Laser-induced spontaneous fluorescence of molecules from a microparticle

A.A. Zemlyanov and Yu.E. Geints

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received August 26, 2004

Spontaneous fluorescence of molecules induced by laser pulses of different duration in a microparticle is considered theoretically. Equations describing the dependence of the power and the spectral cross section of a single-photon spontaneous fluorescence from the microparticle on the particle volume, the concentration of active molecules, and the spectral characteristics of the incident and emitted light are obtained by the method of open-resonator theory with the field vectors expanded in series of quasinormal vibrational eigenmodes of a dielectric sphere. It is shown that the spontaneous fluorescence cross section for the particle excited by a short ($t \ll \tau_s$, where τ_s is the characteristic time of spontaneous fluorescence) and long ($t \gg \tau_s$) laser pulses has the same form provided that it is determined from the energy and power relations, respectively. At the same time, the spectral cross section of a single-photon process can exceed by more than ten times the cross section of spontaneous emission from the same volume of a bulk medium. This excess is proportional to the product of the factors accounting for the focusing properties of the particle and its characteristics as a dielectric microresonator.

Introduction

A weakly absorbing spherical dielectric microparticle with the size essentially exceeding the wavelength of incident radiation can be considered as an open optical resonator. Such a resonator has its own system of electromagnetic vibrational modes with high Q factor, reaching $\sim 10^6$ for liquid particles. The optics of such microresonators is of great interest for diagnostics of aerosols, opto-electronics, and laser physics.[1] The phenomenon of spontaneous emission of atoms and molecules, placed in a high-Q resonator, is traditionally studied by classical and quantum electrodynamics[2,3] with the emphasis on the aspects associated with the quantum characteristics of spontaneous emission of molecules at the resonator modes.

The macroscopic optics of emitting dipole was investigated in Refs. 4–6, where the equations were derived for the power and angular diagram of Raman scattering and spontaneous fluorescence of active molecules in spherical particles in the regime of their stationary excitation by a laser radiation. In the theoretical model used, active fluorophore molecules were represented by a set of classical dipoles, distributed arbitrarily inside a particle, and excited by the electric field of the incident wave. The efficiency of excitation of every dipole is characterized by the effective polarizability of the medium at the point of its position inside the particle and is proportional to the amplitude of the principal wave. The total field of spontaneous emission is a sum of the collective field of emission from the dipoles and some effective field caused by the presence of the particle boundary. Based on the approach developed, Refs. 4–6 reported the results of numerical calculations of these parameters and the analytical equations derived in the approximation of optically small particles.

In recent years, great interest has been shown in the use of significantly nonstationary sources for excitation of molecular fluorescence, such as picosecond and femtosecond lasers.

The excitation of molecules of an active substance in a spherical resonator exhibits strong spatial inhomogeneity of the pumping optical field, manifesting itself in the inhomogeneous (over the volume) profile of the field of spontaneous emission. In case of increasing power density of the radiation incident on the particle, the probability of multiphoton absorption, in addition to single-photon transitions, in molecules increases considerably. Under these conditions, the function of the source, exciting the spontaneous emission, becomes even more inhomogeneous.[7] The fluorescence induced due to one-, two-, and three-photon absorption in coumarin-doped ethanol drops irradiated by femtosecond pulses was observed experimentally in Ref. 6. It was found that the fluorescence is enhanced in the backward direction, opposite to the incident pumping radiation. These results were interpreted within the framework of the stationary model, in which the power (integral over angles) of spontaneous fluorescence from the drops P_s is expressed by the dependence $P_s \propto \sigma_s^{(k)} I_L^k$, where $\sigma_s^{(k)}$ is the cross section of k-photon absorption (k = 1, 2, 3...); I_L is the intensity of the pumping radiation in the particle. In this connection, it is interesting to study this dependence using nonstationary excitation of molecular fluorescence in a particle. For interpretation of physical and numerical experiments, it is also important to obtain analytical equations, allowing the cross section or power of spontaneous fluorescence to be estimated in the case of microparticles irradiated by short and long laser pulses.

In this paper, within the framework of the method of nonstationary wave equation for the electric field strength vector, we have considered theoretically single-photon spontaneous fluorescence of active molecules in a microparticle excited by macroscopic polarization at different duration of the pump pulse t_p. We used the expansion of light fields in terms of eigenfunctions of the stationary problem, which are the quasi-normal vibrational modes of a dielectric sphere.[1] Thus, the equations have been obtained, which establish the dependence of the spectral cross section of spontaneous fluorescence on the parameters of the problem: particle size and optical characteristics, spectral line width of the incident and emitted light, and the concentration of fluorescing molecules.

Macroscopic optics of spontaneous molecular emission in a microresonator

Consider the following formulation of the problem. A weakly absorbing spherical particle of radius a_0, containing some amount of a fluorescent (active) substance, is exposed to a plane electromagnetic wave with the central frequency ω_L. The fluorophore molecules are assumed to be distributed homogeneously over the particle volume and having the concentration C_0, which is much lower than the concentration of molecules of the main substance. Consider the regime of nonstationary excitation of the fluorophore: $t_p \ll \tau_s$, when the molecules absorb light quanta at the principal frequency during the pump pulse, but emit for a longer period. Thus, along with the radiation at the frequency of the incident light (primary radiation), the radiation at the frequencies of spontaneous transitions (secondary radiation) is also present in the microparticle–resonator.

For the periods, longer than the initial pulse duration, the emission of active molecules is largely determined by spontaneous transitions. The only exclusion is the zone of spatial localization of high-Q particle eigenmodes – whispering gallery modes, where the field of the incident light wave stays for a rather long time, about nanoseconds.[8] Under these conditions, stimulated emission can take place within the contour of spontaneous emission. However, the intensity of the pump radiation in such modes is usually low, unless their resonance excitation takes place, and therefore we believe that the influence of stimulated processes in the whispering gallery modes on the spontaneous emission is insignificant.

Taking the above-said into account, we can write the wave equation for the complex vector of the electric field strength of spontaneous radiation inside the particle $\mathbf{E}_s(\mathbf{r};\, t)$:

$$\mathrm{rot\,rot}\,\mathbf{E}_s(\mathbf{r};t) + \frac{\varepsilon_a}{c^2}\frac{\partial^2 \mathbf{E}_s(\mathbf{r};t)}{\partial t^2} + \frac{4\pi\gamma_a}{c^2}\frac{\partial \mathbf{E}_s(\mathbf{r};t)}{\partial t} = -\frac{4\pi}{c^2}\frac{\partial^2 \mathbf{P}_s(\mathbf{r};t)}{\partial t^2}, \qquad (1)$$

where γ_a, ε_a are the conductivity and permittivity of the particulate matter; c is the speed of light in vacuum; $\mathbf{P}_s$ is the medium polarization vector at the frequency of the secondary wave ω_s. The medium is assumed non-magnetic and isotopic; dispersion effects are ignored. The nonlinear interaction of waves is assumed weak, and the pumping depletion is neglected. The polarization $\mathbf{P}_s$ in the right-hand side of Eq. (1) accounts for the field of molecular emission at the frequency of the dipole transition considered. In addition, effective polarization of the medium doped with active molecules occurs at the frequency of the secondary wave, which is taken into account by the second term in the left-hand side of Eq. (1). Thus, we can speak about the existence of two fields of the secondary emission inside a particle, one of which is formed by the dipole emission, while the other one relates to the medium permittivity. In this respect, the formulation of the problem is equivalent to that of the approach used in Ref. 4.

Let us now present the electric field vector of the nonlinear wave as a series expansion in terms of the eigenfunctions of the particle–resonator $\mathbf{E}_n^{TE,TH}(\mathbf{r})$, describing the spatial profile of the fields of vibrational modes with TE- and TH-polarization and eigenfrequencies $\omega_n^{TE,TH}$:

$$\mathbf{E}_s(\mathbf{r};t) = \sum_n \left[A_n(t)\mathbf{E}_n^{TE}(\mathbf{r}) - iB_n(t)\mathbf{E}_n^{TH}(\mathbf{r}) \right], \qquad (2)$$

where the coefficients A_n and B_n account for the contribution of each eigenmode to the total field.[9] The functions $\mathbf{E}_n^{TE,TH}(\mathbf{r})$, forming an orthogonal system within a sphere, satisfy the stationary homogeneous Maxwell equations:

$$\mathrm{rot\ rot}\,\mathbf{E}_n^{TE,TH}(\mathbf{r}) - \varepsilon_a\left(\omega_n^{TE,TH}\right)^2 \big/ c^2\, \mathbf{E}_n^{TE,TH}(\mathbf{r}) = 0 \qquad (3)$$

and can be expressed through the vector spherical harmonics. Note that if spherical harmonics are used in Eq. (2), the index n actually consists of three indices: the mode number n_θ, the radial order n_r, and the azimuth index n_m.

The substitution of Eq. (2) into Eq. (1) after some transformations (see Ref. 9) leads to a system of ordinary differential equations for the coefficients of the secondary wave. Consider only the wave with ÒÅ-polarization, assuming that for ÒH modes the analysis is quite analogous. The corresponding equations for the amplitudes have the form

$$\frac{d^2}{dt^2}A_n(t) + 2\Gamma_n \frac{d}{dt}A_n(t) + \omega_n^2 A_n(t) = J_n(t), \qquad (4)$$

where the “driving force” is expressed as

$$J_n(t) = -\frac{4\pi}{\varepsilon_a}\int\limits_{V_a} \mathrm{E}_n^*(\mathrm{r}')\frac{\partial^2 \mathrm{P}_s(\mathrm{r}';t)}{\partial t^2}\mathrm{d}\mathrm{r}'. \qquad (5)$$

Here V_a is the particle volume; Γ_n is the factor of mode attenuation due to absorption by the particulate matter and losses at the exit of radiation through the particle surface. The integral in the right-hand side of this equation accounts for the spatial overlapping of each eigenmode in the secondary wave field with the field of the polarization source inside the particle. The larger is this overlap, the more active is the excitation of the mode of the secondary field.

The particular solution of the inhomogeneous equation (4), representing only the vibrations under the effect of "external" force, can be written as

$$A_n(t) = \frac{1}{\hat{\omega}_n}\int\limits_0^t J_n(t-t')e^{-\Gamma_n t'}\sin\hat{\omega}_n t'\,\mathrm{d}t', \qquad (6)$$

where $\hat{\omega}_n = \omega_n\sqrt{1-\Gamma_n^2/\omega_n^2}$ is the frequency of free vibrations of the mode with the loss taken into account. Taking Eq. (5) into account and integrating by parts, we can transform the solution (6), under the condition $\mathrm{P}_s(t = 0) = 0$, as:

$$A_n(t) = \frac{4\pi\hat{\omega}_n}{\varepsilon_a}\int\limits_{V_a}\mathrm{E}_n^*(\mathrm{r}')\mathrm{d}\mathrm{r}'\times$$

$$\times\left[\frac{\mathrm{P}_s(\mathrm{r}';t)}{\hat{\omega}_n} + \int\limits_0^t \mathrm{P}_s(\mathrm{r}';t-t')e^{-\Gamma_n t'}\sin\hat{\omega}_n t'\,\mathrm{d}t'\right]. \qquad (7)$$

It follows from this equation that the time dependence of the amplitude of the particle eigenmode includes an "instantaneous" part, showing itself during the pulse at the principal frequency (first term in the square brackets), and the time-integrated contribution (second term).

In choosing the physical model of medium polarization in the case of spontaneous transitions $\mathrm{P}_s(\mathrm{r};\, t)$, we take into consideration the integral character of the influence of spatial changes in polarization on the amplitude of the secondary wave mode A_n, which is expressed by Eq. (5). The macroscopic polarization $\mathrm{P}_s(\mathrm{r};\, t)$ of a small medium volume δV, characterized by the radius-vector r, will be considered as a sum of the dipole moments of individual molecules within this volume:

$$\mathrm{P}_s(\mathrm{r};t) = \sum_j^N d_j(t)\mathrm{p}_j\delta^{(3)}(\mathrm{r}-\mathrm{r}_j), \qquad (8)$$

where N is the number of active (in terms of the dipole transition considered) molecules; p_j is the vector, characterizing the dipole orientation in space ($|\mathrm{p}_j| = 1$); $\delta^{(3)}(\mathrm{r} - \mathrm{r}_j)$ is the Dirac delta in the 3D space. The excitation of dipoles is known to be caused by quantum fluctuations of the field (the so-called zero fluctuations of the field of vacuum[10,11]), and the law of their emission can be represented in the form

$$d_j(t) = d_0\exp(i\omega_0 t - \Gamma_0 t), \qquad (9)$$

where d_0 is the dipole moment amplitude, determined through the quantum mean of the off-diagonal dipole matrix elements of the molecule; ω_0 is the frequency of the dipole transition in the molecule; $\Gamma_0 = 1/T_2$ is the attenuation factor; T_2 is the cross-relaxation time of the dipole transition.

In Eq. (8) for the spontaneous macroscopic polarization, the spatial position of the dipole, characterized by the vector r_j, and its orientation (vector p_j) are random parameters. Thus, $\mathrm{P}_s(\mathrm{r};\, t)$ is a realization of the random field caused by fluctuations of its parameters. The amplitude of the light field in the mode of the microresonator, functionally dependent on $\mathrm{P}_s(\mathrm{r};\, t)$, is, in its turn, a random realization of fluctuations of these parameters. Define the operation of averaging of an arbitrary function f over random realizations of the characteristics r_j and p_j as follows:

$$\langle f\rangle = \int\limits_{\delta V}\frac{\mathrm{d}\mathrm{r}_j}{\delta V}\int\limits_{4\pi}\frac{\mathrm{d}\Omega}{4\pi}f, \qquad (10)$$

where $\mathrm{d}\Omega$ is the solid angle element. Equation (10) means that the statistical averaging is carried out over the position with the uniform probability density $1/\delta V$ and over orientations with the uniform probability density $1/4\pi$.

After the substitution of Eq. (8) into Eq. (7) and the use of Eq. (10), we obtain the following equation for the square amplitude of the eigenmode of nonlinear spontaneous-emission wave field:

$$|A_n(t)|^2 = \frac{16\pi^2\hat{\omega}_n^2}{\varepsilon_a^2}\left\langle\int\limits_{V_a}\mathrm{d}\mathrm{r}'\int\limits_{V_a}\left(\mathrm{E}_n(\mathrm{r}')\mathrm{E}_n^*(\mathrm{r}'')\right)\mathrm{d}\mathrm{r}''\times\right.$$

$$\times\left[\frac{\mathrm{P}_s(\mathrm{r}';t)}{\hat{\omega}_n} + \int\limits_0^t \mathrm{P}_s(\mathrm{r}';t-t')e^{-\Gamma_n t'}\sin\hat{\omega}_n t'\,\mathrm{d}t'\right]\times$$

$$\left.\times\left[\frac{\mathrm{P}_s(\mathrm{r}'';t)}{\hat{\omega}_n} + \int\limits_0^t \mathrm{P}_s(\mathrm{r}'';t-t')e^{-\Gamma_n t'}\sin\hat{\omega}_n t'\,\mathrm{d}t'\right]^*\right\rangle =$$

$$= \frac{16\pi^2|d_0|^2}{3\varepsilon_a^2}\left[e^{-2\Gamma_0 t}\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2 C(\mathrm{r}';t)\mathrm{d}\mathrm{r}' + 2\hat{\omega}_n\times\right.$$

$$\times\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2\mathrm{d}\mathrm{r}'\int\limits_0^t C(\mathrm{r}';t-t')e^{-\gamma_n t'}\sin\hat{\omega}_n t'\cos\omega_0 t'\,\mathrm{d}t' +$$

$$+\hat{\omega}_n^2\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2\mathrm{d}\mathrm{r}'\int\limits_0^t C(\mathrm{r}';t-t')\mathrm{d}t'\times$$

$$\left.\times\int\limits_0^t e^{-\gamma_n(t'+t'')}\sin\hat{\omega}_n t'\sin\hat{\omega}_n t''\cos\omega_0(t'-t'')\,\mathrm{d}t''\right], \qquad (11)$$

where $\gamma_n = \Gamma_n + \Gamma_0$ is the attenuation factor of the secondary field mode in the resonator; $C(\mathrm{r};t) = N(\mathrm{r};t)/\delta V$ is the concentration of excited molecules of the active substance, depending on the spatial coordinates and time. Calculating the internal integral over time in the right-hand side of Eq. (11) and rejecting the terms with the time dependence in the form $\exp\{i(\omega_0+\omega_n)t\}$, we obtain:

$$|A_n(t)|^2 \approx \frac{16\pi^2|d_0|^2}{3\varepsilon_a^2}\Bigg[e^{-2\Gamma_0 t}\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2 C(\mathrm{r}';t)\mathrm{d}\mathrm{r}' + \\ + \tilde{\omega}_n\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2\mathrm{d}\mathrm{r}'\int\limits_0^t C(\mathrm{r}';t-t')e^{-\gamma_n t'}\sin\Delta\omega_n t'\,\mathrm{d}t' + \\ + \frac{g_n}{4}\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2\mathrm{d}\mathrm{r}'\int\limits_0^t C(\mathrm{r}';t-t')e^{-\gamma_n t'}F_n(t')\,\mathrm{d}t'\Bigg]. \quad (12)$$

Here

$$g_n = \tilde{\omega}_n^2\Big/\left(\Delta\omega_n^2+\gamma_n^2\right)$$

characterizes the shape of the spontaneous emission line in the resonator;

$$F_n(t) = \left(\Delta\omega_n\sin(\Delta\omega_n t)+\gamma_n\cos(\Delta\omega_n t)\right);\quad \Delta\omega_n = \omega_0 - \tilde{\omega}_n.$$

It follows from Eq. (12) that the instantaneous component of the intensity of the secondary field mode in the particle attenuates for the cross-relaxation time of the dipole transition and does not depend on the Q-factor for this mode. At the same time, the cumulative contribution of spontaneous transitions, which is present in Eq. (12), at the previous instants contains the spectral function, associated with the resonator properties of the particle and indicating that the square amplitude of the spontaneous emission field mode is maximum at the exact resonance of the mode frequency with the frequency of a molecular transition. In the further analysis, we omit the second term in the right-hand side of Eq. (12) because it is proportional to the frequency detuning of the eigenmode $\Delta\omega_n$ and, consequently, it is negligibly small near the molecular resonance.

The number of emitting dipoles $N(\mathrm{r};t)$ at a particular instant at this point of a particle is determined by the physical mechanism of absorption and emission of light quanta by the molecule and can be found from the solution of the system of kinetic equations for its active levels. For the two-level scheme in the approximation of weak pumping, when $N_2 \ll N_1$, where N_1, N_2 are the numbers of molecules at the lower and upper levels of the working transition, the corresponding equation has the form:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \frac{\sigma_{12}}{\hbar\omega_L}N_1 I_L(\mathrm{r};t) - \Gamma_{21}N_2(t);\quad N_1+N_2 = N_0. \quad (13)$$

In Eq. (13)

$$\sigma_{12} = \frac{4\pi\omega_0|\mu_{12}|^2 g_L}{3c\hbar\sqrt{\varepsilon_a}}$$

is the absorption cross-section of the one-photon transition;

$$g_L = \Gamma_{21}\Big/\left((\omega_0-\omega_L)^2+\Gamma_{21}^2\right)$$

is the Lorenz line width of the transition; Γ_{21} is the rate constant of the spontaneous transition; $I_L(\mathrm{r};t)$ is the intensity of the laser radiation at the principal frequency inside the particle. The solution of Eq. (13) has the form of the convolution integral:

$$N_2(\mathrm{r};t) = \frac{\sigma_{12}}{\hbar\omega_L}N_1\int\limits_0^t I_L(\mathrm{r};t')\,e^{-\Gamma_{21}(t-t')}\mathrm{d}t'. \quad (14)$$

For the field of the pump wave, we also use the representation (2) and take into account that the eigenfunctions are orthogonal, that is,

$$I_L(\mathrm{r};t) = \frac{c\sqrt{\varepsilon_a}}{8\pi}\sum_m |a_m(t)|^2\cdot|\mathrm{E}_m(\mathrm{r})|^2$$

(only TE-modes of the filed are considered as before). Then after the substitution of $N(\mathrm{r};t)$ by the function $N_2(\mathrm{r};t)$ into Eq. (12), we obtain:

$$|A_n(t)|^2 = \frac{2\pi\sigma_{12}c\,C_0|d_0|^2}{3\hbar\omega_L\varepsilon_a\sqrt{\varepsilon_a}}k_n^3 e^{-\Gamma_{21}t}\sum_m \Pi_{nm}^{(1)}\times \\ \times\Bigg[e^{-2\Gamma_0 t}\int\limits_0^t |a_m(t')|^2 e^{\Gamma_{21}t'}\mathrm{d}t' + \\ + \frac{g_n}{4}\int\limits_0^t e^{-(\gamma_n-\Gamma_{21})t'}F_n(t')\,\mathrm{d}t'\int\limits_0^{t-t'}|a_m(t'')|^2 e^{\Gamma_{21}t''}\mathrm{d}t''\Bigg], \quad (15)$$

where C_0 is the concentration of active molecules;

$$\Pi_{nm}^{(1)} = k_n^{-3}\int\limits_{V_a}|\mathrm{E}_n(\mathrm{r}')|^2\cdot|\mathrm{E}_m(\mathrm{r}')|^2\mathrm{d}\mathrm{r}'$$

are the integrals of spatial overlapping of the modes of the primary and secondary fields inside the particle; $k_n = \omega_n/c$.

Consider the case of short pumping of the particle, when the inequality $t_p \ll (\Gamma_{21})^{-1}$ is valid, where t_p is the laser pulse duration. Assume that the medium is excited by a rectangular pulse and by the time $t = t_p$ the population of the upper level of the transition is maximum:

$$N_2^m(\mathrm{r}) \approx \frac{\sigma_{12}}{\hbar\omega_L}N_0 I_{L0}(\mathrm{r})t_p,$$

and $N_2^m \ll N_0$, where

$$I_{L0}(\mathrm{r}) = \frac{c\sqrt{\varepsilon_a}}{8\pi}\sum_m |a_m^0|^2|\mathrm{E}_m(\mathrm{r})|^2$$

is the intensity of the principal wave inside the particle. Once the pumping is terminated ($t > t_p$), N_2

decreases exponentially with time in accordance with Eq. (13):

$$N_2(\mathrm{r};t) = N_2^m(\mathrm{r})\exp\left(-\Gamma_{21}(t-t_\mathrm{p})\right). \qquad (16)$$

Then the square amplitude of the mode of the secondary field takes the following form (for $t > t_\mathrm{p}$):

$$\left|A_n(t)\right|^2 \approx \frac{\pi\sigma_{12}c\left|d_0\right|^2}{6\hbar\omega_\mathrm{L}\varepsilon_\mathrm{a}\sqrt{\varepsilon_\mathrm{a}}}\times$$

$$\times C_0 g_n k_n^3 t_\mathrm{p} e^{-\Gamma_{21}(t-t_\mathrm{p})}\sum_m \left|a_m^0\right|^2 \Pi_{nm}^{(1)}, \qquad (17)$$

where it is taken into account for the attenuation factor that:

$$\Gamma_{21}\ \mathbf{Z}\ \Gamma_n, \Gamma_0. \qquad (18)$$

Introduce the following designation:

$$G_\mathrm{s} = \frac{\pi\sigma_{12}c\left|d_0\right|^2}{6\hbar\omega_\mathrm{L}\varepsilon_\mathrm{a}\sqrt{\varepsilon_\mathrm{a}}}, \qquad (19)$$

which means the rate of conversion of the pump energy absorbed by the active molecule into the energy of spontaneous emission. Multiplying the left- and right-hand sides of Eq. (17) by $\left|\mathrm{E}_n(\mathrm{r}')\right|^2$ and performing summation over all modes of the secondary field, we obtain the equation for the intensity of the field of spontaneous emission in the particle exposed to a short laser pulse:

$$I_\mathrm{s}(\mathrm{r};t) = C_0 C_\mathrm{s} e^{-\Gamma_{21}(t-t_\mathrm{p})}\sum_n\sum_m g_n k_n^3\, w_m^0 \left|\mathrm{E}_n(\mathrm{r})\right|^2 \Pi_{nm}^{(1)}, \qquad (20)$$

where $w_m^0 = \dfrac{c\sqrt{\varepsilon_\mathrm{a}}}{8\pi}\left|a_m^0\right|^2 t_\mathrm{p}$ is the amplitude coefficient in the corresponding expansion of the energy density of the incident wave field inside the particle.

Consider the energy characteristics of the field of spontaneous emission outside the particle. Following the law of energy conservation, the total energy of spontaneous emission W_s, stored in the microparticle–resonator for the whole observation time, converts into the energy of the emitted wave W_r minus the fraction W_ab, converted into heat due to the nonzero conductivity of the resonator matter: $W_\mathrm{s} = W_\mathrm{r} + W_\mathrm{ab}$. Note that here we ignore the energy loss of the spontaneous fluorescence field due to the part of the macroscopic polarization of the medium, associated with stimulated transitions in the molecules, as well as due to the energy exchange between the primary and secondary waves. These issues will be considered in our following papers.

The radiation power in an individual mode of the secondary field inside the microresonator P_n will be determined through integration of Eq. (17) over the particle volume for the fixed index n:

$$P_n(t) = \frac{\varepsilon_\mathrm{a}\omega_n^4}{8\pi c^3} C_0 G_\mathrm{s} g_n e^{-\Gamma_{21}(t-t_\mathrm{p})}\sum_m w_m^0\, \Pi_{nm}^{(1)}.$$

Then the total energy of radiation spontaneously emitted from inside the particle can be expressed as follows:

$$W_\mathrm{s} = \frac{\varepsilon_\mathrm{a}}{8\pi c^3\Gamma_{21}} C_0 G_\mathrm{s}\sum_n \eta_n\, \omega_n^4 g_n \sum_m w_m^0 \Pi_{nm}^{(1)};\ t > t_\mathrm{p}. \qquad (21)$$

Here

$$\eta_n = 1 - 4\pi\gamma_\mathrm{a}/(\varepsilon_\mathrm{a}\overset{\vdash}{\omega}_n).$$

Introduce the total cross-section of spontaneous emission of the particle for single-photon transitions upon the nonstationary excitation $\sigma_\mathrm{s}^{(1)}$ as the ratio of the energy of the secondary field W_s emitted to the energy density of the incident pulse. For the rectangular-shaped pump pulse we have:

$$\sigma_\mathrm{s}^{(1)} = \frac{W_\mathrm{s}}{I_0 t_\mathrm{p}} = \frac{\varepsilon_\mathrm{a}}{8\pi c^3\Gamma_{21}} C_0 G_\mathrm{s}\sum_n \eta_n\, \omega_n^4 g_n \sum_m \left|\bar{a}_m^0\right|^2 \Pi_{nm}^{(1)}, \qquad (22)$$

where $\left|\bar{a}_m^0\right|^2 = \left|a_m^0\right|^2/\left|E_0\right|^2$, E_0 is the electric field strength of the incident light wave.

In the regime of a long pump pulse, the stationary solution for the power of spontaneous emission into the mode follows from Eq. (15):

$$P_n^\mathrm{st} = \frac{\varepsilon_\mathrm{a}\omega_n^4}{8\pi c^3\Gamma_{21}} C_0 G_\mathrm{s} g_n \sum_m \left|a_m^0\right|^2 \Pi_{nm}^{(1)},$$

which also leads to the equation, identical to Eq. (22), for the cross section of stationary spontaneous emission.

Thus, from the analysis of equations obtained we can draw some conclusions.

The radiation emitted spontaneously by a spherical particle–resonator has, in the general case, a wider line as compared to that in an extended medium $\gamma_n \ge \Gamma_0$. At a strong attenuation of modes in the resonator, when $\Gamma_n \gg \Gamma_0$, the line width is determined by the resonant properties of the particle $g(\Delta\omega_n)\ \mathbf{W}\ Q_n^{-1}$, where Q_n is the loaded Q of the resonant mode.

At a pulsed excitation of spontaneous fluorescence in the particle, the time behavior of the power of the spontaneous emission field, upon the fulfillment of the condition (18), is characterized by the exponential attenuation with the constant, equal to the time of the excited level depopulation of the active molecule. The influence of attenuation within the resonator on the time behavior of spontaneous emission is negligible, as long as the condition $\Gamma_n \gg \Gamma_{21}$ is valid, and reduces to only the broadening of the fluorescence spectral line, mentioned above.

One of the features of spontaneous emission from a microparticle is the fact that the intensity of spontaneous component of the field at every point depends on the degree of its spatial overlap with all other modes of the pump field. In other words, the resonator morphology, determining the spatial structure of the interacting fields, influences the energy characteristics of the incoherent signal induced.

Influence of resonator morphology on the power of spontaneous emission

Consider the overlap integrals $\Pi_{nm}^{(1)}$ for the spherical resonator in a more detail. In this case, the eigenfunctions $\mathrm{E}_n^{\mathrm{TE,TH}}(\mathrm{r})$ are expressed, as was noted above, through the spherical vector-harmonics $\mathrm{M}_n^{(1)}$ and $\mathrm{N}_n^{(1)}$ [Ref. 12] in the basis $(\mathrm{e}_r;\mathrm{e}_\theta;\mathrm{e}_\varphi)$:

$$\mathrm{E}_n^{\mathrm{TE}} \equiv (\mathrm{E}_{n_\theta\,(n_m)}^{n_r})^{\mathrm{TE}} = h_{n_\theta\,(n_m)}^{\mathrm{TE}}(k_{n_\theta}^{n_r}a_0)\,\mathrm{M}_{n_\theta\,(n_m)}^{(1)}(k_{n_\theta}^{n_r}r,\theta,\varphi),$$
$$\mathrm{E}_n^{\mathrm{TH}} \equiv (\mathrm{E}_{n_\theta\,(n_m)}^{n_r})^{\mathrm{TH}} = h_{n_\theta\,(n_m)}^{\mathrm{TH}}(k_{n_\theta}^{n_r}a_0)\,\mathrm{N}_{n_\theta\,(n_m)}^{(1)}(k_{n_\theta}^{n_r}r,\theta,\varphi), \tag{23}$$

where $k_{n_\theta}^{n_r} = \omega_{n_\theta}^{n_r}/c$. The scaling coefficients $h_{n_\theta\,(n_m)}^{\mathrm{TE}}$ and $h_{n_\theta\,(n_m)}^{\mathrm{TH}}$ are determined from the condition of the eigenfunctions normalization to unity:

$$h_{n_\theta\,(n_m)}^{\mathrm{TE}}(k_{n_\theta}^{n_r}a_0) = \left(\rho_{n_\theta\,(n_m)}/f_{n_\theta}\right)^{1/2},$$

$$h_{n_\theta\,(n_m)}^{\mathrm{TH}}(k_{n_\theta}^{n_r}a_0) = \left(\rho_{n_\theta\,(n_m)}/g_{n_\theta}\right)^{1/2}.$$

Here

$$\rho_{n_\theta\,(n_m)} = \frac{(2n_\theta+1)(n_\theta-n_m)!}{2\pi n_\theta(n_\theta+1)(n_\theta+n_m)!(1+\delta_{0n_m})};$$

$$f_{n_\theta} = \frac{1}{2\left(k_{n_\theta}^{n_r}\right)^3}\psi_{n_\theta}(k_{n_\theta}^{n_r}a_0)\left[\psi'_{n_\theta}(k_{n_\theta}^{n_r}a_0) - \frac{1}{k_{n_\theta}^{n_r}a_0}\psi_{n_\theta}(k_{n_\theta}^{n_r}a_0)\right];$$

$$g_{n_\theta} = \frac{1}{2k_{n_\theta}^{n_r}}\psi_{n_\theta}(k_{n_\theta}^{n_r}a_0)\,\psi'_{n_\theta}(k_{n_\theta}^{n_r}a_0),$$

where ψ_n are the spherical Riccati–Bessel functions, the dash denotes the derivative with respect to the entire argument; δ_{nm} is the Kronecker delta. Then the factor of overlapping among the TE-modes $\Pi_{nm}^{(1)}$ is the integral of the product of squared absolute values of vector harmonics with different indices and different eigenfrequencies:

$$\Pi_{nm}^{(1)} = \left(k_{n_\theta}^{n_r}\right)^{-3}\left|h_{n_\theta\,(n_m)}^{\mathrm{TE}}\right|^2\left|h_{m_\theta\,(m_m)}^{\mathrm{TE}}\right|^2\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\sin\theta\mathrm{d}\theta\times$$
$$\times\int_0^{a_0}\left|\mathrm{M}_{n_\theta\,(n_m)}^{(1)}(k_{n_\theta}^{n_r}r;\theta;\varphi)\right|^2\cdot\left|\mathrm{M}_{m_\theta\,(m_m)}^{(1)}(k_{m_\theta}^{m_r}r;\theta;\varphi)\right|^2 r^2\mathrm{d}r.$$

Figure 1 shows the overlap integral $\Pi_{nm}^{(1)}$ as a function of the effective dimensionless half-width of the resonance contour of eigenmodes of the field $\bar{\Gamma}_{nm} = \bar{\Gamma}_n + \bar{\Gamma}_m = \Gamma_n/\omega_n + \Gamma_m/\omega_m$. The following model case was considered. It was assumed that, in the rhodamine-doped water drop exposed to the radiation with $\lambda_\mathrm{L} = 0.53$ μm, the fluorescence at the wavelength $\lambda_\mathrm{s} = 0.6$ μm with the spectral line width $\Gamma_0 = 2\cdot10^{13}$ Hz is induced. As an example, we took a particle having the radius $a_0 = 10$ μm and considered three modes of the secondary field: $\mathrm{TE}_{125(1)}^2$ (¨), $\mathrm{TE}_{119(1)}^3$ (i), and $\mathrm{TE}_{115(1)}^4$ (Δ), having equal eigenfrequencies ω_n (but different Γ_n) and falling within the spectral contour of the fluorescence. For each of these modes, we calculated the array of overlap integrals with different principal field modes, sampled randomly from the ranges of the indices $m_\theta = 1$–$(2x_\mathrm{a})$, $m_r = 1$–5, $m_\varphi = 1$, where $x_\mathrm{a} = 2\pi a_0/\lambda_\mathrm{L}$. The obtained values of $\Pi_{nm}^{(1)}$ were constructed as functions of the combined parameter $\bar{\Gamma}_{nm}$.

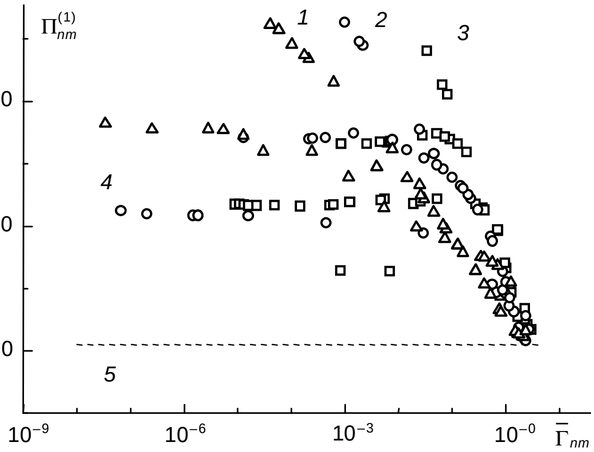

Fig. 1. Integral of the mode overlap $\Pi_{nm}^{(1)}$ as a function of the parameter $\bar{\Gamma}_{nm}$ in the water drop ($a_0 = 10$ μm). The groups of points *1 – 3* correspond to the overlapping eigenmodes with identical radial indices: $n_r = 2$ (*1*), 3 (*2*), 4 (*3*); and with different radial indices (group *4*). Line *5* shows the level of $\Pi_{nm}^{(1)} = 1$.

It follows from Fig. 1 that the whole array of the values of the overlap coefficient can conditionally be divided into two groups of points. One of them (with the numbers *1–3*) characterizes the situation of the optimal spatial overlap of the modes and the high values of the coefficient $\Pi_{nm}^{(1)}$, which allows one to speak about the resonance character of the process of wave interaction. In this case, the spatial profiles of the interacting modes are in a rather accurate correspondence, and the detailed analysis carried out in Ref. 13 showed that the overlap the radial modes (coincidence of the radial mode numbers n_r) is of critical importance here. This can also be from Fig. 2, which shows the spatial distribution of the integrand function $\left|\mathrm{E}_n(r;\theta)\right|^2\cdot\left|\mathrm{E}_m(r;\theta)\right|^2$ for two combinations of the overlapping modes with the same and different values of the radial index n_r. The increase of the Q-factor of the interacting modes (decrease of the parameter $\bar{\Gamma}_{nm}$) for this group of points leads to the corresponding increase of the overlap factor.

Another group of points in Fig. 1 (group *4*) represents overlapping of the eigenmodes with different radial indices n_r. The values of $\Pi_{nm}^{(1)}$ for this type of overlap are much lower, especially, in the range of narrow spectral contours of the modes, and, in contrast to the previous case, have the tendency to saturation with the decrease of $\bar{\Gamma}_{nm}$ (increase of the Q-factor of the modes). This saturation is caused by the increasing degree of spatial inhomogeneity of the modes and the contraction of the zone of their efficient overlap.

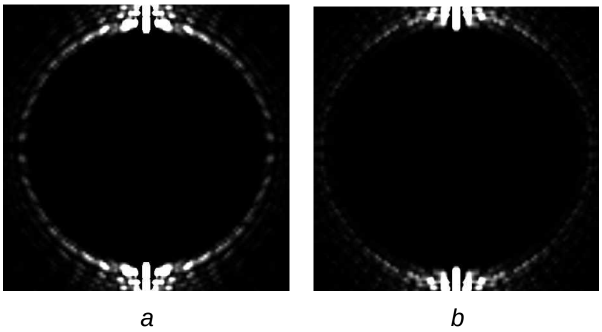

Fig. 2. Spatial profile of the function $|E_n(r;\theta)|^2 \cdot |E_n(r;\theta)|^2$ at the principal cross section of the water drop for different combinations of eigenmodes of the internal optical field: (*a*) $TE^3_{119(1)} - TE^3_{84(1)}$ ($\Pi_{nm}^{(1)} = 34$); (*b*) $TE^3_{119(1)} - TE^1_{84(1)}$ ($\Pi_{nm}^{(1)} = 21$).

In the limiting case of the low-Q modes (high $\bar{\Gamma}_{nm}$), both of the groups of points fall in the same range of close-to-unity values of the factor $\Pi_{nm}^{(1)}$. In fact, this type of interaction is analogous to spontaneous fluorescence in the free space, when the eigenfunctions of the problem are traveling waves: $E_n(r) \sim e^{ikr}$, and the overlap factor $\Pi_{nm}^{(1)} \approx 1$.

The dependence $\Pi_{nm}^{(1)}(\bar{\Gamma}_{nm})$ shown in Fig. 1, regardless of the fact that it is calculated for the fixed size of the particle, is nevertheless rather universal for the mode overlap in the particles of different size. The increase or decrease of the particle radius will change the combination of the eigenmodes of the primary and secondary fields, taking part in the nonlinear interaction, because $\omega_n \sim 1/a_0$. In this case, the spectral contour of spontaneous emission $\omega = \omega_0 \pm \gamma_n$ will overlap for example, with the decreased particle radius, the eigenmodes of the secondary field with smaller indices and, consequently, larger values of the parameter $\bar{\Gamma}_n$. Correspondingly, the number of modes of the primary field, which really take part in the interaction, will decrease. Thus, the decrease or increase of a_0 will correspond to the movement along the dependence shown in Fig. 1 from the left to the right or from the right to the left, respectively.

Estimate the cross section of spontaneous fluorescence of the particle. Assume that the spatial overlap of the modes of the primary and secondary fields is characterized by some identical effective value of the integral coefficient $[\Pi^{(1)}]_{\text{eff}}$. Then the internal sum in Eq. (22) over the modes of the pump field can be expressed through the factor of spatial inhomogeneity of the field $\bar{B}_L = 1/V_a \sum_m |\bar{a}_m^0|^2$, averaged over the particle volume, as follows:

$$\sum_m |\bar{a}_m^0|^2 \Pi_{nm}^{(1)} \approx [\Pi^{(1)}]_{\text{eff}} \sum_m |\bar{a}_m^0|^2 = [\Pi^{(1)}]_{\text{eff}} V_a \bar{B}_L . \quad (24)$$

Note that the dependence of the factor $\bar{B}_L$ on the diffraction parameter of the particle $x_a = \omega_L a_0 / c$ (Fig. 3) has the pronounced resonance character. The observed peaks are connected with the fulfillment of the condition of resonant excitation of the corresponding modes of the pump field in the particle: $\omega_L = \omega_m$ (the so-called *input* resonances), and the value of the factor $\bar{B}_L$ in this case can be more than an order of magnitude greater that the non-resonant background, where $\bar{B}_L \approx 1.5–2$. Consequently, as the particle radius varies, the cross-section of spontaneous fluorescence follows the input resonances of the pump field.

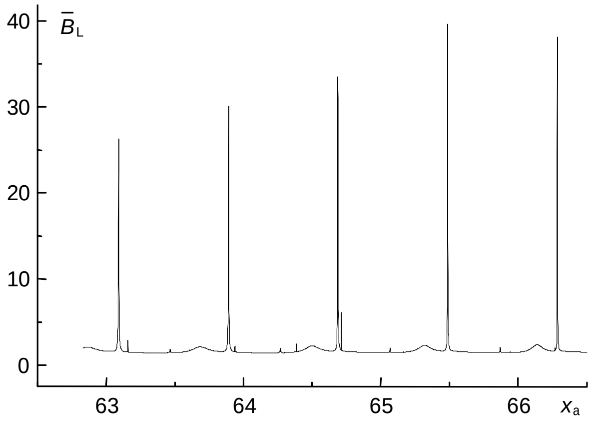

Fig. 3. Volume-averaged factor of inhomogeneity of the internal optical field as a function of the diffraction parameter of a particle with the refractive index $n_a = 1.33$.

Re-write Eq. (22) taking into account Eq. (24):

$$\sigma_s^{(1)} \cong \frac{\varepsilon_a G_s}{8\pi c^3 \Gamma_{21}} C_0 [\Pi^{(1)}]_{\text{eff}} V_a \bar{B}_L (x_a) \sum_n \eta_n \omega_n^4 g_n . \quad (25)$$

As can be seen from this equation, the cross section of spontaneous emission of the particle $\sigma_s^{(1)}$ is proportional to the particle volume V_a and the concentration of active molecules C_0, as was noticed in the experiment (Ref. 14). In the regime of saturation of the fluorophore absorption, the linear dependence of the cross-section $\sigma_s^{(1)}$ on the concentration breaks, and $\sigma_s^{(1)}$ transits into the regime of saturation.

The radiation spontaneously emitted from the resonator is usually a multimode one. Under these conditions, the equation obtained can be analyzed only numerically. For analytical estimation, consider the unimodal regime of spontaneous emission from the particle. In this case, in the sum of the Lorentz contours of the secondary field modes in Eq. (25), under the condition $\omega_n = \omega_0$ (the so-called *output* resonance), the corresponding term will dominate. The cross section of particle fluorescence in the unimode regime takes the form:

$$\sigma_s^{(1)}(\omega_n = \omega_0) \cong C_0 \frac{\varepsilon_a \omega_0^4}{8\pi c^3 \Gamma_{21}} \times$$

$$\times G_s \eta_n \frac{\omega_0^2}{(\Gamma_n + \Gamma_0)^2} [\Pi^{(1)}]_{\mathrm{eff}} V_a \bar{B}_L(x_a). \qquad (26)$$

If the dominant mode is a high-Q mode, that is, $\Gamma_n \ll \Gamma_0$, then the fluorescence cross section is inversely proportional to the squared natural line width of spontaneous emission Γ_0. For the low-Q mode ($\Gamma_n \gg \Gamma_0$), the decisive role in $\sigma_s^{(1)}$ belongs to the natural attenuation within the resonator.

Compare Eq. (26) with the cross section of spontaneous fluorescence in an extended medium $\sigma_{s\infty}^{(1)}$. The ratio of the fluorescence cross section of the particle in the regime of excitation of a single mode of the secondary field to that in a spherical area without the pronounced resonant properties, containing the same number of the active molecules and having the same volume, is the following:

$$\sigma_s^{(1)} \big/ \sigma_{s\infty}^{(1)} = \frac{1}{(1 + \Gamma_n/\Gamma_0)^2} \bar{B}_L [\Pi^{(1)}]_{\mathrm{eff}}. \qquad (27)$$

For numerical estimation, let us take water drop with the refractive index $n_a = 1.33$. At the mean value of the overlap integral $[\Pi^{(1)}]_{\mathrm{eff}} \approx 20$, we have the sought ratio of fluorescence cross-sections in the absence of input resonance ($\bar{B}_L \sim 2$): $\sigma_s^{(1)} \big/ \sigma_{s\infty}^{(1)} \sim 0.1$ for low-Q modes ($\Gamma_n \gg \Gamma_0$) and $\sigma_s^{(1)} \big/ \sigma_{s\infty}^{(1)}\ \mathrm{W}\,40$ for high-Q modes ($\Gamma_n \ll \Gamma_0$). At the resonance excitation of spontaneous fluorescence by the incident wave (input resonance conditions), when $\bar{B}_L \gg 1$, these estimates should be increased by more than an order of magnitude.

Thus, upon the excitation of spontaneous fluorescence in microparticles, the spectral cross section of a single-photon process for some modes can exceed the cross section of spontaneous emission for the same volume of an extended medium, and this excess is proportional to the product of the factors accounting for the focusing properties of the particle and its characteristics as a dielectric microresonator. The spherical shape causes the appearance of local peaks in the spatial intensity distribution of the pump field and the secondary wave inside the microparticle. As a result, excitation of active molecules in these zones is more efficient as compared to the extended medium. It can be stated that this is just the main cause for the asymmetry in the angular distribution of the fluorescence field from particles (observed in some experiments, see, for example Ref. 6), whereas the spontaneous fluorescence from a bulky medium has the isotropic angular distribution.

Acknowledgments

This work was supported, in part, by the Russian Foundation for Basic Research (Grant No. 03–05–64228) and CRDF (Grant RP0–1390–TO–03).

References

1. Yu.E. Geints, A.A. Zemlyanov, V.E. Zuev, A.M. Kabanov, and V.A. Pogodaev, *Nonlinear Optics of Atmospheric Aerosol* (SB RAS Publishing House, Novosibirsk, 1999), 260 pp.
2. F.V. Bunkin and A.N. Oraevskii, Izv. Vyssh. Uchebn. Zaved., Radiofiz. 11, No. 2, 181–186 (1959).
3. A.N. Oraevskii, Usp. Fiz. Nauk 164, No. 4, 415–427 (1994).
4. H. Chew, P.J. McNulty, and M. Kerker, Phys. Rev. A 13, 396–404 (1976).
5. G. Schweiger and S. Lange, J. Opt. Soc. Am. B 13, No. 9, 1864–1872 (1996).
6. S.C. Hill, Y. Pan, S. Holler, and R.K. Chang, Phys. Rev. Lett. 85, No. 1, 54–57 (2000).
7. A.A. Zemlyanov, Yu.E. Geints, and E.K. Panina, Proc. SPIE 5396, 205–211 (2003).
8. A.A. Zemlyanov and Yu.E. Geints, Atmos. Oceanic Opt. 15, No. 5, 316–325 (2001).
9. A.A. Zemlyanov and Yu.E. Geints, Atmos. Oceanic Opt. 15, No. 12, 988–993 (2002).
10. V.M. Fain, *Quantum Radiophysics*. Vol. 1. *Photons and Nonlinear Media* (Sov. Radio, Moscow, 1972), 472 pp.
11. D.N. Klyshko, *Physical Principles of Quantum Electronics* (Nauka, Moscow, 1986), 296 pp.
12. C. Bohren and D. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York–London, 1983).
13. A.A. Zemlyanov and Yu.E. Geints, J. Opt. Soc. Am. B 20, No. 12, 2477–2486 (2003).
14. S.C. Hill, R.G. Pinnick, S. Niles, N.F. Fell, Yong-Le Pan Jr., J. Bottiger, B.V. Bronk, S. Holler, and R.K. Chang, Appl. Opt. 40, No. 18, 3005–3013 (2001).