spectral distribution of the group *A* shown in Fig. 2*a* coincides with the spectral behavior of the liquid dye fluorescence. The spectral distribution of the group *B* is shown in Fig. 2*b* (points). The signals of the group *B* are in the red spectral range, that is characteristic of the single droplet lasing of rhodamine 6G (Fig. 4).

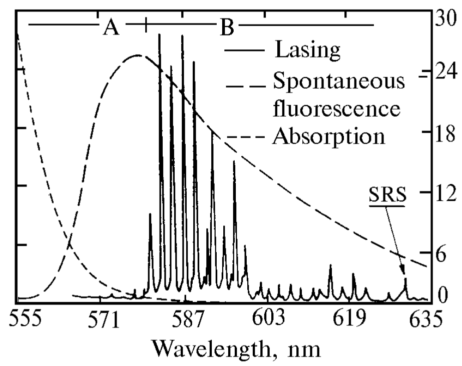

FIG. 4. Spectral dependence of the stimulated fluorescence of the single droplet.[1]

Thus, the fact of the presence of the distribution $H_1(y)$ in the histogram is a reliable criterion of lasing. In addition, the "separated" distributions makes it possible to investigate the fluorescence characteristics of both generating and nongenerating polydisperse system of droplets independently.

In the general case, the conditions of separation of the mixture are not always fulfilled, the distributions considered overlap, but, in any case, the distribution $P(y/H_1^i)$ has a heavier right "tail" under the hypothesis H_1^i than the distribution $P(y/H_0^i)$ (Fig. 5, $p \gg p_0$). One can use this fact for constructing of a solving rule of the form (7), but in this case it should be based on the maximum ordinal statistics, i.e.

$$T(\overline{y}^i) = \max_{j\in[1-N_i]} y_i \begin{cases} \overset{H_1^i}{\geq} & d_i \\ \underset{H_0^i}{\leq} & d_i \end{cases} . \quad (10)$$

In other words, the maximum element is found in the record sheet y^i and then it is compared with the threshold d_i that is determined experimentally. For example, any number from the range (40, 60) can be accepted as a threshold in the situation presented in Fig. 1*d*.

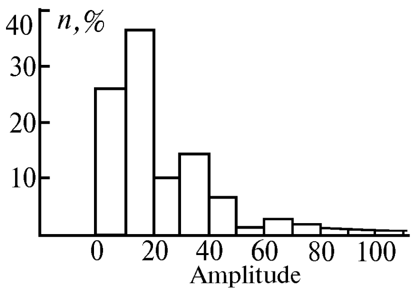

FIG. 5. Histogram of the fluorescence signals of dye droplets at $p \gg p_0$.

We have considered several statistical criteria which provide for a reliable separation of the lasing effect and usual droplet fluorescence. The experiments we have carried out prove the applicability of the criteria considered for identification of the stimulated fluorescence phenomenon in a polydisperse droplet cloud when using spectral measurements with the resolution comparable with the spectral width of the single peak of lasing (10Å).

ACKNOWLEDGMENT

The work was supported in part by the grant of the MOPO competition Center of Fundamental Natural Sciences at Sankt-Petersburg State University (grant No. 95–05.5–32).

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