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Abstract

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The ability to generate radiation is a universal property of solutions of organic dyes and other complex molecules ([1]). The absence of generation may be regarded as an exception requiring a special explanation. Generation has been obtained in many dozens of different compounds, even for molecules with a negligible luminescence quantum yield, of the order of 0.001%. The principal difficulties are connected only with the accumulation of particles in the triplet state and with absorption of radiation by excited particles. Practical limitations are sometimes associated with the absence of intense pump sources at a frequency ν_p close to the frequency of the maximum of the absorption band.

In papers ([2]) a method was developed for calculating the principal energy characteristics of generators based on organic dyes excited by monochromatic radiation. However, in ([2]) the possible absorption of radiation by excited particles in transitions from levels 2 and 3 to higher electron-vibrational levels 4 and 5 was not taken into account (see Fig. 1). The analysis carried out in the present work shows that absorption of pump radiation in transitions $2 \to 4$ and $3 \to 5$ is relatively small. At the same time, absorption of the generated energy usually constitutes the main source of losses. The calculation is performed under the assumption that the accumulation of particles at levels 4 and 5 is small. The formulas obtained apply to the transverse version of the generator.

Fig. 1. Level scheme

The condition of quasistationarity of generation at frequency ν_g has the form ([1]):

$$k_\mathrm{us} = \frac{h\nu_\mathrm{g}}{v}\left[B_{31}(\nu_\mathrm{g})n_3 - B_{13}(\nu_\mathrm{g})n_1 - B_{35}(\nu_\mathrm{g})n_3 - B_{24}(\nu_\mathrm{g})n_2\right] = k_\mathrm{pot}, \qquad (1)$$

where $k_{\text{pot}} = \rho + \ln(1/r_1 r_2)/2l$. Taking into account the relations $n_3 p_{32} = n_2 p_{21}$, $B_{13}(\nu_{\text{g}}) = B_{31}(\nu_{\text{g}}) e^{-a}$, where $a = h(\nu_{\text{el}} - \nu_{\text{g}})/kT$, and introducing the notation $\chi_{\text{g}} = B_{31}(\nu_{\text{g}}) n h \nu_{\text{g}}/v$ and

$$\theta_{\text{g}} = B_{35}(\nu_{\text{g}})/B_{31}(\nu_{\text{g}}) + B_{24}(\nu_{\text{g}}) p_{32}/B_{31}(\nu_{\text{g}}) p_{21}, \tag{2}$$

instead of (1) we obtain

$$\frac{\chi_{\text{g}}}{n} \left[n_3 - n_1 e^{-a} - n_3 \theta_{\text{g}} \right] = k_{\text{pot}}. \tag{3}$$

Since $n_1 + n_2 + n_3 = n$, it follows from (2) that

$$\frac{n_3}{n} = \frac{1}{C}(\delta + e^{-a}), \qquad \frac{n_1}{n} = \frac{1}{C}\left[1 - \theta_{\text{g}} - \left(\frac{1 + p_{32}}{p_{21}}\right)\delta\right], \tag{4}$$

where $\delta = k_{\text{loss}}/\chi_{\text{g}}$, $C = 1 + (1 + p_{32}/p_{21}) e^{-a} - \theta_{\text{g}}$.

The absorption coefficient of the pump radiation of frequency ν_{p} is equal to

$$(\chi_{\text{p}} = B_{13} n h \nu_{\text{p}}/v, \qquad b = (\nu_{\text{p}} - \nu_{\text{el}})/kT),$$

$$\begin{aligned} k_{\text{abs}} &= \frac{h\nu_{\text{p}}}{v} \left[B_{13}(\nu_{\text{p}}) n_1 - B_{31}(\nu_{\text{p}}) n_3 + B_{35}(\nu_{\text{p}}) n_3 + B_{24}(\nu_{\text{p}}) n_2 \right] \\ &= \frac{\chi_{\text{p}}}{C} \left[1 - e^{-(a+b)} - \delta(1 + e^{-b} + p_{32}/p_{21}) - \theta_{\text{g}} + \theta_{\text{p}}(e^{-a} + \delta) \right]. \end{aligned} \tag{5}$$

Here θ_{p} is given by expression (2) with ν_{g} replaced by ν_{p}.

The absorption power of an active layer of length z is

$$W^0_{\text{abs}} = l y v u_{\text{p}}(0) \left[1 - e^{-k_{\text{abs}} z} \right], \tag{6}$$

where $u_{\text{p}}(0)$ is the density of the radiation incident on the input face of the cuvette, and ly is the cross-sectional area of the cuvette.

Formula (6) determines the total power absorbed in all three channels: $1 \to 3$, $2 \to 4$, $3 \to 5$. For generation, only the power spent on excitation of level 3 is used. Since $W^{1-3}_{\text{abs}}/W^0_{\text{abs}} = k^{1-3}_{\text{abs}}/k_{\text{abs}}$, then

$$W^{1-3}_{\text{abs}} = \Phi_{\text{p}} l y v u_{\text{p}}(0)[1 - e^{-k_{\text{abs}} z}], \tag{7}$$

where

$$\Phi_{\rm p} = \{1 + \theta_{\rm p}(e^{-a} + \delta)/[1 - e^{-(a+b)} - \theta_{\rm g} - \delta(1 + e^{-b} + p_{32}/p_{21})]\}^{-1}. \quad (8)$$

In developing generators it is advisable to use only those molecules for which $\theta_{\rm p}(e^{-a} + \delta)$ and $\theta_{\rm g}$ are considerably less than unity and, consequently, $\Phi_{\rm p}$ is close to unity. The number of such molecules is sufficiently large.

Since $\nu_{\rm g} < \nu_{\rm p}$, Stokes losses always exist; part of the power is expended on frequency conversion. To take this fact into account, it is sufficient to multiply (7) by $\nu_{\rm g}/\nu_{\rm p}$.

Fig. 2. Dependences of the absorption, luminescence, and heat-release powers on the length of the generating layer z. 1–$W^0_{\rm abs}$; 2–$\Phi_{\rm p} W^0_{\rm abs}$; 3–$\Phi_{\rm p} W^0_{\rm abs}\nu_{\rm g}/\nu_{\rm p}$; 4 –$Q$.

In Fig. 2 the dependences of the powers $W^0_{\rm abs}$, $W^{1-3}_{\rm abs}$, and $W^{1-3}_{\rm abs}\nu_{\rm g}/\nu_{\rm p}$ on the layer length are plotted. The difference I between the horizontal straight line $lyvu_{\rm p}(0)$ and the curve $W^0_{\rm abs}$ characterizes the pump-power losses associated with incomplete absorption of the incident radiation in the layer z. Difference II characterizes the pump-energy losses in the channels $3 \to 5$ and $2 \to 4$, and difference III the Stokes losses. Fig. 2 also shows the straight line

$$Q(z) = \frac{A_{31}}{\eta} lyn_3 z = \frac{A_{31}}{C\eta} lynh\nu_{\rm g}(e^{-a} + \delta)z, \quad (9)$$

which determines the losses associated with luminescence in the channel $3 \to 1$ and heat release in the channels $3 \to 2 \to 1$ (A_{31} is the probability of the spontaneous optical transition, η is the quantum yield of luminescence).

The difference

$$W^0_{\rm gen}(z) = \Phi_{\rm n} ly\nu u_{\rm n}(0)[1 - e^{-k_{\rm abs}z}]\, \nu_{\rm g}/\nu_{\rm n} - Q(z) \quad (10)$$

(the difference V in Fig. 2) gives the value of the power of stimulated radiation of frequency $\nu_{\rm g}$ in the channel $3 \to 1$, i.e., the value of the total generation power. As z increases from zero to a certain point $z_{\rm opt}$, the value of $W^0_{\rm gen}$ increases continuously. Increasing z beyond $z_{\rm opt}$ has no meaning, since generation is absent in the region $z > z_{\rm opt}$ (see (2)). The optimal value of z is

$$z_{\rm opt} = \ln Y/k_{\rm abs}, \quad (11)$$

where

$$Y = \{\eta B_{13}(\nu_{\rm n})u_{\rm n}(0)[1 - e^{-(a+b)} - \theta_{\rm g} - \delta(1 + e^{-b} + p_{32}/p_{21})]\}\times$$
$$\times[A_{31}(e^{-a} + \delta)]^{-1}. \quad (12)$$

The optimal value of W^0_{gen} is

$$W^0_{\mathrm{gen}}(z \geq z_{\mathrm{opt}}) = \Phi_{\mathrm{n}} l y \nu u_{\mathrm{n}}(0) \left[1 - \frac{1}{Y}(1 + \ln Y)\right] \frac{\nu_{\mathrm{g}}}{\nu_{\mathrm{n}}}. \tag{13}$$

Generation in the optimal regime is realized only for $Y > 1$. From this the threshold value of the pump-radiation density is determined:

$$\eta u^{\mathrm{thr}}_{\mathrm{n}}(0) = \frac{A_{31}(e^{-a} + \delta)}{B_{13}(\nu_{\mathrm{n}})[1 - e^{-(a+b)} - \theta_{\mathrm{g}} - \delta(1 - e^{-b} + p_{32}/p_{21})]}. \tag{14}$$

If $u_{\mathrm{n}}(0) \to u^{\mathrm{thr}}_{\mathrm{n}}(0)$, then $z_{\mathrm{opt}} \to 0$; at small pump intensities the generation process is concentrated in a very thin layer at the entrance face of the cuvette. Estimates of $\eta u^{\mathrm{thr}}_{\mathrm{n}}(0)$ for typical parameter values (and $\theta_{\mathrm{g}} = 0$) show that $\eta u^{\mathrm{thr}}_{\mathrm{n}}(0) \sim 1\ \mathrm{erg} \cdot \mathrm{cm}^{-3}$. At pump densities $\sim 10^4\ \mathrm{erg} \cdot \mathrm{cm}^{-3}$, characteristic of a single-pulse ruby generator operating at the fundamental frequency, the threshold is exceeded by a very large amount. Generation is sometimes possible even when the cuvette is irradiated by ruby radiation in the free-generation regime. To achieve stationary generation, lamps are needed that provide pump-radiation fluxes of $3 \div 5\ \mathrm{kW} \cdot \mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$.

The effect of absorption of radiation in the channels $2 \to 4$ and $3 \to 5$ on the generation threshold can be substantial only if the value of θ_{g} is close to unity.

The radiation generated in the stimulated transitions $3 \to 1$ is partially absorbed in the channels $2 \to 4$ and $3 \to 5$. To take this fact into account, it is sufficient to multiply (10) or (13) by the quantity $k_{\mathrm{loss}}/k_{\mathrm{loss}} + B_{35}(\nu_{\mathrm{g}})n_3 + B_{24}(\nu_{\mathrm{g}})n_2$, equal to

$$\Phi_{\mathrm{g}} = \frac{\delta C}{\delta C + \theta_{\mathrm{g}}(\delta + e^{-a})}. \tag{15}$$

For $Y \gg 100$, the energy losses associated with incomplete absorption of the pump energy, as well as with luminescence and heat release in the channels $3 \to 1$ and $3 \to 2 \to 1$, are insignificant; in this case the limiting value of the generation power is reached. The limiting efficiency is

$$\gamma^{\mathrm{lim}}_{\mathrm{gen}} = (W^0_{\mathrm{gen}})_{\mathrm{lim}}/l y \nu u_{\mathrm{n}}(0) = \Phi_{\mathrm{n}} \Phi_{\mathrm{g}} \nu_{\mathrm{g}}/\nu_{\mathrm{n}}. \tag{16}$$

The quantity $\gamma^{\mathrm{lim}}_{\mathrm{gen}}$ depends on the ratio of the parameters δ, e^{-a}, p_{32}/p_{21}, θ_{p}, and θ_{g}. For $\delta \simeq 0$, $\Phi_{\mathrm{n}} \sim 1$, but $\Phi_{\mathrm{g}} \sim 0$. As δ increases, the value of Φ_{g} increases slowly, tending to the limiting value (for small θ_{g}, close to unity). At the same time, the value of Φ_{n} usually depends little on δ in the region of small δ and very rapidly tends to zero as it approaches

δ to $\left(1 - e^{-(a+b)} - \theta_\text{g}\right) / \left(1 + e^{-b} + p_{32}/p_{21}\right)$. It follows from this that, in the transverse configuration, it is advisable to work with very high loss coefficients. In order for Φ_g and Φ_n to be simultaneously close to unity, the condition must be fulfilled

$$\frac{1 - e^{-(a+b)} - \theta_\text{g}}{1 + e^{-b} + p_{32}/p_{21}}\,\chi_\text{r} > \rho + \frac{1}{2l}\ln\frac{1}{r_1 r_2} \gg \frac{\theta_\text{g}}{C - \theta_\text{g}}\,e^{-a\chi_\text{r}}. \qquad (17)$$

The inequality under consideration can be realized only in molecules with small θ_g and p_{32}/p_{21}. If these conditions could be fulfilled, then the value of γ_p would be close to $\nu_\text{g}/\nu_\text{n}$, i.e., to $0.8 \div 0.9$. A decrease in $r_1 r_2$ and l should, as a rule, lead to an increase in γ_gen and then, very sharply, to disruption of generation. The search for the optimal value k_opt is simplest to carry out experimentally, since the values of θ_g, θ_n, and p_{32}/p_{21} are usually unknown.

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