ON THE POLARIZED GENERATION RADIATION OF SOLUTIONS OF ORGANIC DYES

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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE POLARIZED GENERATION RADIATION OF SOLUTIONS OF ORGANIC DYES

All known cases of polarized luminescence of solutions of organic dyes have been interpreted quite well within the framework of various oscillator models ($^{1-4}$).

We have investigated the polarization of radiation during generation in glycerol and alcohol solutions of cryptocyanine, whose molecule is usually modeled by a linear oscillator, and AlCl PhC, whose molecule corresponds to a planar oscillator (^{5}). A cuvette with the substance under investigation was placed in a resonator with mirrors r_1, r_2 (Fig. 1a) and was excited by completely polarized radiation from a single-pulse ruby optical quantum generator. The direction of excitation coincided with the x-axis, and the polarization vector of the exciting light with the z-axis.

Fig. 1. a—for calculating the anisotropy of the gain coefficient $K^0(u\ \ , \psi)$; b—dependence of $K^0(u\ \ , \psi)$ on ψ

As a result of the measurements it was established that, for such a direction of the polarization vector of the exciting light, the stimulated radiation of dye solutions proves to be completely polarized, and the polarization vector of this radiation coincides with the polarization vector of the exciting light.

As in work (^{6}), a model of the working substance is considered consisting of two electronic levels containing a large number of vibrational sublevels. Let us consider the radiation of an elementary layer along the direction oy. We shall specify the polarization of this radiation by the vector $\mathbf{p}$, which lies in the xoz plane and whose direction is determined by the angle ψ. The radiation power can be represented as the sum of the powers of spontaneous and stimulated radiation with frequency ν:

$$W_y(\nu, u\ \ , \psi) = W\ \ (\nu, u\ \ , \psi) + W\ \ (\nu, u\ \ , \psi). \qquad (1)$$

In the presence of generation, the second term may be written in the form [7]

$$W^{\mathrm{gen}}(\nu, u^{\mathrm{ex}}, \psi) = -\frac{\nu}{a}\,[K^0_{\mathrm{us}}(\nu, u^{\mathrm{ex}}, \psi) - K_{\mathrm{loss}}]. \tag{2}$$

The expression for K^0_{us} can be written as follows:

$$K^0_{\mathrm{us}}(u^{\mathrm{ex}}, \psi) = \frac{h\nu}{\nu}\int_{\Omega} b(\nu, \Omega, \psi)\, n_2(u^{\mathrm{ex}}, \Omega)\, d\Omega. \tag{3}$$

According to [4], for $n_2(u^{\mathrm{ex}}, \Omega)$ and $b(\nu, \Omega, \psi)$ we have the expressions

$$n_2(u^{\mathrm{ex}}, \Omega) = \frac{\dfrac{1}{4\pi}n_2^0 + \dfrac{n}{8\pi}\alpha u^{\mathrm{ex}}\cos^2\theta}{1 + \alpha u^{\mathrm{ex}}\cos^2\theta}, \tag{4}$$

$$b(\nu, \Omega, \psi) = \frac{8\pi^3}{h}\,|D_{21}|^2\cos^2\Theta = 3B(\nu)\cos^2\Theta, \tag{5}$$

where n_2^0 is the population of the second level corresponding to the equilibrium distribution; n is the total number of molecules; α is the nonlinearity coefficient in the excitation channel; θ is the angle between the dipole moment and the electric vector of the exciting light; Ω determines the direction of the dipole moment; $B(\nu)$ is the integral Einstein coefficient; Θ is the angle between the vector $\mathbf{p}$ and the direction of the dipole moment D_{21}. After integration, for K^0_{us} we obtain the expression

$$K^0_{\mathrm{us}} = \frac{1}{2}\varkappa\,[\beta\sin^2\psi + \gamma\cos^2\psi], \tag{6}$$

where $\varkappa = B(\nu)h\nu n/\nu$ is the limiting gain coefficient. In addition, the following notation has been introduced here:

$$\beta = 1 + \frac{3}{2\alpha u^{\mathrm{ex}}} - \frac{3}{2}\left[\frac{1}{(\alpha u^{\mathrm{ex}})^{1/2}} + \frac{1}{(\alpha u^{\mathrm{ex}})^{3/2}}\operatorname{arc\,tg}(\alpha u^{\mathrm{ex}})^{1/2}\right], \tag{7}$$

$$\gamma = 1 - \frac{3}{\alpha u^{\mathrm{ex}}} + \frac{3}{(\alpha u^{\mathrm{ex}})^{3/2}}\operatorname{arc\,tg}(\alpha u^{\mathrm{ex}})^{1/2}. \tag{8}$$

Figure 1b presents the graphical dependence of K^0_{us} on ψ, for various densities of the exciting light. It is seen from the figure that the gain coefficient of an active substance excited by linearly polarized light depends on the direction of the polarization vector of the amplified light.

By analogy with the dependence of the absorption coefficient of a substance on the polarization of the absorbed light, called dichroism, let us introduce the quantity D_{ku}, which will characterize the dependence of the gain coefficient of the substance on the polarization of the amplified light:

$$D_{\text{ku}} = (K_{\text{us}}^{0\,\max} - K_{\text{us}}^{0\,\min})/(K_{\text{us}}^{0\,\max} + K_{\text{us}}^{0\,\min}). \tag{9}$$

Like ordinary dichroism, the dichroism of an amplifying medium may be natural (for example, in ruby optical quantum generators) and induced, as occurs in the case under consideration, when

$$D_{\text{ku}}^{\text{ind}} = (\gamma - \beta)/(\gamma + \beta). \tag{10}$$

The presence of dichroism of the amplifying medium proves to be essential for the amplification and generation of polarized radiation. Since the generation condition for an amplifying medium is fulfilled first of all at the maximum of the gain coefficient, and $\gamma > \beta$, in the system under consideration radiation generation will occur with the same direction of polarization as that of the exciting light. Let us also note that, in this case, the effect of burning out modes with a definite polarization plays an essential role. In deriving formula (6), the medium was assumed to be rigid. It should be pointed out, however, that the quantity D_{ku} will be different from zero also for

in the presence of rotations of the excited molecule, i.e., the stimulated emission of organic dyes in all solvents, even those having a very low viscosity, will always be polarized if the excitation is produced by polarized or by natural light according to the scheme shown in Fig. 1.

The value of the generation power along the direction oy is obtained if in (2) we substitute the value $K_{yc}^{0}\,(\psi = 0, u^{\text{exc}})$ from equality (6):

$$W^{\text{gen}}\,(\nu, u^{\text{exc}}, \psi = 0) = \frac{\nu}{a}\left[\frac{1}{2}\varkappa(\nu)\gamma - K_{\text{loss}}\right]. \tag{11}$$

Relation (11) makes it possible to study experimentally the dichroism of the amplifying medium. For this purpose a polarizer should be introduced into the resonator with the active substance and, rotating it through different angles ψ about the y axis, the generation power should be measured. Substituting the obtained values into equality (11), one can determine K_{yc}^{0} for different ψ.

In [4] expressions are given for the luminescence power with electric vectors along the axes oz and ox as a function of the density of the linearly polarized exciting light:

$$W_{\text{lum}}^{z}\,(\nu, u^{\text{exc}}, \psi = 0) = \frac{1}{8\pi} W_{\infty}^{\text{lum}}\gamma, \tag{12}$$

$$W_{\text{lum}}^{x}\left(\nu, u^{\text{exc}}, \psi = \frac{\pi}{2}\right) = \frac{1}{8\pi} W_{\infty}^{\text{lum}}\beta, \tag{13}$$

where $W_{\infty}^{\mathrm{lum}}$ is the limiting value of the luminescence.

Equalities (11), (12), and (13) make it possible to trace the dependence of the polarization of the radiation on the density of the exciting light. As U^{exc} changes from zero to the values $U_{\mathrm{thr}}^{\mathrm{exc}}$, at which generation begins, the radiation will consist only of luminescence, whose polarization is described by equations (12) and (13). The degree of polarization of the luminescence decreases with increasing U^{exc}. When U^{exc} exceeds the threshold value, the main part of the radiation will be the completely polarized stimulated emission.

In Fig. 2 (curve I) the dependence of the degree of polarization p of the radiation emerging from the resonator on U^{exc} is represented graphically. This curve was calculated for rigidly fixed dipoles, which in fact corresponds to the case of glycerin solutions. For alcohol solutions the radiation will be practically unpolarized over the entire range of values of U^{exc} from 0 to $U_{\mathrm{thr}}^{\mathrm{exc}}$, jumping to 100% at $U^{\mathrm{exc}} > U_{\mathrm{thr}}^{\mathrm{exc}}$.

It was considered expedient to carry out the calculation of K_{yc}^{0} also for the case when the electric vector of the exciting light is directed along the resonator, along the oy axis. In this case the expression for K_{yc}^{0} has the form

$$K_{yc}^{0} = \frac{1}{2}\varkappa\beta, \tag{14}$$

i.e., the dichroism of the amplifying medium is absent. The radiation generated in this case is completely depolarized, which is confirmed experimentally for both glycerin and alcohol solutions of cryptocyanine and AlCl PhC. The generation power for this case is written in the form

$$W^{\mathrm{gen}}\left(\nu, u^{\mathrm{exc}}, \psi\right) = \frac{\nu}{a}\left[\frac{1}{2}\varkappa(\nu)\beta - K_{\mathrm{loss}}\right]. \tag{15}$$

Equalities (11) and (15) can easily be checked experimentally if one considers the ratio of the generation powers for both directions of polarization of the exciting light. The duration of the generation pulse in both cases is 8–10 nsec at the 0.5 level; therefore the ratio of powers can be replaced by the ratio of energies, i.e.,

$$E_{\mathrm{gen}}^{z}\left(u_{H}^{z}\right)/E_{\mathrm{gen}}^{z}\left(u_{H}^{y}\right) = \left(\frac{1}{2}\varkappa\gamma - K_{\mathrm{loss}}\right) / \left(\frac{1}{2}\varkappa\beta - K_{\mathrm{loss}}\right). \tag{16}$$

Let us carry out a numerical estimate of this equality.

The energy of the exciting monopulse was 0.5 J at a duration of 20 nsec, which corresponds to $U^{\mathrm{exc}} \approx 10^{4}$. According to (3),

$$\alpha(\nu) = B_{12}(\nu)/p_{21} = B_{12}^{(\nu)}\tau.$$

For cryptocyanine $B_{12}(\nu_{\text{rub}}) = 1.6 \cdot 10^6$ ($\sigma = 0.55 \cdot 10^{15}$), and $\tau = 10^{-9}$ (7), i.e. $\alpha(\nu) = 1.6 \cdot 10^{-3}$, $\alpha u^{\text{exc}} = 30$. Substituting the obtained values of the quantities into (7) and (8), we obtain $\gamma = 0.633$ and $\beta = 0.18$.

In our experiments a cuvette of size 0.2×1.5 cm and mirrors with reflectances 0.98 and 0.8 were used, which corresponds to the loss coefficient

$$K_{\text{loss}} = \frac{1}{e} \ln \frac{1}{\sqrt{r_1 r_2}} = 0.08.$$

The initial transmission of the cuvette along the direction of excitation was 0.1. This corresponds to $\chi = 11.5$. Substituting the found values χ, β, γ, and K_{loss} into (16), we obtain for

$$E^z_{\text{gen}}(u^z_{\text{H}})/E^z_{\text{gen}}(u^y_{\text{H}}) = 1.6.$$

For cryptocyanine in glycerin, the measured value of this ratio is approximately 1.8, which agrees well with the calculated value. The change in the polarization direction of the exciting light was achieved by rotating the O.K.G. about the axis of the ruby rod through an angle $\pi/2$.

Fig. 2. Dependence on the density of the exciting light of the degree of polarization p (1) and

$$K = E^z_{\text{gen}}(u^z_{\text{H}})/E^z_{\text{gen}}(u^y_{\text{H}})$$

for $\alpha u^{\text{exc}} = 30$ (solid curve) and $\alpha u^{\text{exc}} = 65$ (dashed curve)

In Fig. 2, curve 2 corresponds to the calculated dependence

$$K = E^z_{\text{gen}}(u^z_{\text{H}})/E^z_{\text{gen}}(u^y_{\text{H}})$$

on the density of the exciting flux. The behavior of the curve shows that the magnitude of this ratio decreases with increasing density of the exciting light.

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Note: Figure translations are in progress. See original paper for figures.