
Light quenching effects at high-saturation conditions

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Received: 16.10.2013

Abstract. Computer modelling of fluorescence light quenching is performed with no limitations on the optical wave intensities. The main attention is paid to searching for such combinations of polarizations of the interacting waves that provide minimal polarization changes for the waves passing through a cell. From the viewpoint mentioned above, the most appropriate case is circular polarization of the pumping wave. The efficiency parameter of amplification of the quenching wave can be used for checking mutual orientations of the dipoles responsible for absorption and emission. We show that the light quenching can produce appreciable changes in the polarization of fluorescence light passing through the cell.

Keywords: light quenching, polarization, fluorescence

PACS: 33.50.Hv; 42.55.Ja

UDC: 537.37; 535.665.7+535.428; 535.51

1. Introduction

Induced transitions from a fluorescence-related state of complex organic molecules can result in a significant decrease of fluorescence intensity. This phenomenon is known as ‘light quenching’ [1]. The induced transitions can be initiated by both the exciting radiation and independent radiation sources. As the light quenching is associated with selective deactivation of the excited states, the effect exhibits a strong dependence on the polarizations of exciting and quenching radiations, thus exerting influence on the luminescence polarization [2–4]. Because of this, the light quenching has been extensively used to study different characteristics of complex molecular compounds [3–5]. The induced transitions from the excited states have attracted even greater interest of researchers since the introduction of a new high-resolution microscopy method, a stimulated-radiation depletion (STED) microscopy [6, 7].

It should be noted that rather high powers of luminous fluxes used for excitation in the studies of the light quenching effects lead to noticeable depletion of the population of the ground state [8]. As a consequence, even a weak light flux giving rise to the stimulated radiation processes can be markedly enhanced, its characteristics being indicative of orientational molecular distribution in the excited state. On the other hand, amplification of the quenching radiation may, in its turn, result in a new molecular distribution which is inevitably manifested in the characteristics of both the exciting radiation and the luminescence.

We consider a variant of a classical pump-probe scheme, where the probe wave is no longer weak. There is no possibility to solve such a complex self-consistent problem on the basis of rate equations usually used when studying the light quenching [2–4, 8]. As will be shown later, this problem hardly allows derivation of analytical solutions even for relatively simple cases. A general theory for the light quenching in strong optical fields can be developed as a technique enabling computations performed for particular molecular systems and specific experimental measuring

schemes. This is why in this article we touch upon somewhat narrower problems. As our principal subject is still the luminescence polarization governed by the orientational molecular distribution of the excited state, these problems are mainly concerned with a possibility for selecting polarizations of the exciting and quenching waves such that their changes during propagation inside a medium under study be minimal. Another problem is finding out whether it is possible to obtain information about the structure and properties of the molecules studied issuing from the analysis of variable parameters of the quenching wave.

2. Theoretical model

To describe the evolution of a polarized monochromatic plane wave in the approximation of slowly varying amplitudes, we use a reduced wave equation [9] of the form

$$\frac{d}{dz} \vec{E} + \frac{1}{2} \sigma \vec{E} = \frac{i\mu_0 \omega c}{2n} \vec{P}_{NL}, \quad (1)$$

where \vec{E} denotes the wave amplitude vector, σ the linear absorption factor of a medium, μ_0 the magnetic constant, ω the cyclic wave frequency, n the refractive index at the frequency ω , c the vacuum speed of light, and \vec{P}_{NL} the nonlinear polarization vector.

The main problem is to choose the approach for computing the quantity \vec{P}_{NL} . In the majority of cases, the Kerr approximation [9] is used, which imposes considerable restrictions on the intensity of optical waves. At the same time, a high-power radiation (at least, for excitation) is generally used to study the light quenching. Then the saturation effects become appreciable. This is revealed, e.g., by a considerable decrease in the ground-state population [8]. However, it is very difficult to include the saturation effects into calculations of the vector parameter \vec{P}_{NL} due to necessity for orientational averaging. Because of this, we adopt the approach developed in Refs. [10, 11] using the technique of spherical basis tensors. It enables one to derive \vec{P}_{NL} in a fairly compact form as

$$\vec{P}_{NL} = \hat{R} \vec{E}, \quad (2)$$

where \hat{R} is a second-rank tensor of which components are functions of the optical field intensity.

The calculations have been performed using the following scheme. Let us consider an ensemble of chaotically though rigidly oriented identical molecules, and two parallel plane waves propagating through this ensemble along the axis z of a laboratory coordinate system. To describe the light quenching process, we use a four-level model for the formation of fluorescence [8]. Let us assume that an exciting wave of the frequency ω_0 causes a transition from lower-lying vibrational levels of the ground state S_0 to upper vibrational sublevels of the first excited state S_1 , or of higher excited states, which is followed by a rapid vibrational relaxation (with the characteristic time τ_r) to lower sublevels of the first excited state S_1 . Deactivation of the molecular system from these sublevels can proceed in the two ways: due to spontaneous emission with the characteristic time τ_f , or due to stimulated emission under the effect of quenching wave at the frequency ω_1 . As a result of deactivation, the system goes to the upper vibrational sublevels of the ground state S_0 , with subsequent relaxation to the lower sublevels. For simplicity, we make the following assumptions in our further calculations: (i) the field frequencies ω_0 and ω_1 are separated enough so that a direct interaction of these waves (implemented via populating their

molecular states) can be neglected; (ii) we ignore possible ‘upward’ transitions at the frequency ω_1 ; and (iii) we assume identical times of the vibrational relaxation in both the ground and excited states.

Basing on the model system adopted, one solves an equation for the density matrix and derives the induced dipole moments at the frequencies ω_0 and ω_1 (the appropriate relations are cumbersome and so we omit them further on; notice that the similar formulae may be found in Ref. [11]). The next procedures are associated with orientational averaging, in a complete agreement with the approach given in Ref. [11], and derivation of expressions for the vectors $\vec{P}_{NL}(\omega_0)$ and $\vec{P}_{NL}(\omega_1)$. Notice that it is impossible to obtain these expressions in the analytical form.

Assuming that the effect of the quenching wave on the exciting one can be neglected and the exciting wave has a linear polarization (according to the work [10], this polarization is the eigenvector even under conditions of strong saturation), we arrive at a scalar nonlinear equation for the relative intensity $s_0 = I_0/I_{s0}$ of the exciting wave. It coincides with the equation for the two-level system given in Ref. [11] and has the form

$$\frac{ds_0}{dz} = 3\sigma_0 \left(-1 + \frac{\arctan(\sqrt{s_0})}{\sqrt{s_0}} \right). \quad (3)$$

Here $\sigma_0 = \frac{1}{3} \frac{\hbar\omega_0\Delta N^e}{\tau_f I_{s0}}$, ΔN^e represents the equilibrium difference of populations in the states S_0 and S_1 with no excitation, which can be assumed as equal to the concentration of dye molecules for the majority of cases; I_{s0} is the saturation intensity in the excitation channel. Notice that the z values are normalized basing on the relation $z = \beta\sigma_0 z_0$, where z_0 denotes the normalized coordinate, and the factor β has been chosen to optimize numerical computations for the particular molecular structures. Specifically, we have $\beta = 35$ for a standard ethanol solution of Rhodamine 6G dye associated with all computations performed in this work (the data are taken from Ref. [12]).

As testified by solving Eq. (3) numerically, the function $s_0(z)$ is close to the ordinary Bouguer decay only if $s_{00} = s_0(z=0) \ll 1$. If we have $s_{00} = 0.5$, the deviations from the Bouguer decay law can be $\sim 10\text{--}15\%$. With increasing s_{00} , the evolution $s_0(z)$ becomes more and more dependent on the initial polarization state of the quenching wave. As a result, it is impossible to fit the appropriate approximation function to the evolution $s_0(z)$ and, hence, to divide the solution of the problem into two independent parts. Because of this, the problem has been solved with direct numerical techniques.

3. Results of numerical simulation

As the evolutions of intensities of the exciting and quenching waves are greatly dependent on the ratio of their initial polarizations, at first we have studied the situations when the polarizations of the waves represent the eigenvectors [10, 11] and so remain invariable during the propagation process. These are the four combined cases: (1) coincident circular polarizations of the both

waves; (2) circular polarization of the exciting wave and linear polarization of the quenching wave; (3) linear polarization of the exciting wave and circular polarization of the quenching wave; and (4) coincident linear polarizations of the both waves.

As follows from our analysis, effective amplification of the quenching wave takes place for $z_{00} > 0.5$. The character of the quenching-wave intensity amplification reveals no principal differences for all of the above-mentioned combined cases (i) to (iii) (see Fig. 1).

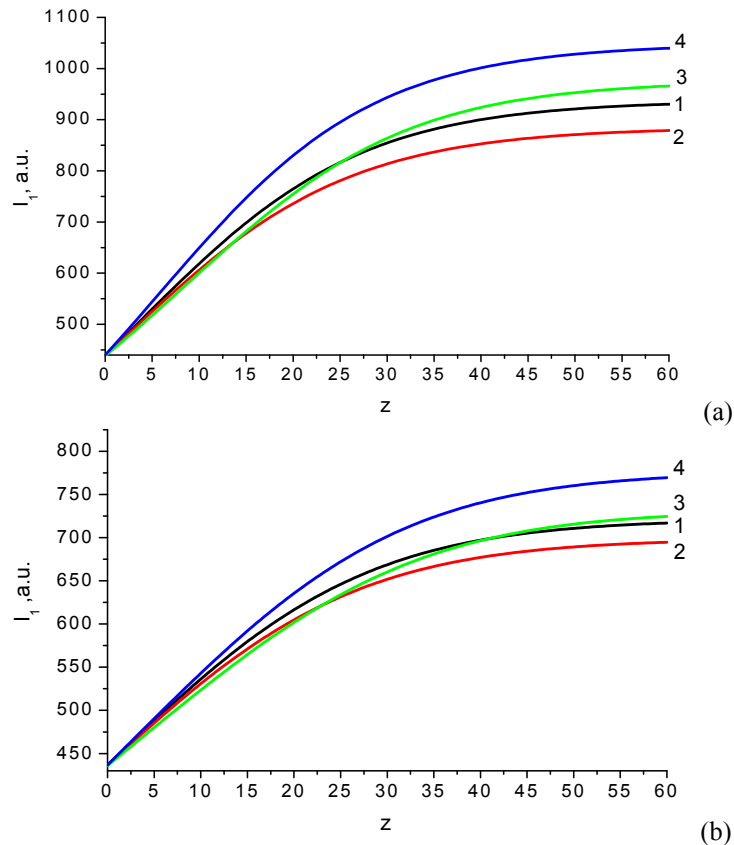


Fig. 1. Intensity of the probe wave versus coordinate z for the probe wave propagating in amplifying media for the cases (1)–(4) of polarizations of the interacting waves ($s_{00} = 1.5$): absorption and emission dipoles are parallel (a) and orthogonal (b).

As seen from the analysis, the amplification efficiency for the quenching wave is higher for the coincident linear polarizations, irrespective of the structure of absorbing molecules. It would be interesting to ascertain the situation when the interacting waves are both linearly polarized and the angle ϑ between their polarization vectors is variable. Then the molecular structure effect is especially marked. When the dipole moments of transitions at the frequencies ω_0 and ω_1 are parallel, the amplification efficiency slowly decreases with increasing angle ϑ . When they are orthogonal, a substantial reverse effect is observed (see Fig. 2).

Among the particular cases for the polarization of the exciting and quenching waves considered above, the case (2) is the most interesting because the orientation of the quenching-wave polarization vector may be chosen arbitrarily and, hence, its effect on the orientational molecular distribution in the excited state can vary essentially. The numerical calculations demonstrate that the circular polarization of the exciting wave is preferable from the viewpoint of

the effect exerted on the polarization of the quenching (i.e., amplified) wave. To illustrate this point, Fig. 3 shows variations in the ellipticity η for the quenching wave as functions of polarization (circular or linear) of the exciting wave propagating in the medium. As seen from Fig. 3, the variations for the case of circular polarization of the exciting wave are insignificant for any initial ellipticity. At the same time, the ellipticity decreases markedly for the linearly polarized exciting wave. This effect is exhibited over a wide range of the initial pumping-wave and quenching-wave intensities.

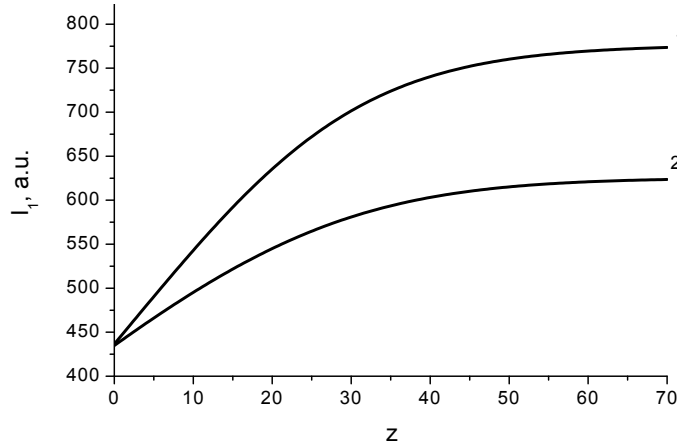


Fig. 2. Dependences of intensity of the quenching wave on the coordinate z for orthogonal absorption and emission dipoles ($s_{00} = 1.5$): $\vartheta = 90^\circ$ (1) and 0° (2).

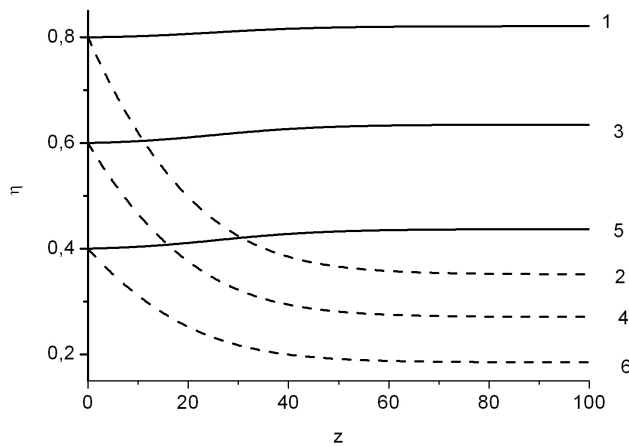


Fig. 3. Ellipticity of the quenching wave versus the coordinate z as calculated for different initial ellipticities ($s_{00} = 1.5$). Polarization of the exciting wave is linear (dashed lines) or circular (solid lines). The ellipticity initial values are $\eta_0 = 0.8$ (1, 2), 0.6 (3, 4) and 0.4 (5, 6).

Let us proceed to the analysis of the most common situation when the both fluxes have linear polarizations differing from each other. Our numerical solutions demonstrate that a decrease in the ϑ angle occurs along z at rather small variations of ellipticity for the both waves when the initial ϑ values are not equal to zero (parallel orientation). However, this effect leads to no significant changes in the behaviour of luminescence polarization at relatively low initial intensities of the quenching wave. Fig. 4 presents the ‘polarization degrees’ of the luminescence recorded along the direction orthogonal to the propagation direction of the fluxes (in particular, for the case of $\vartheta = \pi/4$). Here the ‘polarization degree’ is defined by the classical relation

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}, \quad (4)$$

where the direction of the selected axis is given by the polarization vector of the exciting wave.

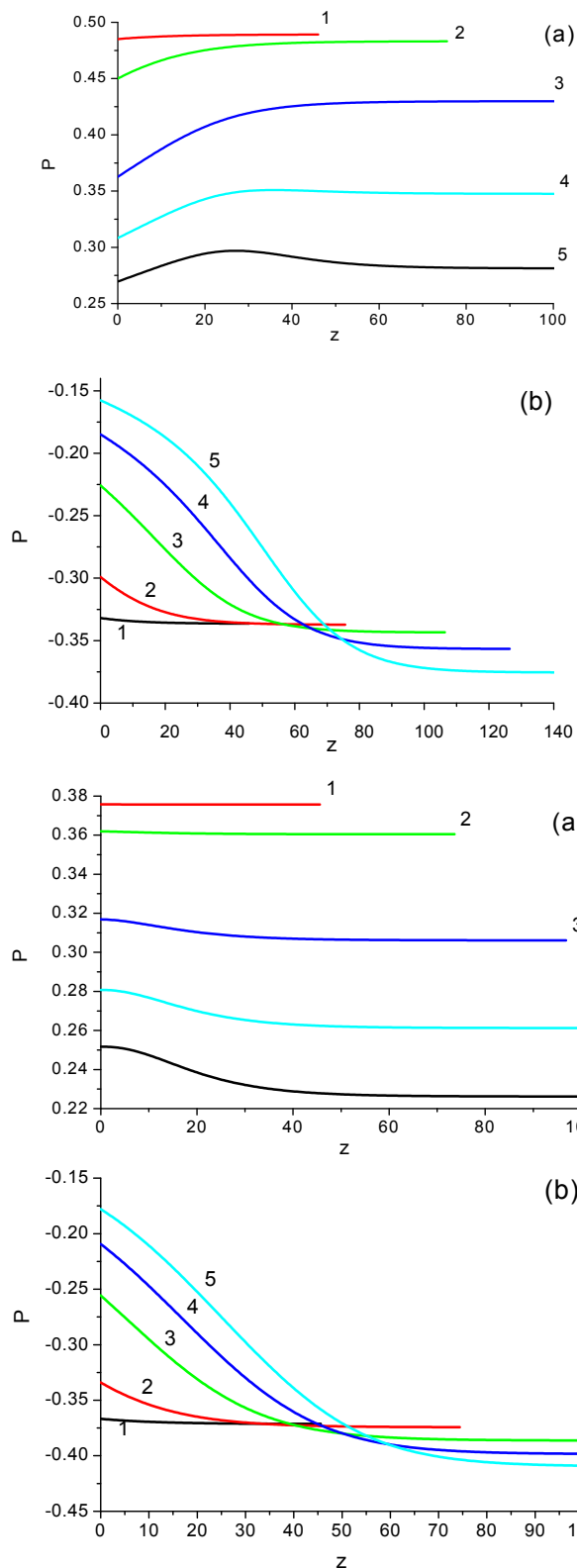


Fig. 4. Dependences of luminescence polarization degree on the cavity length as functions of the pump intensity: $s_{00} = 0.05$ (1), 0.5 (2), 2.5 (3), 5.0 (4) and 8.0 (5). Dipole orientations for the absorption and emission are parallel (a) and orthogonal (b). The initial relative intensity of the quenching wave is $s_{10} = I_1(z=0)/I_{0s} = 0.1$.

Fig. 5. Dependences of luminescence polarization degree on the cavity length as functions of the pump intensity: $s_{00} = 0.05$ (1), 0.5 (2), 2.5 (3), 5.0 (4) and 8.0 (5). Dipole orientations for the absorption and emission are parallel (a) and orthogonal (b). The quenching wave intensity is $s_1 = 2.1$.

As seen from Fig. 4a, some increase in the luminescence polarization degree is observed under increasing cell length that contains the solution when the dipole moments of the transitions related to the absorption and emission are parallel. This is associated with the fact that the effect of exciting radiation decay is much greater and so the saturation effects in the orientational distribution of the excited molecules are weaker than the effect due to amplification of the quenching wave. However, these effects amplify each other for the case of orthogonal dipole moments of the transitions with the absorption and emission (see Fig. 4b), thus leading to appreciable increase in the polarization degree.

Assume that the initial intensity of the quenching radiation increases (see Fig. 5). When the dipole moments of the transitions with the absorption and emission are parallel (see Fig. 5a), the effect exerted by the quenching wave amplification becomes pronounced and the polarization degree decreases. This effect becomes stronger with increasing intensity of the exciting flux. However, the effect remains the same as in the case of relatively low intensities of the quenching flux whenever the dipole moments of the transitions with the absorption and emission are orthogonal (see Fig. 5b). In other words, for the orthogonal dipole moments the observed effect is qualitatively independent of the quenching wave intensity.

4. Conclusion

We have presented the results of our numerical simulation for the light quenching effect within the scope of approximated theoretical approach. The results demonstrate that the quenching wave can be appreciably amplified, whereas the polarizations of both the quenching and exciting fluxes can be changed during this process. It seems that, among the four possible combinations of intrinsic polarizations analyzed in our study, the combination of circular polarization of the exciting wave and linear polarization of the quenching wave is the most convenient for the light-quenching processes. Besides, the changes in the polarization of the quenching radiation are minimal for the circular polarization of the pump radiation. In this case we expect that the description based on the rate equations for the averaged intensities of the exciting and quenching fluxes should be quite adequate.

The computational results point to the fact that the amplification effect of the polarized quenching radiation differs considerably for different orientations of the dipole moments of the transitions with the absorption and emission. This is promising for investigations of the structure of complex polyatomic molecules. As the quenching-radiation amplification effects result in variations of polarization degree of the luminescence along the cell length, one can develop the methods appropriate for studying different molecular solutions and ascertaining character of spatial evolution of the amplified radiation.

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M. Jadan. 2014. Light quenching effects at high-saturation conditions. Ukr.J.Phys.Opt. **15**: 38 - 45.

***Анотація.** Здійснено комп'ютерне моделювання загасання флуоресценції без обмежень на інтенсивність оптичних хвиль. Основну увагу надано пошуку таких комбінацій поляризації взаємодіючих хвиль, що забезпечують мінімальні зміни поляризації для хвиль, які проходять крізь комірку. З цієї точки зору найзручнішою є циркулярна поляризація хвилі нагнітання. Параметр ефективності підсилення хвилі загасання можна використати для встановлення взаємної орієнтації диполів, відповідальних за поглинання і випромінювання. Показано, що загасання світла може приводити до помітних змін поляризації флуоресценції, що проходить крізь комірку.*