

LASERS BASED ON SOLUTIONS OF ORGANIC DYES

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1. INTRODUCTION

THE number of substances in use as the active elements of lasers is very large at present. The most varied are the gas lasers. Several tens of atoms, ions, and simple molecules are being used to give laser action. Rare-earth ions in glasses and crystals, and also the trivalent chromium ion in ruby, serve as the active centers in solid-state lasers. The semiconductors constitute a special class of laser materials. Rare-earth ions incorporated into complicated organic complexes (chelates) soluble in organic solvents were used exclusively in liquid lasers until recently.

Laser action was obtained in 1966 in a solution of neodymium in selenium oxychloride.^[1]

In all the listed classes of substances (except the semiconductors), laser action arises from transitions characterized by more or less narrow luminescence lines. In the case of optical excitation, the upper laser level is always metastable. The existence of a metastable level and narrow luminescence lines was considered one of the most important criteria marking a substance as showing promise for laser action.^[2-5] Undoubtedly, this opinion has hindered the search for new active substances.

The discrete set of generable frequencies made possible by the set of discussed materials covers a broad spectral range.

However, it is highly limited, and does not satisfy the demands of experiment. As a rule, the possibilities of continuous frequency shift are small, since the range of generable frequencies is limited by the width of the luminescence line.

Recently the list of generating substances was supplemented by a new practically unlimited class of objects, namely solutions of organic dyes. In contrast with other laser materials, the luminescence band width of the dyes is very large (up to 2000 Å), while the upper laser level is labile (the lifetime of the excited state is of the order of 10^{-8} – 10^{-9} sec). Furthermore, laser action in these objects arises from stimulated transitions to the ground state from the same electronic level as is excited in the pumping process.

The mechanism of laser action in organic dyes is described by a system of two broadened (electronic-vibrational) levels, and differs from the three- and four-level systems characterizing ordinary laser materials. In this sense, organic-dye lasers are somewhat reminiscent of semiconductor lasers, although the physical mechanism and characteristics of laser action substantially differ for substances of these two classes.

The possibility of obtaining amplification in solutions of complex molecules was first noted in a study by Ivanov,^[6] which was made before lasers were invented. Analogous ideas were later expressed, as applied to

color centers in crystals.^[7] The principles of obtaining laser action within the system of electronic-vibrational transitions of semicomplex molecules of the anthracene type have been discussed in^[8]. Some calculations of the characteristics of laser action are given in^[9,10], with the existence of the vibrational structure taken into account.

Some studies performed in 1965^[11-14] made a detailed theoretical analysis of the processes that take place under intense excitation of complex molecules, and it was established that they can generate radiation, both in a three-level and in a two-level system. In these studies they derived simple formulas required for calculating the threshold and power of laser action, and they characterized the fundamental features of laser action in complex molecules. In particular, they predicted a subsequently-confirmed dependence of the generated frequency on the concentration of active particles and the loss coefficient of the resonator. The calculation showed that the threshold for laser action in organic dyes is close to that in ruby and neodymium glass.

The possibility was discussed in^[15] of exciting laser action in dyes by ruby-laser pulses. The optimum solute concentrations, frequencies of generated radiation, and threshold pumping values were calculated from measurements of transition probabilities for five different phthalocyanines.

Laser action in solutions of organic dyes excited by single ruby-laser pulses was obtained independently in^[16-18] in 1966.

Subsequent studies^[19,20] have made a detailed analysis of the requirements for substances showing promise for laser action, and have compared the theory with the experimental results.

Dyes excited by single ruby-laser pulses generate radiation in the near infrared. Pumping with the second harmonic of ruby and neodymium lasers has made it possible to obtain induced emission from dyes at various wavelengths in the visible, from the blue to the red.^[21-23] The number of dyes that have shown laser action is already several times larger than the total number of all other solid and liquid active substances. More than 50 molecules of various classes, substantially differing both in structure and in spectral-luminescent characteristics, show laser action when excited by a laser.

Laser action was obtained in 1967 from several dyes pumped directly by pulsed lamps.^[23,24] This showed that solutions of organic dyes can be used not only for conversion of the emission spectrum of solid-state lasers, but also as independent, highly efficient lasers.

One of the remarkable properties of dye lasers is that one can control the frequency of the generated radiation. It was shown experimentally in^[25,26] that dyes can emit narrow spectral lines of 1–2 Å width in a resonator having selective losses, and the line positions

can be varied within the limits of the broad luminescence band.

2. PHYSICAL ASSUMPTIONS

A sufficiently high amplification must be produced in the medium for laser action to arise. This is impossible with optical pumping in a system having two narrow levels.^[27] In fact, the absorption coefficient of such a system (Fig. 1a)

$$k_{\text{abs}} = \frac{h\nu}{v} (n_1 B_{12} - n_2 B_{21}) = \frac{h\nu}{v} n_1 B_{12} \left(1 - \frac{n_2}{n_1} \frac{g_1}{g_2}\right) \quad (1)$$

is always positive. In Eq. (1), B_{12} and B_{21} are the Einstein coefficients ($B_{12}g_1 = B_{21}g_2$), g_1 and g_2 are the degeneracies of the levels, and n_1 and n_2 are their degrees of population. In a steady state of excitation, the following relation holds:^[28]

$$\frac{g_1}{g_2} \frac{n_2}{n_1} = \frac{B_{21}u_{21}}{p_{21} + B_{21}u_{21}} < 1; \quad (2)$$

Here p_{21} is the overall probability of spontaneous optical and non-optical $2 \rightarrow 1$ transitions, and u_{21} is the density of the exciting radiation. As $u_{21} \rightarrow \infty$, the ratio in (2) approaches unity, while the absorption coefficient in (1) approaches zero.

Thus, a pure two-level system is not suitable for laser action. Consequently, one ordinarily uses three- and four-level systems (Fig. 1b and c). Ruby works on a three-level system, and glasses, crystals and solutions containing rare earths on a four-level system.

A three-level system is characterized by the following fundamental properties: efficient absorption of the pumping radiation by the transition $1 \rightarrow 3$, metastability of the level 2, and the existence of a narrow emission line in the laser-action channel $2 \rightarrow 1$. One has to transform more than half of the total number of active centers to the metastable state to obtain laser action.

In a four-level system, the lower laser level 2 lies considerably higher than the ground state 1, and hence the number n_2 of particles is small. In order to avoid an increase in n_2 during the laser process, the level 2 must have a very short lifetime. As in the previous case, the upper laser level 3 is metastable in this system. However, we need not raise the majority of the particles to this level to get amplification and laser action. Population inversion is ensured even at small values of n_3 .

In these systems, the upper laser level is metastable, and hence the probability of stimulated transitions from this level is relatively small. For ruby, it is

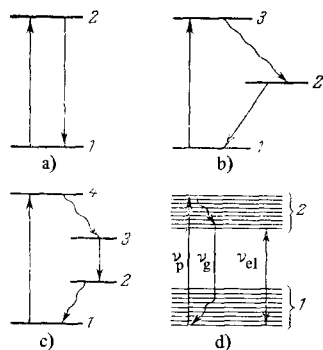


FIG. 1. System of energy levels.

characterized by an Einstein coefficient $B(\nu) \sim 1.5 \times 10^2 \text{ erg}^{-1} \text{ cm}^3 \text{ sec}^{-1}$, and for neodymium glass by a coefficient $B(\nu) \sim 1.8 \times 10^4 \text{ erg}^{-1} \text{ cm}^3 \text{ sec}^{-1}$.

We shall now proceed to evaluate the possibilities of obtaining amplification within a system of two substantially broadened electronic levels.^[11-14,20] The lower laser level is the electronic ground state, and the upper level is labile (Fig. 1d). The broadening of the levels can involve either interaction with the medium, or the existence of a continuous set of vibrational sublevels characteristic of the molecule itself. The amplification coefficient at the frequency ν is

$$k_{21}(\nu) = \alpha_{21}(\nu) \left[\frac{n_2}{n} - \frac{n_1}{n} \frac{B_{12}(\nu)}{B_{21}(\nu)} \right], \quad (3)$$

Here

$$\alpha_{21}(\nu) = \frac{h\nu}{v} n B_{21}(\nu) = n \sigma_{21}(\nu) \quad (4)$$

is the limiting amplification coefficient, which holds when $n_2 = n$; $\sigma_{21}(\nu)$ is the cross-section corresponding to the limiting amplification;

$$B_{21}(\nu) = \int B_{21}(E_2, \nu) \rho_2(E_2) dE_2, \quad (5)$$

$$B_{12}(\nu) = \int B_{12}(E_1, \nu) \rho_1(E_1) dE_1 \quad (6)$$

are the Einstein coefficients for stimulated emission and absorption averaged over all the vibrational sublevels of E_2 and E_1 ; $\rho_1(E_1)$ and $\rho_2(E_2)$ are the distribution functions of the particles over the sublevels in the ground and excited states. If the probabilities of redistribution of the particles over the sublevels of E_1 and E_2 are considerably greater than the probabilities of optical and non-optical transitions between the electronic states, then the functions $\rho_i(E_i)$ correspond to thermal equilibrium:

$$\rho_i(E_i) = C_i g_i(E_i) e^{-E_i/kT}, \quad (7)$$

Here $g_i(E_i)$ is the degeneracy, T is the temperature of the medium, and C_i is a normalizing factor. If the statistical weights of the electronic levels are the same, then $C_1 = C_2$. If we substitute (7) into (5) and (6), and take into account the relation $B_{21}(E_2, \nu) g_2(E_2) = B_{12}(E_1, \nu) g_1(E_1)$ between the Einstein coefficients, as well as the equality $E_2 = E_1 + h(\nu - \nu_{e1})$, we obtain^[29]

$$\frac{B_{12}(\nu)}{B_{21}(\nu)} = \frac{C_1}{C_2} e^{-h(\nu_{e1} - \nu)/kT}. \quad (8)$$

Equation (8) is independent of the width of the ground and excited levels. Hence, it is universal whenever there is an equilibrium distribution of the particles over the sublevels.

If we substitute (8) into (3) and assume that $C_1 = C_2$, we get

$$k_{21}(\nu) = \alpha_{21}(\nu) \left[\frac{n_2}{n} - \frac{n_1}{n} e^{-h(\nu_{e1} - \nu)/kT} \right]. \quad (9)$$

According to (9), amplification will arise at the frequency ν if

$$\frac{n_2}{n_1} > e^{-h(\nu_{e1} - \nu)/kT}. \quad (10)$$

For frequencies $\nu \geq \nu_{e1}$, this condition is fulfilled only if a population inversion of levels 2 and 1 is formed. However, such a requirement is not obligatory for fre-

quencies $\nu < \nu_{e1}$, and amplification will occur even when n_2 is smaller than n_1 . The greater $\nu_{e1} - \nu$ is, the lower the required values of n_2/n_1 are, and the easier it is to get amplification.

In order to give an appreciable amplification effect, the active substance must satisfy several fundamental requirements. First of all, (3) and (4) imply that molecules having a high value of $\sigma_{21}(\nu)$ are the most advantageous. At the same time, the value of $\nu_{e1} - \nu$ must be high enough. Since the frequency ν cannot lie outside the limits of the luminescence band,* we can attain large values of $\nu_{e1} - \nu$ only for molecules having a very large half-width $\Delta\nu$ of the band. Large values of $\sigma_{21}(\nu)$ and $\Delta\nu$ are realized among molecules having large probabilities of spontaneous optical transitions.

However, we must convince ourselves that adopting molecules having large values of $\Delta\nu$ will not interfere with accumulation of particles in level 2 and thus decrease the value of $k_{21}(\nu)$. It is rather simple to calculate n_2 and n_1 for a steady state, with excitation by monochromatic radiation of frequency ν_p and density u_p . The equations of balance of the particles are $n_1 B_{12}(\nu_p) u_p = n_2 [p_{21} + B_{21}(\nu_p) u_p]$ and $n_1 + n_2 = n$, where p_{21} is the total probability of spontaneous radiative and radiationless $2 \rightarrow 1$ transitions. They imply that

$$\frac{n_2}{n} = \frac{e^{h(\nu_p - \nu_{e1})/kT}}{\frac{8\pi h \nu_p^3}{v^3} \frac{\Delta\nu}{\eta u_p} \frac{\kappa_{21}(\nu_l)}{\kappa_{21}(\nu_p)} + 1 + e^{h(\nu_p - \nu_{e1})/kT}} \quad (11)$$

In deriving (11), we represented the probability p_{21} in the form $p_{21} = A_{21}(\nu_l) \Delta\nu/\eta$ (where $A_{21}(\nu_l)$ is the spectral probability of spontaneous emission at the frequency ν_l of the maximum of the luminescence band, $\Delta\nu$ is the half-width of the band, and η is the quantum yield of luminescence), and we have also taken into account Eq. (8) and the relation between the Einstein coefficients $A_{21}(\nu)$ and $B_{21}(\nu)$.

In order to study the relation of the amplification coefficient (9) to the half-width $\Delta\nu$ of the band, with account taken of (11), we must assume that $\nu_{e1} - \nu \cong \Delta\nu$, and $\nu_p - \nu_{e1} \cong \Delta\nu/2$ (with excitation at the peak of the absorption band). An analysis made under these assumptions gives the following results. At small $\Delta\nu$ ($h\Delta\nu \ll kT$), the amplification coefficient is negative. Then, as $\Delta\nu$ increases, the square bracket in (9) becomes positive and increases, approaching unity in the limit. This corresponds to creation of an amplification coefficient, which then increases up to the limiting value $\kappa_{21}(\nu)$. If increase in $\Delta\nu$ is not accompanied by decrease in $\kappa_{21}(\nu)$, then molecules having very large values of $\Delta\nu$ are the most advantageous. For some classes of molecules, increase in $\Delta\nu$ involves decrease in $\sigma_{21}(\nu)$, and hence in $\kappa_{21}(\nu)$. Then the relation of $k_{21}(\nu)$ to $\Delta\nu$ has a maximum, which usually occurs at $\Delta\nu \sim 1000-2000 \text{ cm}^{-1}$.

Equations (9) and (11) also imply that we should use molecules having high values of η and use more intense excitation sources in order to increase the amplification.

Thus, a system of two broadened levels can provide considerable amplification. The optimum conditions are

*The contour of the band of limiting amplification $K_{21}(\nu)$ is proportional to the contour of the luminescence band divided by ν^3 .^[14] When ν lies far from the center of the band, the value of $K_{21}(\nu)$ become very small.

attained in substances having very wide luminescence bands and very high probabilities A_{21} of spontaneous transition (or if the value of η is fixed, having very small lifetimes of the excited state). These requirements are satisfied best of all by the organic dyes.

Dyes are an especial class of complex organic compounds. Their distinctive feature is high absorptivity in the visible.^[30,31] The chemical structure of dyes is characterized by combination of six-membered benzene (C_6H_6), pyridine (C_5H_5N), azine ($C_4H_4N_2$) and other rings, as well as five-membered pyrrole rings (C_4H_5N). These rings can be joined either directly, or through a central atom (C, N), or a linear chain having conjugated bonds $-(CH=CH)_n-$. The hydrogen atoms in the cyclic part are often replaced by radicals (e.g., the CH_3 or C_2H_5 groups). This considerably changes the absorptivity of the dyes and the spectral position of the bands.

Dye molecules have a planar skeleton, with only the groups of the radicals sometimes lying outside the common plane. The structural formulas of some types of dyes are given in Fig. 2.

Many dyes can luminesce. Favorable conditions for luminescence are created when the dye molecules can ionize or be polarized, and are shielded from mutual influence. These conditions are best attained at low temperatures and in solid solutions having low concentrations of the particles. Temperature rise and the diffusional movements that occur in liquids somewhat impair the conditions for luminescence. Nevertheless, many solutions of low viscosity luminesce with a high quantum yield.

The absorption and emission spectra of dyes in the visible usually consist of one broad band (of widths up to 7000 cm^{-1}). Typical absorption spectra are given in Fig. 3. In accord with the Stokes-Lommel law, the emission band is always shifted to longer wavelengths than the absorption band. In many cases, the absorption and luminescence bands exhibit mirror symmetry.^[31] The contours of these bands are related by the universal relation^[29,32]

$$\frac{W_I(\nu)}{k_{\text{abs}}(\nu)} = C \nu^3 e^{h(\nu_{e1} - \nu)/kT}, \quad (12)$$

where C is a constant depending on the excitation conditions. Equation (12) permits one to determine the form of the function $W_I(\nu)$ from the measured function $k_{\text{abs}}(\nu)$, and vice versa.

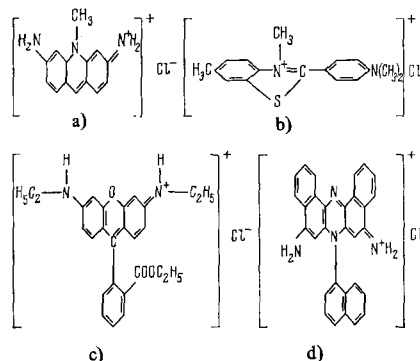


FIG. 2. Structural formulas of some dyes: a) trypaflavin; b) rhoduline yellow; c) rhodamine 6G; d) magdala red.

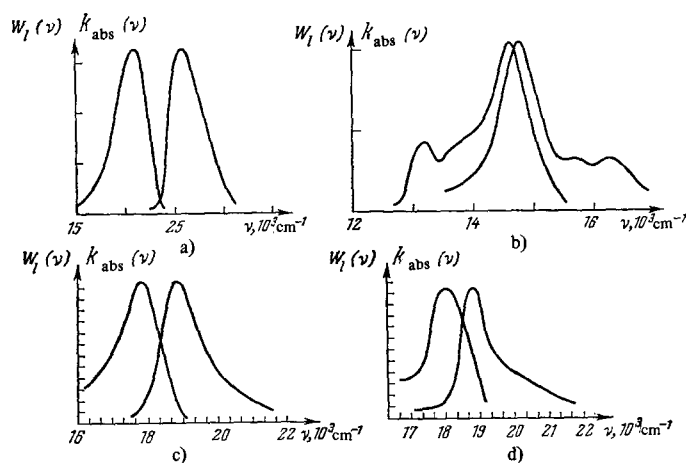


FIG. 3. Typical absorption (at right) and luminescence spectra of dyes: a) 3-aminophthalimide in ethanol; b) Mg phthalocyanine in quinoline; c) rhodamine 6G in acetone; d) eosine B extra in isoamyl alcohol.

The most important property of dyes is their extremely high value of the cross-section for limiting amplification $\sigma_{21}(\nu)$. It usually amounts to about 10^{-15} cm^2 ($B_{21}(\nu_l) \sim 10^7 \text{ erg}^{-1} \text{ cm}^3 \text{ sec}^{-1}$). This is almost five orders of magnitude larger than for the R_1 line of ruby. This makes it possible to obtain considerable amplifications even when the population of the upper level is small. Thus, for example, let us assume $\sigma \sim 0.5 \times 10^{-15} \text{ cm}^2$, $\Delta\nu \sim 1000 \text{ cm}^{-1}$, and $n \sim 10^{16} \text{ cm}^{-3}$. Then, according to (9), transferring only 2% of all the particles to the excited level is sufficient to produce an amplification coefficient of 0.1 cm^{-1} . If $\eta \cong 0.5$, $\nu_p - \nu_{el} \sim 500 \text{ cm}^{-1}$, and $\kappa_{21}(\nu_l)/\kappa_{21}(\nu_p) \sim 10$, then a relative population n_2/n of 0.02 is attained at $u_p \sim 0.4 \text{ erg} \cdot \text{cm}^{-3}$. This is about the same density as is necessary to attain an analogous amplification in ruby when pumped by the green monochromatic line. The cited data show that dyes should have very low thresholds for laser action.

The pumping efficiency of dyes is considerably connected not only with the radiation density, but also with the position of the frequency of the incident radiation on the contour of the absorption band. According to (11), increase in $\nu_p - \nu_{el}$ increases n_2 . However, shift of ν_p outside the limits of the peak of the absorption band lowers the efficiency of absorption. Hence, there is an optimum value of ν_p at which a given pumping density u_p will provide a maximum value of n_2 , and hence, of

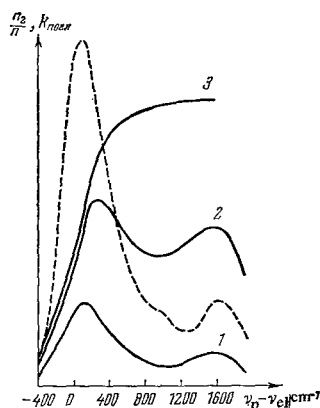


FIG. 4. Dependence of n_2/n on $\nu_p - \nu_{el}$ for various exciting-light densities. The pumping density increases from 1 to 3. The absorption contour of the dye is given by the dotted line.

$k_{21}(\nu)$. The value of ν_p^{opt} depends on u_p . When u_p is small, it is suitable as a rule to excite at the maximum of the absorption band. The value of ν_p^{opt} shifts to shorter wavelengths with increasing u_p . For example, Fig. 4 gives the relation of n_2/n to the position of the frequency of the exciting light on the absorption band of a substance for different pumping intensities.

Equation (11) implies that the limiting population of the upper level, which is attained as $u_p \rightarrow \infty$,

$$\left(\frac{n_2}{n}\right)_{\text{lim}} = \frac{1}{1 + e^{-h(\nu_p - \nu_{el})/kT}} \quad (13)$$

can be very large. When $h(\nu_p - \nu_{el}) \ll kT$, i.e., in a system of two narrow levels, it is 0.5. However, even when $h(\nu_p - \nu_{el}) \sim 1000 \text{ cm}^{-1}$, it amounts to as much as 0.993. Thus, it is possible not only to get with the organic dyes amplification based on individual electronic-vibrational transitions, but also to raise almost all the particles to the excited state.

We shall now take up the spectral properties of the amplification coefficient of (9). We can find them by determining experimentally the shape of the function $\kappa_{21}(\nu)$, which is proportional to $W_l(\nu)/\nu^3$. Figure 5a shows the results of calculating $k_{21}(\nu)$ by Eq. (9) for various values of n_2/n . Negative values of $k_{21}(\nu)$ correspond to absorption, and positive values to amplification. As n_2/n increases, not only does absorption decrease and amplification increase, but the shape and position of the bands change. The maxima of the bands are shifted to shorter wavelengths. When all the particles are raised to the excited state, absorption disappears, while the amplification spectrum coincides with the luminescence spectrum divided by ν^3 . Fig. 5b shows the analogous construction for absorption and luminescence-amplification spectra having two maxima. As we see from the diagram, the relation between the sizes of the amplification peaks depends considerably on n_2 . When n_2 is small, the short-wavelength maximum is smaller than that at longer wavelengths, and vice versa for large n_2 .

In general, the maximum amplification coefficient

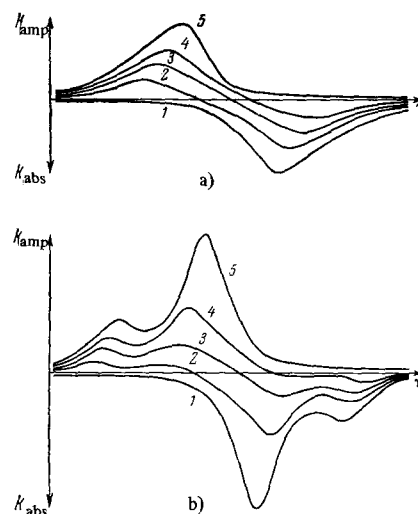


FIG. 5. Relation of the absorption and amplification bands to n_2/n for various forms of spectra: 1 - $n_2/n = 0$; 5 - $n_2/n = 1$; 2 - 4 - intermediate cases.

$k_{21}^{\max}(\nu)$, which is attained as $u_p \rightarrow \infty$, does not coincide with the limiting value $\kappa_{21}(\nu)$. It is

$$k_{21}^{\max}(\nu) = \frac{1}{1 + e^{-h(\nu_p - \nu_{e1})/kT}} \kappa_{21}(\nu) [1 - e^{-h(\nu_p - \nu)/kT}]. \quad (14)$$

The value of k_{21}^{\max} approaches closer to $\kappa_{21}(\nu)$ as the difference $\nu_p - \nu_{e1}$ increases, or the temperature decreases. At room temperature with $\nu_p - \nu_{e1} > 500 \text{ cm}^{-1}$, the functions $k_{21}^{\max}(\nu)$ and $\kappa_{21}(\nu)$ practically coincide. However, when $\nu_p - \nu_{e1} \leq 0$, then the functions $k_{21}^{\max}(\nu)$ and $\kappa_{21}(\nu)$ differ considerably (see Fig. 5).

We shall now discuss excitation of a dye by radiation of broad spectral composition. Amplification can be obtained even here. Let us assume that the spectral density of the incident radiation $u_p(\nu)$ varies slightly within the limits of the absorption and emission bands. The probabilities of direct and reverse stimulated transitions are $B_{12} u_p(\nu)$ and $B_{21} u_p(\nu)$, where $B_{ij} = \int B_{ij}(\nu) d\nu$. By analogy with (11), we can easily derive

$$\frac{n_2}{n} = \frac{\beta}{\frac{8\pi h \nu^3}{v^3} \frac{1}{\eta u_p(\nu)} + 1 + \beta}, \quad (15)$$

Here $\beta = B_{12}/B_{21}$ is a quantity equal to the ratio of areas of the absorption and luminescence bands normalized to unity at the maximum. According to (15), the population of the levels does not depend on the lifetime of the excited state, nor on the widths of the bands. The amplification coefficient is determined by Eq. (9).

Equation (15) implies that the spectral density of the pumping radiation required to transform 2% of all the particles to the excited state is $\sim 10^{-3} \text{ erg} \cdot \text{cm}^{-3} \text{ cm}^{-1}$, when $\beta = 1$, $\eta = 0.5$, and $\nu_l \sim 18,000 \text{ cm}^{-1}$. It can be attained with standard pulsed xenon lamps. In the region of $18,000 \text{ cm}^{-1}$, such a value of the intensity $u_p(\nu)$ corresponds to a Planck emitter at a temperature $\sim 8000^\circ \text{K}$.

Laser action in dyes having a two-level system can be complicated by the harmful influence of extra levels, as shown in Fig. 6. The odd numbers denote singlet, and the even numbers triplet states. Pumping and amplification are localized in the channel $1 \leftrightarrow 3$. One has to take account in the calculations of $3 \rightarrow 5$ transitions, of deactivation of the level 3 in $3 \rightarrow 2$ transitions, and $2 \rightarrow 4$ and $2 \rightarrow 1$ transitions. As a rule, the triplet state 2 is deactivated by a non-optical pathway, and in some molecules the probability p_{21} can be very large. The amplification coefficient with account taken of absorption in the channels $3 \rightarrow 5$ and $2 \rightarrow 4$ is

$$k_{31}(\nu) = \frac{h\nu}{v} [n_3 B_{31}(\nu) - n_1 B_{13}(\nu) - n_5 B_{35}(\nu) + n_5 B_{53}(\nu) - n_2 B_{24}(\nu) + n_4 B_{42}(\nu)]. \quad (16)$$

Since the probabilities of non-optical deactivation of the

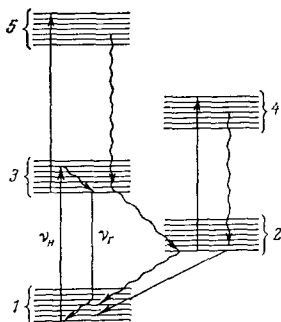


FIG. 6. System of energy levels, with the triplet states taken into account.

levels 4 and 5 are usually large, n_3 and n_5 are small. Hence, we can neglect the fourth and fifth terms of (16). In this approximation,

$$k_{31}(\nu) = \kappa_{31}(\nu) \left[\frac{n_3}{n} (1-c) - \frac{n_1}{n} e^{-a} - \frac{n_2}{n} d \right], \quad (17)$$

where $\kappa_{31}(\nu) = B_{31}(\nu) nh\nu_{31}/v = \sigma_{31}(\nu)n$ is the limiting amplification coefficient, $a = h(\nu_{e1} - \nu)/kT$, $c = B_{35}(\nu)/B_{31}(\nu)$, and $d = B_{24}(\nu)/B_{31}(\nu)$. The existence of the transitions $3 \rightarrow 5$ and $2 \rightarrow 4$ and the accumulation of particles in level 2 can considerably decrease $k_{31}(\nu)$. When $c \geq 1$, amplification is completely impossible. Absorption in the channel $2 \rightarrow 4$ is characteristic of complex molecules, and has been studied many times.^[33-35] However, it is substantial only when n_2 is large.

In order to estimate the effect of the triplet level on the amplification coefficient $k_{31}(\nu)$, we must find n_1 , n_2 , and n_3 . We shall assume that the density of the excited radiation is spectrally uniform. We shall assume for simplicity that $\beta = 1$, i.e., $B_{12} = B_{21} = B$. The solution of the kinetic equations of balance for a square irradiation pulse has the form^[36]

$$\frac{n_1}{n} = e^{-\alpha_1 t} [C_1 (p_{31} + p_{32} - \alpha_2) - C_2 (p_{31} + p_{32} - \alpha_1) e^{-\alpha_1 t}] + D (p_{31} + p_{32} + Bu_p), \quad (18)$$

$$\frac{n_3}{n} = [e^{-\alpha_2 t} (C_1 - C_2 e^{-\alpha_1 t}) + D] Bu_p, \quad (19)$$

$$\frac{n_2}{n} = 1 - \frac{n_1}{n} - \frac{n_3}{n}, \quad (20)$$

Here $D = p_{21}/y$, $y = p_{21}(p_{31} + 2Bu_p) + p_{32}(p_{21} + Bu_p)$, $\alpha_1 = \sqrt{z^2 - 4y}$, $\alpha_2 = (z - y)/2$, and $z = p_{31} + p_{32} + 2Bu_p$. The constants C_1 and C_2 are determined by the initial conditions.

The time variation of the populations is determined primarily by the parameters α_1 and α_2 . When $\alpha_1 > \alpha_2$, as usually happens with dyes, the process of redistribution of the particles over the electronic levels runs as follows. Initially, the particles are rapidly accumulated in level 3 within the time $t_1 \sim 1/\alpha_1$. Then n_2 gradually increases and n_3 declines up to the instant $t_2 \sim 1/\alpha_2$. The function $n_3(t)$ has a maximum. In the region of the maximum, we can use Eq. (15) to estimate n_3 , with $\eta = A_{31}/(p_{31} + p_{32})$. That is, the effect of the metastable level is neglected.

A steady state sets in when $t \gg t_2$:

$$\frac{n_3}{n} = \frac{Bu_p}{p_{31} + p_{32} + Bu_p (2 + p_{32}/p_{21})}, \quad (21)$$

$$\frac{n_2}{n} = \frac{Bu_p p_{32}/p_{21}}{p_{31} + p_{32} + Bu_p (2 + p_{32}/p_{21})}, \quad (22)$$

$$\frac{n_1}{n} = \frac{p_{31} + p_{32} + Bu_p}{p_{31} + p_{32} + Bu_p (2 + p_{32}/p_{21})}. \quad (23)$$

If we substitute (21)–(23) into (17), we get

$$k_{31}^{\text{st}}(\nu) = \kappa_{31}(\nu) \frac{Bu_p \{1 - [c + e^{-a} + d(p_{32}/p_{21})] - (p_{31} + p_{32}) e^{-a}\}}{p_{31} + p_{32} + Bu_p (2 + p_{32}/p_{21})}. \quad (24)$$

In the steady state, amplification occurs only when the following conditions are satisfied:

$$c + e^{-a} + d \frac{p_{32}}{p_{21}} < 1 \quad (25)$$

and

$$Bu_p > \frac{(p_{31} + p_{32}) e^{-a}}{1 - [c + e^{-a} + d(p_{32}/p_{21})]}. \quad (26)$$

The maximum value of the steady-state amplification can be attained as $u_p \rightarrow \infty$. It is

$$k_{31}^{st \max}(\nu) = \kappa_{31}(\nu) \frac{1 - [c + e^{-a} + d(p_{32}/p_{21})]}{2 + p_{32}/p_{21}} \quad (27)$$

According to (24)–(26), the degree of amplification depends considerably on the absorption of light in the system of triplet levels (2 → 4 transitions). If the ratio p_{32}/p_{21} is large (as is true of many dyes), then even very small values of d will considerably decrease the amplification and increase the amount of pumping necessary to attain a given value of $k_{31}(\nu)$. However, if $d \ll p_{21}/p_{32}$, then we can neglect the 2 → 4 absorption. Then the harmful effect of the triplet level will be manifested only when a significant number of particles accumulate in it. This effect is especially substantial for large p_{32}/p_{21} , and can considerably reduce the amplification.

If p_{32}/p_{21} and d are large, then we can get appreciable amplification only in a non-steady state, in the interval of time between $t_1 > 1/\alpha_1$ and $t_2 < 1/\alpha_2$. The size of this interval depends on the pumping intensity. At low pumping powers, $1/\alpha_1 \cong 1/(p_{31} + p_{32})$, and $1/\alpha_2 = 1/p_{21}$. When $u_p \rightarrow \infty$, $1/\alpha_1 \rightarrow 1/2Bu_p$, and $1/\alpha_2 \rightarrow 2/p_{32}$.

Thus the existence of an intensive 3 → 2 conversion not only decreases (or renders impossible) steady-state amplification, but it also shortens the interval of time during which one can observe non-steady-state amplification. We should choose for laser action molecules having a large value of p_{21} and a small value of p_{32} . In all cases we should avoid molecules having appreciable triplet-triplet absorption at the laser frequency.

3. CALCULATION OF THE THRESHOLD AND POWER OF LASER ACTION^[37,20]

Let us consider a dye solution placed within a resonator having selective losses. We use monochromatic radiation of frequency ν_p for pumping. The frequency ν_g of the generated radiation is unambiguously fixed by the characteristics of the resonator. Laser action will set in whenever the amplification coefficient of (17) at the frequency ν_g has become equal to the loss coefficient.* Hereinafter, the loss coefficient and the amplification coefficient will be assumed equal. That is, the following condition for laser action will be satisfied:

$$n_3(1-c) - n_1e^{-a} - n_2d = n\delta, \quad (28)$$

where $\delta = k_{\text{LOSS}}/k_{31}(\nu_g)$.

We can find the populations n_1 , n_2 , and n_3 of the levels during laser action by solving Eq. (28) simultaneously with the equations

$$n = n_1 + n_2 + n_3, \quad (29)$$

$$\frac{dn_2}{dt} = p_{32}n_3 - p_{21}n_2. \quad (30)$$

This gives

$$\frac{n_3}{n} = \frac{\delta + e^{-a}}{G} \left[p_{21} + \frac{(e^{-a}-d)p_{32}}{1-c+e^{-a}} e^{-at} \right] - \frac{(e^{-a}-d)n_2(0)}{1-c+e^{-a}}, \quad (31)$$

*This is true for resonators having a small length L . If L is large, a certain time t_0 is necessary for laser action to develop. At large amplifications it is approximately equal to $(3-5)L/v$, where L/v is the time that light takes to pass through the distance L . When $L \sim 10$ cm, $t_0 \sim 10^{-9}$ sec.

$$\frac{n_2}{n} = \frac{\delta + e^{-a}}{G} p_{32} (1 - e^{-at}) + n_2(0), \quad (32)$$

$$\frac{n_1}{n} = \frac{1}{G} \left[(1-c-\delta)p_{21} - (\delta+d)p_{32} + \frac{(\delta+e^{-a})(1-c+d)p_{32}}{1-c+e^{-a}} e^{-at} \right] - \frac{(1-c+d)n_2(0)}{1-c+e^{-a}}, \quad (33)$$

where

$$\alpha = \frac{G}{1-c+e^{-a}}, \quad (34)$$

$$G = (e^{-a}-d)p_{32} + p_{21}(1-c+e^{-a}); \quad (35)$$

and $n_2(0)$ is the number of particles accumulated in the triplet level in the period preceding the onset of laser action. At the high irradiation intensities attained in a single pulse of a ruby laser, the firing time is very short, and hence $n_2(0)$ is practically zero.

When $n_2(0)$ is small, the populations of the levels in a state of laser action do not depend on the pumping intensity. When u_p is small, the values of $n_2(0)$ may prove to be appreciable, and the variations $n_1(u_p)$, $n_2(u_p)$, and $n_3(u_p)$ considerable.

The value of the laser power (per unit volume)

$$W_g = [B_{31}(\nu_r)n_3 - B_{13}(\nu_g)n_1]u_p h\nu_g \quad (36)$$

can be found from the equation of balance of particles in level 3:

$$\frac{dn_3}{dt} = B_{13}(\nu_p)u_p(n_1 - n_3e^{-b}) - B_{31}(\nu_g)u_g[n_3(1+c) - n_1e^{-a}] - (p_{31} + p_{32})n_3, \quad (37)$$

where $b = h(\nu_p - \nu_{e1})/kT$. Taking (31)–(33) into account, we get

$$W_g = h\nu_g \left\{ B_{13}(\nu_p)u_p \left[n_1 \left(1 - \frac{(e^{-a}-d)e^{-b}}{1-c+d} \right) - n \frac{(\delta+d)e^{-b}}{1-c+d} \right] - \frac{p_{31} + p_{32}}{1-c+d} [n(\delta+d) + n_1(e^{-a}-d)] + \frac{n(\delta+e^{-a})(e^{-a}-d)p_{32}}{1-c+e^{-a}} e^{-at} \right\} \frac{n(\delta+d) + n_1[ce^{-a}-d(1+e^{-a})]}{n(\delta+d)(1+c) + n_1[2ce^{-a}-d(1+e^{-a}+c)]}, \quad (38)$$

where n_1 is given by Eq. (33).

Equation (38) permits us to estimate the relation of the laser power both to the parameters of the system a , b , c , d , p_{31} , p_{32} , and $B_{13}(\nu_p)$; and to external parameters: the density u_p of the exciting radiation, the loss coefficient of the resonator, the concentration of particles, and also the time.

In the first stage of study it is convenient to neglect the accumulation of particles in the triplet level 2. This is valid for molecules having $p_{32} \ll p_{21}$. In this case $n_1 = n(1-c-\delta)/(1-c+e^{-a})$, $n_2 = 0$, $n_3 = n(\delta+e^{-a})/(1-c+e^{-a})$,

$$W_g = nh\nu_g \frac{1 - e^{-(a+b)} - \delta(1+e^{-b}) - c}{1+e^{-a}-c} B_{13}(\nu_p) (u_p - u_p^{\text{thr}}) \frac{\delta(1+e^{-a}) + ce^{-a}}{\delta(1+e^{-a}) + c(\delta+2e^{-a})} \quad (39)$$

where

$$u_p^{\text{thr}} = \frac{8\pi h\nu_g^3}{v^3} \frac{\Delta\nu}{\eta} \frac{\kappa_{13}(\nu_l)}{\kappa_{31}(\nu_p)} \frac{\left[e^{-h(\nu_l - \nu_g)/kT} + \frac{k_{\text{LOSS}}}{n\sigma(\nu_g)} e^{-h\Delta\nu_M/2kT} \right]}{1 - e^{-h(\nu_p - \nu_g)/kT} - [1 + e^{-h(\nu_p - \nu_{e1})/kT}] \frac{k_{\text{LOSS}}}{n\sigma(\nu_g)} - c} \quad (40)$$

is the threshold value of the density of exciting radiation, $\Delta\nu$ is the half-width of the luminescence band, $\Delta\nu_M$ is the distance between the maxima of the absorption and luminescence bands, ν_l is the frequency at the maximum of the luminescence band, and η is the luminescence quantum yield in the 1 → 3 band, and η is the luminescence quantum yield in the 1 → 3 band, which is equal to $A_{31}/(p_{31} + p_{32})$. We have assumed here that the absorption and luminescence spectra are mirror images

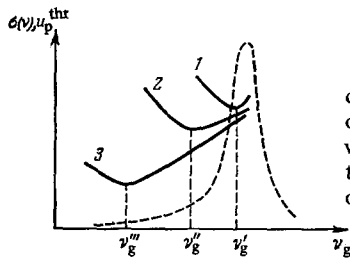


FIG. 7. Limiting-amplification contour (dotted curve) and shape of the function $u_p^{\text{thr}}(\nu_g)$ for various values of k_{loss}/n . In going from 1 to 3, k_{loss}/n diminishes by a factor of three.

of one another.

The populations of the levels and laser power are constant in time in the case being considered. If u_p should depend on t , then n_3 and n_1 remain invariant, while the shape of the laser pulse will reproduce that of the pumping pulse. This conclusion is well confirmed by experiment.

Equation (40) implies that the optimum value of ν_p is somewhat higher than the frequency at the peak of the absorption band, which is determined by the shape of the function $B_{13}(\nu)$. It is extremely unfavorable to adopt an excitation region near ν_{e1} , and especially near ν_g , since this involves a sharp increase in the threshold and decline in the laser power.

Figure 7^[12] shows the relation of the threshold to ν_g for one particular shape of luminescence band for various values of δ . The optimum value of ν_g lies on the long-wavelength side of the band. The smaller k_{loss}/n is, the smaller ν_g^{opt} is. Tuning the laser frequency can lead to a substantial change in u_p^{thr} . However, if one exceeds the threshold considerably, the laser power depends weakly on ν_g (except when c is anomalously large). W_g is considerably more dependent on ν_p .

The threshold is linearly dependent on k_{loss}/n for small δ . If k_{loss} is increased greatly, as can happen if the solution is overheated and becomes turbid, the denominator of (40) approaches zero, and u_p^{thr} approaches infinity. Consequently laser action breaks down.

If the luminescence quantum yield were independent of the concentration, then the threshold would be lowered and the laser power would increase with increasing n . In actual situations, concentration quenching of luminescence, decline in η , and rapid increase in the threshold set in at large n . Therefore there is an optimum concentration n (in the range 10^{16} – 10^{17} cm^{-3}).

Temperature decrease is accompanied by decrease in u_p^{thr} and increase in W_g .

The threshold and laser power for dyes depend considerably on the properties of the molecules, and primarily on the half-width $\Delta\nu$ of the bands, the distance $\Delta\nu_m$ between the maxima of the bands, and the luminescence quantum yield η . For estimating, we shall assume that $\nu_p \sim \nu_{\text{abs}}^m$, $\nu_g - \nu_l \sim \Delta\nu/2$, $\nu_l \sim 13,000$ cm^{-1} , $c = 0$, $\exp(-h\Delta\nu/2kT) \ll 1$, and $\exp(-h\Delta\nu_m/2kT) \ll 1$. Then

$$u_p^{\text{thr}} \approx 0.01 \frac{\Delta\nu}{\eta} \frac{\kappa_{13}(\nu_l)}{\kappa_{13}(\nu_p)} \frac{e^{-h\Delta\nu/2kT} + \frac{k_{\text{loss}}}{n\sigma(\nu_p)} e^{-\Delta\nu_m/2kT}}{1 - k_{\text{loss}}/n\sigma(\nu_g) - c}, \quad (41)$$

where $\Delta\nu$ is expressed in cm^{-1} . If we should drop the factor $\kappa_{31}(\nu_l)/\kappa_{13}(\nu_p)$ out of (41), then the optimum value of $\Delta\nu$ would be close to $2kT$. However, this factor also

declines with increasing $\Delta\nu$, and hence the optimum value $\Delta\nu_{\text{opt}}$ is considerably larger. We can assume that it is most advantageous to use molecules having the largest values of $\Delta\nu$ and $\Delta\nu_m$ in order to decrease the threshold. The value of the threshold is inversely proportional to η . Absorption of the generated radiation in the channel $3 \rightarrow 5$ is taken into account by the quantity $c = B_{35}(\nu_g)/B_{31}(\nu_g)$, and can be considerable when c is close to unity.

Equation (41) permits us to estimate the numerical values of the threshold. In typical cases, $\Delta\nu \sim 1000$ cm^{-1} , $\kappa_{13}(\nu_g)/\kappa_{13}(\nu_p) \sim 0.01$, $k_{\text{loss}} < 1$ cm^{-1} , and $n\sigma(\nu_g) > 20$ cm^{-1} . Then $u_p^{\text{thr}} \sim 0.01/\eta$. Even when $\eta \sim 10^{-4}$, i.e., for non-luminescent molecules, $u_p^{\text{thr}} \sim 10^2$ $\text{erg} \cdot \text{cm}^{-3}$. Since a single-pulse ruby laser produces a value $u_p \sim 10^4$ $\text{erg} \cdot \text{cm}^{-3}$, laser action is possible even under such unfavorable conditions. For good luminescent molecules, the value of u_p^{thr} is several orders of magnitude smaller than u_p .

When $u_p \gg u_p^{\text{thr}}$, the expression (39) for the laser power is greatly simplified. This implies that with a proper choice of ν_p and ν_g , all dyes having large values of $\Delta\nu$ have similar values of W_g . This result also agrees well with experiment.

Now we shall consider substances in which particles accumulate in level 2 within the duration of the pumping pulse. These substances are easily distinguished experimentally by studying the time characteristics of the luminescence and their tendency to become bleached by the incident radiation. Let us assume that $|e^{-a} - d| p_{32} \gg p_{21}$. If we also assume that $e^{-a} \ll 1$, $e^{-b} \ll 1$, and $c = 0$, then (31)–(33) imply that

$$\frac{n_3}{n} = (\delta + e^{-a}) e^{(d-e^{-a})p_{32}t}, \quad (42)$$

$$\frac{n_2}{n} = \frac{\delta + e^{-a}}{d - e^{-a}} [e^{(d-e^{-a})p_{32}t} - 1], \quad (43)$$

$$\frac{n_1}{n} = \frac{d + \delta - (\delta + e^{-a})(1+d)e^{(d-e^{-a})p_{32}t}}{d - e^{-a}}. \quad (44)$$

With increasing t , n_2 increases and n_1 declines. The direction of variation of n_3 is determined by the sign of the difference $d - e^{-a}$. The effect of accumulation of particles in level 2 is especially marked for large d , i.e., when there is considerable absorption of the radiation by metastable particles.

In this case, according to (38), the decline of n_1 with time will rapidly weaken the laser action, and then stop it. We can easily determine the limiting value of n_1 at which laser action is still possible by equating (38) to zero. To the same degree of approximation, this gives

$$n_1^{\text{min}} = \frac{(p_{31} + p_{32})(d + \delta) + (1 + d)(\delta + e^{-a})(d - e^{-a})p_{32}e^{(d-e^{-a})p_{32}t}}{B_{13}(\nu_p)u_p(1+d) + (p_{31} + p_{32})(d - e^{-a})} n. \quad (45)$$

By equating the expressions (44) and (45), we can find the instant of breakdown of laser action:

$$t_{\text{lim}} = \frac{1}{(d - e^{-a})p_{32}} \ln \frac{(d + \delta)B_{13}(\nu_p)u_p}{(\delta + e^{-a})[B_{13}(\nu_p)u_p(1+d) + (p_{31} + p_{32})(d - e^{-a}) + p_{32}(d - e^{-a})^2]}. \quad (46)$$

If t_{lim} is considerably longer than the duration Δt of the pumping pulse, then accumulation of particles in the metastable level will not affect the laser process appreciably. Conversely, when $t_{\text{lim}} \ll \Delta t$, laser action ceases long before the pumping pulse ends. In this case,

the laser power will be very small, and the efficiency low. It is also necessary that t_{lim} should be larger than $t_0 \cong (3-5) L/v$, since otherwise laser action will not set in at all, and only amplified luminescence will be observed.

Table I gives the results of calculating $p_{32}t_{\text{lim}}$ for various values of d and $p_{32}/B_{13}(\nu_p)u_p$.

For certain values of the system parameters, t_{lim} proves to be negative. Laser action is impossible in these systems (even at the initial instant of time). The condition for realizing laser action when $d > e^{-a}$ has the form

$$B_{13}(\nu_p)u_p > \frac{(\delta + e^{-a})[(p_{31} + p_{32})(d - e^{-a}) + p_{32}(d - e^{-a})^2]}{d - e^{-a} - d(\delta + e^{-a})}. \quad (47)$$

When d is large, laser action is possible only with very intense pumping to compensate for the diminution of the amplification coefficient by $2 \rightarrow 4$ transitions. For small d , laser action is possible at relatively small values of u_p . Then laser action ceases only when the lower level has been very highly depleted.

Let us consider the data of Table I as applied to a single-pulse excitation system ($B_{13}(\nu_p)u_p \sim 10^{11} \text{ sec}^{-1}$, $\Delta t \sim 10^{-8} \text{ sec}$). If, e.g., $d \sim 1$, then $t_{\text{lim}} \approx 2/p_{32}$ over the range of values of p_{32} from zero to 10^{10} sec^{-1} . If, furthermore, $p_{32} \geq 10^9 \text{ sec}^{-1}$, then $t_{\text{lim}} \leq 2 \times 10^{-9} \text{ sec} \ll \Delta t$. Then laser action will stop at the very onset of the pumping pulse, or won't occur at all. Intense laser action can occur only when $p_{32} \leq 10^8 \text{ sec}^{-1}$. The situation is analogous when $d \sim 0.3$. The value of t_{lim} is an order of magnitude greater only in the improbable case when $d < 0.01$.

The cited data show that when p_{21} is very small (the condition for validity of Eqs. (42)–(44)), laser action can be observed only in systems having a large quantum yield of luminescence ($p_{32} \sim A_{31}$). Substances having low η can show laser action only when p_{21} is large, so as to ensure depletion of level 2 (Eqs. (39)–(40)).

When the solution is pumped by a laser operated in the spiked mode, ($B_{13}(\nu_p)u_p$ at the spike maximum = $10^8 - 10^9 \text{ sec}^{-1}$, spike width $\Delta t \sim 10^{-6}$), then even a minute accumulation of particles in level 2 will hinder the appearance of laser action. It can be accomplished only in especially favorable cases.

Upon substituting (44) into (38), we get an expression for the laser power, with account taken of accumulation of particles in the metastable level:

$$W_g(t) = nh\nu_g \frac{d + \delta - (\delta + e^{-a})(1+d)e^{(d-e^{-a})p_{32}t}}{d - e^{-a}} B_{13}(\nu_p) [u_p(t) - u_p^{\text{thr}}], \quad (48)$$

where

$$u_p^{\text{thr}} = \frac{8\pi h\nu_g^3}{v^3} \frac{\Delta\nu}{\eta} \frac{\kappa_{13}(\nu_l)}{\kappa_{13}(\nu_p)} \times e^{-\Delta\nu_m/2kT} \frac{(d - e^{-a})(\delta + e^{-a}) \left[1 + d \left(1 + \frac{p_{32}}{p_{31} + p_{32}} \right) \right] e^{(d-e^{-a})p_{32}t}}{(\delta + d) - (\delta + e^{-a})(1+d)e^{(d-e^{-a})p_{32}t}} \quad (49)$$

The threshold increases with increasing time, and the laser power declines (for $u_p = \text{const}$). The laser pulse shape will coincide with the pumping pulse shape $u_p(t)$ only when $u_p(t) > u_p^{\text{thr}}$ and $dp_{32}t$ is small.

Let us make some numerical estimates of the threshold at the end of a pumping pulse having $\Delta t \sim 10^{-8} \text{ sec}$. If $\Delta\nu \sim 1000 \text{ cm}^{-1}$, $\kappa_{13}(\nu_l)/\kappa_{13}(\nu_p) \sim 0.01$, $d \sim 1$, $e^{-a} \sim 0.1$, $p_{32} \sim 10^8 \text{ sec}^{-1}$, $p_{31} = p_{32}$, and $\eta \sim 0.01$, then $u_p^{\text{thr}} \sim 20 \text{ erg} \cdot \text{cm}^{-3}$. With these values of the parameters, the density of the exciting radiation (single-pulse

 Table I. Values of $p_{32}t_{\text{lim}}$

d	$p_{32}/B_{13}(\nu_p)u_p$			
	0	0.1	1	10
0.001	46	46	41	27
0.01	29	29	28	14
0.3	4.8	4.7	3.8	—
1	2.0	1.9	1.3	—
2	1.1	1.0	0.46	—
5	0.47	0.40	0.12	—
10	0.24	0.17	0.002	—

ruby laser) is far above the threshold. However, if $\Delta t \sim 10^{-7}$, with the same values of the parameters, then the laser threshold at the end of the lifetime of the pumping pulse is infinite, and laser action is impossible at that time.

Equations (48) and (49) permit us to discuss the relation of u_p^{thr} and W_g to the system parameters. The threshold is related to $\Delta\nu$, $\Delta\nu_m$, and η in the same way as in the previous case where p_{21} is large. Accumulation of particles in the metastable level will lead to an increase in the threshold with increasing d , p_{32} , and Δt .

The discussed extreme cases ($p_{21} \gg p_{32}$ or $|e^{-a} - d|p_{32} \gg p_{21}$, $e^{-a} \ll 1$, $e^{-b} \ll 1$, $c = 0$) permit us to describe the properties of only a fraction of the molecules. In the general case we must use Eqs. (31)–(38).

We can calculate the percent conversion of the energy of the exciting flux into radiation energy generated by the solution by using the expressions for the laser power and the populations of the levels. We only have to take into account the variation of u_p throughout the layer. If the degree of transition of particles into the triplet level is small, while the relative luminescence losses are small (strong pumping), the percent conversion is very high. Values of $\sim 50\%$ have been attained recently. Further optimization of the parameters is possible. Only the Stokes losses cannot be avoided in principle. They amount to $\sim 10\%$ when the excitation is in a long-wavelength absorption band, but can rise as high as 50% when ultraviolet bands are used for pumping.

We shall now proceed to calculate W_g and u_p^{thr} for non-monochromatic excitation of the solution by ordinary pulsed lamps.

Since the probability of $1 \rightarrow 3$ transitions is relatively small for irradiation by lamps, it takes much time to accumulate particles in level 3. Within this time, part of the particles drop to level 2. The populations n_1 , n_2 , and n_3 of the levels are given by Eqs. (31)–(33) as before, but $n_2(0) \neq 0$. In this case, they depend on the pumping density u_p via $n_2(0)$.

The laser power is determined by formulas like (37), taking the non-monochromatic excitation into account. For $c = 0$, it is

$$\frac{W_g}{h\nu_g} = \int [B_{13}(\nu) n_1(t) - B_{31}(\nu_p) n_3(t)] u_p(\nu_p, t) d\nu_p - (p_{31} + p_{32}) n_3(t) - \frac{dn_3}{dt}$$

The threshold value of the frequency-average of the spectral radiation density is determined by the formula

$$\bar{u}_p^{\text{thr}}(\nu_p, t) = \frac{(p_{31} + p_{32}) n_3(t) - (dn_3/dt)}{B_{13}n_1(t) - B_{31}n_3(t)}, \quad (51)$$

where

$$B_{13} = \int B_{13}(\nu_p) d\nu_p, \quad B_{31} = \int B_{31}(\nu_p) d\nu_p.$$

If no particles accumulate in level 2 ($p_{32} \ll p_{21}$), then

$$\frac{W_g}{nh\nu_l} = \frac{B_{13}}{1 - e^{-u}} \left[1 - \delta - \frac{1}{\beta} (\delta + e^{-u}) \right] [u_p(\nu_p, t) - u_p^{\text{thr}}], \quad (52)$$

$$u_g^{\text{thr}} = \frac{8\pi l \nu_l^3}{v^3 \eta} \frac{\delta + e^{-u}}{\beta(1-\delta) - \delta - e^{-u}}, \quad (53)$$

where $\eta = A_{31}/(p_{31} + p_{32})$, and $\beta = B_{13}/B_{31}$ is the ratio of the area of the absorption band and the area of the curve of $W_l(\nu)/\nu^3$ normalized to unity at the peak.

To estimate the threshold, we can assume that $\delta = 0.005$, $e^{-u} \sim 0.03$, and $B_{13}/B_{31} \sim 1.2$. For $\nu_l \sim 18,000 \text{ cm}^{-1}$ and $\eta = 0.75$, this gives $u_p^{\text{thr}} \sim (2-3) \times 10^{-4} \text{ erg} \cdot \text{cm}^{-3} \cdot \text{cm}$. Standard tube-type pulse lamps permit a density of pumping radiation almost an order of magnitude greater. Thus, laser action is quite possible, but only in dyes having high values of η . Dyes are advantageous that have high values of $\nu_{e1} - \nu_g$, i.e., have a large band half-width. The requirements on the loss coefficient are as before.

The laser power at small δ and large u is $B_{13} u_p^{\text{thr}} nh \nu_g (X - 1)$, where X is the ratio of pumping power to threshold. For typical dyes, $B_{13} \sim 0.3 \times 10^{10} \text{ erg}^{-1} \text{cm}^3 \text{sec}^{-1}$. If $X = 5$, $n \sim 10^{16} \text{ cm}^{-3}$, and $h\nu_g \sim 3 \times 10^{-12}$, then $W_g \sim 40 \text{ kW/cm}^3$. The actual powers are determined by the possibility of appearance of pumping within the solution. Under optimal conditions, the output powers should be greater than with a ruby laser.

If part of the molecules accumulate in the metastable level during excitation, then we should use Eq. (50) to calculate the laser power and threshold. Increase in n_2 raises the threshold. However, laser action can occur when p_{32} and d are not too high.

Up to now we have been discussing laser action in dyes in a resonator having selective properties. That is, losses were high at all frequencies except ν_g . If the losses are the same at all frequencies, then the laser frequency corresponds to the peak of the amplification band. We have showed above that the spectral position of this peak depends on the relative population n_3/n (see Fig. 5). Calculation of the amplification spectrum for various values of n_3/n permits us to establish an unequivocal relation between the maximum value of the amplification coefficient and the value of ν_g (see Fig. 8, which is drawn from the data of Fig. 5). Since the maximum amplification coefficient in the laser process equals the loss coefficient, the curves in Fig. 8 essentially reflect the dependence of the laser frequency on the loss coefficient of the resonator. In dye lasers, ν_g can be varied over a wide range without using any selective apparatus, but simply varying the loss coefficient (which is equal to $\rho - (\ln r_1 r_2)/2l$, where ρ is the coefficient of harmful losses). That is, one varies the thickness l of the layer, or the reflection coefficients r_1 and r_2 of the resonator mirrors. Increase in l , r_1 , or r_2 , or decrease in ρ shifts ν_g to shorter frequencies. Increase in the dye concentration gives an analogous effect. In fact, Eqs. (3) and (4) imply that increase in n is accompanied by a proportional increase in the amplification coefficient (the dotted curve in Fig. 8a). If the losses remain constant, then increase in n brings about a decrease in ν_g . Fig. 8b shows the analogous curves for the case in which the amplification spectrum has two maxima. In this case, variation in k_{loss} or n can lead

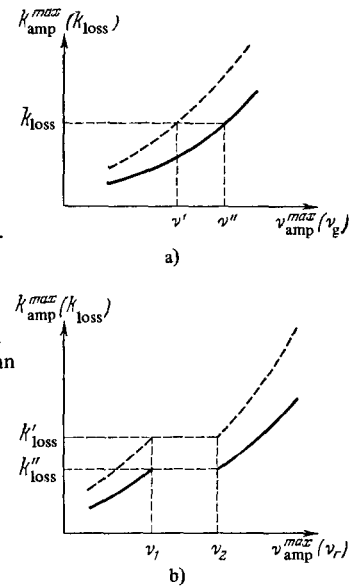


FIG. 8. Relation of the amplification coefficient at the band maximum to $\nu_{\text{amp}}^{\text{max}}$ for two forms of spectra at two concentrations. The dotted curve corresponds to a concentration 1.5 times higher than for the solid curve.

to a jump in the laser frequency from one maximum to the other. Sometimes laser action can occur simultaneously at both frequencies.

The discussed relations are well confirmed by experiment.

One can also calculate the frequency of the generated radiation by using the expressions (40), (49), or (53) for the laser threshold. The frequency manifested in the laser spectrum will correspond to the minimum of the function $u_p^{\text{thr}}(\nu)$ (see Fig. 7).*

4. EXPERIMENTAL DATA

More than ten studies by different authors^[18-23, 38, 39] have been concerned with experimental study of laser action in dye solutions. A number of results have been reported at the All-union Conference on Quantum Electronics (Erevan, 1967), the International Symposium on Non-linear Optics (Erevan, 1967), and the All-union Conference on Luminescence (Leningrad, 1967).^[25, 26, 37, 40-45] In most cases, the dyes were excited either by radiation from a single-pulse ruby laser,^[16-19, 26, 41, 44] or by the second harmonic of a neodymium or ruby laser.^[20-23, 42, 43, 45] Laser action pumped directly by pulsed lamps has been described only in^[20, 23, 24, 26, 40, 48]

A. Laser Action in Dye Solutions Excited by Lasers

Dyes can show laser action in longitudinal and transverse variants under laser excitation (Fig. 9). In the

*The analysis carried out here refers to the case in which laser action is due to the stimulated-emission process. However, another mechanism of laser action in complex molecules is possible in principle. As estimates have shown, conditions can be satisfied in some cases for efficient stimulated Raman scattering when pumped by laser radiation. The smaller the probability of energy exchange between the vibrational degrees of freedom of the molecule is, and the more intense the exciting radiation is, the more favorable the conditions are for appearance of laser action by stimulated Raman scattering. Laser action by stimulated Raman scattering can differ considerably in its properties from the process discussed above. These distinctions can be used in each concrete case to identify the mechanism of laser action, and also to determine certain parameters of the generating molecules.

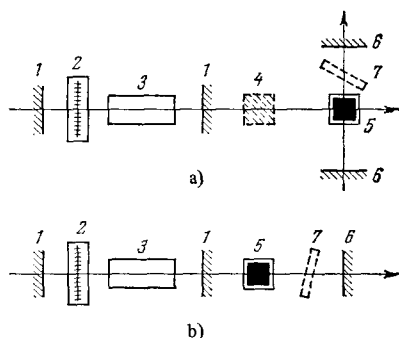


FIG. 9. Longitudinal (a) and transverse (b) variants of excitation of dye solutions. 1 – mirrors; 2 – optical shutter; 3 – ruby (or neodymium glass); 4 – KDP crystal; 5 – cuvette containing the solution; 6 – mirrors; 7 – Fabry-Perot interferometer.

transverse variant, the flux of radiation being generated is perpendicular to the exciting flux. Then the length of the cuvette containing the solution must match the diameter of the pumping light beam. In^[18], for example, a rectangular cuvette of dimensions $1.5 \times 3 \times 3$ cm³ was used, and the length of the generating layer amounted to 1.5 cm. The accuracy of optical working of the cuvette met the usual standards imposed on the working materials of solid-state lasers.

Laser action in dyes is usually observed without focusing the exciting beam on the cuvette. However, it is advantageous in a number of cases to set a cylindrical lens in front of the cuvette. The dye resonator can be formed by external mirrors or by mirrors directly deposited on the faces of the cuvette. The reflectivities of the mirrors in different cases have amounted to from 4 to 99%.

Whenever the second harmonic of a ruby or neodymium laser is used for pumping, a KDP crystal and a light filter to isolate the harmonic from the fundamental are installed between the cuvette and the exciting laser.

The power of the light flux incident on the cuvette in different experiments ranges from tens of kilowatts to a hundred megawatts.

The longitudinal variant of the laser is most efficient when the central mirror (see Fig. 9a) is spectrally selective, transmitting well the radiation of the pumping laser and reflecting the radiation generated by the dye.^[46]

Some dyes can show laser action in Fresnel reflection from the walls of the cuvette (both in the transverse and longitudinal variants).

Laser action has been obtained thus far from more than fifty different dyes. The chemical structures and luminescence-spectroscopic properties of these substances are highly varied. The spectral positions of the absorption and luminescence bands vary for different compounds over the entire visible and near infrared. The half-widths of the bands range from 230 to 1600 Å. The luminescence quantum yields of dyes differ substantially from one another. The best of them are characterized by a yield of $\sim 95\%$. For many others, η is extremely small, less than 0.001%. Table II gives data on the luminescence quantum yield and positions and widths of the absorption and luminescence bands of most of the dyes showing laser action that have been described in the literature. The spectral properties of the

radiation that they generate are also indicated here.

When using the second harmonic of ruby or neodymium lasers for excitation, people have used mainly substances that have relatively high quantum yields of luminescence. When pumped by the fundamental frequency, practically all objects show laser action if they have absorption bands overlapping even slightly the laser line of ruby.^[19] We can consider it now proved that ability to generate radiation is characteristic not of individual types of complex molecules, but is a universal property of all organic dyes. Only individual substances or groups of them can show exceptions. Certain phthalocyanines serve as an example of such an exception. It has not been possible to excite laser action in vanadyl, copper, aluminum bromide, and zinc phthalocyanines, even at pumping powers considerably above 50 MW. This is explained by accumulation of particles in the triplet level. The rate of the process is so great in copper and vanadyl phthalocyanines that it is completely impossible to obtain amplification in the $3 \rightarrow 1$ channel. In particular, this is indicated by the lack of luminescence in this channel at pumping powers that cause a substantial decrease in absorption (i.e., bleaching) of the substance.^[15] In the other phthalocyanines, amplification can be had only for a short interval of time insufficient for laser action ($t_2 < t_0 \sim (3-5) L/v$). At present, the only phthalocyanines showing laser action are free phthalocyanine, magnesium phthalocyanine, and aluminum chloride phthalocyanine.

Laser action in dyes has been obtained in various organic solvents, and also in water and sulfuric acid (see Table II).

We shall discuss briefly the fundamental characteristics of laser action in solutions of organic dyes excited by radiation from solid-state lasers.

The threshold for exciting laser action differs in different dyes. Some dyes, e.g., 3,3'-diethylthiocarbocyanine bromide,^[17] begin to show laser action at powers ~ 100 kW/cm². Others do so at powers exceeding 100 MW/cm². Dyes having a low threshold can show laser action even when pumped with a ruby laser operating in a free-running mode (e.g., a solution of cryptocyanine in certain viscous solvents^[19,20]). Some dyes are excited either by the second harmonic of a neodymium laser ($\lambda_{\text{pum}} = 530$ nm) or by the second harmonic of ruby ($\lambda_{\text{pum}} = 347$ nm). The pumping powers required to excite laser action in the two cases are about the same.^[22] Usually they are 1–2 MW/cm². The differences in the values of $u_{\text{pum}}^{\text{thr}}$ for different dyes agree with the results of calculations by Eqs. (40) and (49). Exact comparison is hindered by lack of information on the values of p_{32} , p_{21} , c , and d .

The value of $u_{\text{p}}^{\text{thr}}$ depends considerably on the concentration of active particles. If we increase n , we observe a decline at first, and then a rapid growth in $u_{\text{p}}^{\text{thr}}$. The latter involves enhanced concentration quenching of luminescence and impaired conditions for the pumping radiation to penetrate the system. If we keep the level of excitation constant, then we can determine the minimum and maximum concentrations beyond which laser action is not seen in the given dye. For the dye brilliant green at a pumping density $u_{\text{p}} \cong 10^4$ erg/cm³, the threshold concentrations amount to 3.6 and 0.2 g/liter, respectively.

Table II. Quantum yield η , half-width of luminescence band $\Delta\lambda_{lum}$, width of laser spectrum $\Delta\lambda_{las}$, λ_{abs}^{max} , λ_{lum}^{max} , λ_{las} , and λ_{pum} (pumping by laser radiation)

Dye	Solvent	η , %	$\Delta\lambda_l$ nm	λ_{abs}^{max} nm	λ_l^{max} nm	λ_g nm	$\Delta\lambda_g$ nm	λ_p nm
Aluminum chloride phthalocyanine ^[16,49]	Ethanol	40	20	690	685	755		694
3,3'-Diethylthiotricarbocyanine bromide ^[17]	Methanol		50		810	835		694
	Acetone					808		
3,3'-Diethylthiotricarbocyanine iodide ^[17]	Methanol					731		694
1,1'-Diethyl- γ -cyano-2,2'-dicarbocyanine tetrafluoborate ^[17]	Methanol					740		694
1,1'-Diethyl- γ -nitro-4,4'-dicarbocyanine tetrafluoborate ^[17]	Methanol					796		694
	Ethanol					805		694
	Acetone					814		
	Dimethylformamide					815		
	Pyridine					821		
	Benzonitrile					822		
1,1'-Diethyl- γ -acetoxy-2,2'-dicarbocyanine tetrafluoborate ^[17]	Methanol					797		694
1,1'-Diethyl-2,2'-dicarbocyanine iodide ^[38]	Glycerol		~50	720	750	750		694
						790		
1,1'-Diethyl-4,4'-carbocyanine iodide (cryptocyanine) ^[38]	Glycerol							694
	Methanol	0.2				740	4	
	Ethanol					to	to	
	Isoamyl alcohol					810	15	
Rhoduline blue 6G ^[19]	Glycerol	0.001	65	640	690	758	25	694
Brilliant green ^[19]	Glycerol	0.5	50	633	666	759	49	694
Echtblau B ^[19]	Glycerol	1.5	50	650	667	753	33	694
Rapid-filter grün ^[19]	Glycerol	0.02	72	693	755	795	9	694
Victoria blue ^[19]	Glycerol	~0.001	85	620	645	809	11	694
Victoria blue R ^[19]	Glycerol	~0.001	75	610	700	814	21	694
Naphthalene green ^[19]	Glycerol	~0.01	90	650	725	756	44	694
Thionin ^[19]	Sulfuric acid	<0.001	160	630		850	21	694
Blatt grün ^[19]	Sulfuric acid	<0.001	130	710		800	17	694
Toluidine blue ^[19]	Sulfuric acid	<0.001	150	680		848	11	694
Methylene green ^[19]	Sulfuric acid	<0.001	140	640		823	20	694
Methylene blue ^[19]	Sulfuric acid	<0.001	140	670		829	7	694
Dicyanine ^[19]	Glycerol	3.77	32	663	690	756	12	694
	Isobutanol		32			765		
	Quinoline					{ 723		
						{ 752		
Magnesium phthalocyanine ^[18]	Quinoline	80	62	668	683	759	1	694
Phthalocyanine ^[18]	Sulfuric acid		110			863	1	694
Methylene blue ^[18]	Sulfuric acid	<0.001	120	670	820	835	4	694
Rhodamine B ^[21-23,26]	Isoamyl alcohol	~90	30	552	585	610	10	347
								530
Rhodamine 3B ^[26,43]	Isoamyl alcohol	78	23	555	580	620	8	347
								530
Rhodamine 6G ^[22,26,43]	Isoamyl alcohol	98	30	530	560	580	15	347
								530
Pyronine G ^[26,43]	Isoamyl alcohol	95	32	535	566	590	12	347
								530
Rapid-filter gelt ^[43]	Isoamyl alcohol	44	30	548	580	620	10	347
								530
Violetrot ^[43]	Isoamyl alcohol	50	23	554	580	620	10	347
								530
3-Aminophthalimide ^[43]	Isoamyl alcohol	60	80	370	490	500	7	347
Lucegenin ^[43]	Water + H ₂ SO ₄	~40	90	440	512	600	12	347
Fluorescein ^[21,22]	Glycerol/NaOH	90	50	490	530	550	9	347
Pina(orthol) ^[43]	Ethanol					565	8	347
Trypaflavin ^[22,43]	Ethanol					505	11	347
Lachs ^[43]	Glycerol					540	5	347
Sodium salt of 3-ethylaminopyrene-5, 8, 10-trisulfonic acid ^[21]	Water					441		347
2, 4, 6-Triphenylpyryl fluoborate ^[21]	Methanol					485		347
Uranine ^[43,49]	Ethanol					560		347
Eosine ^[43]	Ethanol					600		347
Dibromofluorescein ^[43]	Glycerol					568		347
Monobromofluorescein ^[43]	Glycerol					560		347
Isoquinoline red ^[43]	Water					620		347
3,3'-Diethylthiotricarbocyanine iodide ^[49,52]	Methanol			757	798	796		694
	Acetone				801	801.5		694
	Ethanol			762		803		694
	1-Propanol			764		807		694
	Ethylene glycol			766		808		694

Table II. (Continued)

Dye	Solvent	$\eta, \%$	$\Delta\lambda_1$ nm	$\lambda_{\text{abs}}^{\text{max}}$ nm	λ_1^{max} nm	λ_g nm	$\Delta\lambda_g$ nm	λ_p nm
	Dimethylformamide			766		808		694
	Glycerol			775		809		694
	Butanol			766		809		694
	Dimethylsulfoxide			772		816		694
Fluorescein Na ^[49]	Water				527			347
	Ethanol				527			347
Acridone ^[49]	Ethanol				437			347
Acridine red ^[49]	Ethanol				580			347

As the distance L between the mirrors is increased, u_p^{thr} increases. Each dye is characterized by its own critical resonator length, such that laser action ceases when it is exceeded. For example, laser action ceases in a solution of dicyanine in glycerol in a cuvette of thickness 1.5 cm even when $L \sim 6$ cm. For a solution of brilliant green in glycerol, the critical length is 50 cm.

The impairment of conditions for laser action observed with increasing L is mainly due to increase in the time t_0 required for laser action to set in. The value of t_0 declines with increase in the excess of the initial amplification coefficient over the loss coefficient. It also declines with decreasing ratio of the length L of the resonator to the thickness l of the layer of working substance. If t_0 is longer than the pumping time (~ 20 – 30 nsec), laser action does not set in. In the discussed case of short-acting pumping, we should emphasize in this regard that the threshold amplification coefficient required for development of laser action when the distances L are long can considerably exceed the loss coefficient of the resonator.

In agreement with the results of theoretical analysis, the laser power of dyes depends on the quantum yield of luminescence, the shapes and mutual positions of the absorption and luminescence bands, and also on the position of the frequency of the exciting light relative to ν_{el} . When excited by the fundamental frequency of a ruby laser, the dyes of the polymethine series work most effectively.^[17, 18, 41, 44, 46] In these dyes, the conversion of excitation energy into laser energy amounts to 20–35%. In a longitudinal excitation system using a selective mirror, the efficiency rises as high as 50%.^[46] This is considerably higher than the limiting value of the corresponding conversion for a ruby laser.^[14]

Among the dyes showing laser action in the visible, the most efficient are pyronine G, rhodamine 6G, trypanflavin, 3-aminophthalimide, and some others. In these cases the conversion is $\sim 15\%$.^[22, 26]

In many dyes, the energy of the generated radiation is considerably reduced by absorption in the channels $3 \rightarrow 5$ and $2 \rightarrow 4$. However at high excitation intensities, the value of u_g may attain values that bleach these channels. Then increase in u_g will be accompanied by decline in the losses and a consequent increase in W_g at a rate faster than linear. This probably explains the form of relation of W_g to u_p shown in Fig. 10.^[17]

A characteristic feature of laser action in dye solutions is the relatively small angular divergence of the beam. Sometimes the angle of divergence amounts to 5×10^{-4} radians, i.e., considerably smaller than in a ruby laser. Therefore, in some solutions the intensity of the generated beam is 2–3 times higher than in the

ruby laser used for pumping. The small angle of divergence involves the high optical homogeneity of the liquid.

The time course of laser action duplicates the shape of the exciting pulse in solutions when $u_p \gg u_p^{\text{thr}}$. With less intense pumping, the duration of laser action is somewhat shortened (5–10 nsec).^[16, 22]

The laser bands of different compounds differ considerably. Their spectral widths in resonators having a non-selective loss distribution varies from 10 to 5000 Å.^[18–20] The large width of the spectrum primarily involves the non-steady-state nature of the process. The populations of the levels oscillate somewhat during the time of laser action. Owing to the high transition probabilities, this corresponds to considerable oscillations of the amplification coefficient about the value defined by the losses of the resonator. This allows the condition for laser action to be satisfied for a wide range of frequencies about the peak of the amplification band. At the same time, the oscillations in the intensity of the generated flux arising from the pulsations in the populations are relatively small. This situation is the opposite of that in the ruby laser, where slight oscillations in the amplification are accompanied by sharp pulsations in the intensity of the emerging flux.

Broadening of the spectrum of the generated radiation can also involve changes in time in the losses of the resonator owing to heating of the solution.

The laser spectra of most dyes show a series of sharp equidistant lines (Fig. 11). Their spacings depend on the properties of the resonator.^[19, 20, 25, 26, 41, 44] These lines are due to the interference conditions in the complex resonator, which includes a large number of reflecting surfaces (four surfaces of the cuvette and four surfaces of the external mirrors). If one eliminates the effect of the interference conditions (in a resonator having feedback via scattering), the structure of the spectra vanishes.^[45]

In line with the theoretical conclusions of the previous section, decrease in the concentration, in the reflectivi-

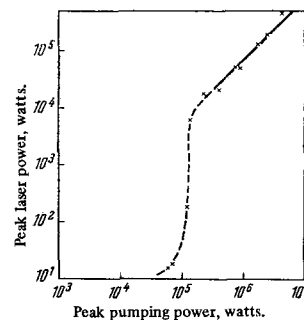


FIG. 10. Relation of the peak emission power from 3,3'-diethylthiobarbituric acid bromide to the peak pumping power.^[17]

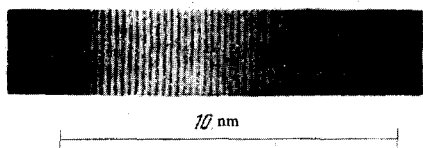


FIG. 11. Structure in the laser spectrum of 3-aminophthalimide ($\lambda_g = 500$ nm).^[43]

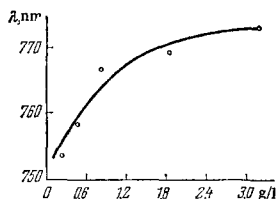


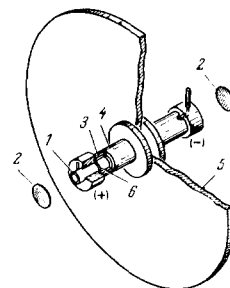
FIG. 12. Concentration-dependence of the laser wavelength of brilliant green.^[40]

ties of the mirrors, or in the length of the cuvette, as well as increase in the resonator length while keeping the cuvette length constant,* will increase the frequency of the generated light.^[18-20,25,38-41] Variation of the cited parameters permits one to vary the position of the laser band over a range of ~ 150 Å. As an example, Fig. 12 gives an experimental relation of λ_g to the dye concentration. In some cases (dicyanine, phthalocyanine, cryptocyanine, etc.), one can observe simultaneous generation at two frequencies corresponding to different maxima in the amplification spectrum.^[18,20,41] At first, if one reduces the concentration and the reflectivities of the mirrors, only one line is generated, corresponding to the long-wavelength luminescence peak. At certain concentrations (or with certain mirrors), laser action occurs simultaneously at two frequencies corresponding to both peaks. Finally, only the short-wavelength component appears at high concentrations. The experimental data fully agree with the theory.

The large width of the laser spectra can be used to build broad-band amplifiers.^[50] On the other hand, if one has to obtain narrow bands of $\sim 1-2$ Å width, then, as is shown in^[25], one must introduce a frequency selector into the resonator in the form of an inclined Fabry-Perot interferometer having a short spacing (~ 20 μ).^{*} Introducing the interferometer does not diminish the output power substantially. Inclining the interferometer permits one smoothly to tune the frequency of the generated radiation over a range of ~ 100 Å.^[25] Using an interferometer in conjunction with different dyes makes it possible to obtain narrow, intense laser lines at any given frequencies in the visible and near infrared.^[40,43] One can get even narrower laser lines (~ 0.6 Å) from dyes by using a resonator containing a plane diffraction grating.^[51]

The polarization properties of the generated radiation are of interest. Since the pumping light (ruby radiation or its harmonics) is usually linearly polarized, this gives rise to stimulated anisotropy of absorption and

FIG. 13. Design of a laser head containing a flash lamp. 1 – cuvette containing the dye; 2 – mirrors; 3 – discharge region of the flash lamp; 4 – contact; 5 – condenser; 6 – electrode.^[24]



amplification in the excited region of the solution. Consequently, the conditions for laser action are satisfied for only one polarization direction, and the radiation generated by the dye proves to be linearly polarized. The degree of polarization is usually close to unity.* As in the case of luminescence, the degree of polarization of the generated radiation is positive when pumped in the long-wavelength absorption band, and negative when pumped in the ultraviolet bands. For example, in a solution of rhodamine 6G in ethanol, the generated radiation has a degree of polarization $P = -0.9$ when excited by the second harmonic of a ruby laser ($\lambda_p = 347$ nm). When excited analogously at a wavelength $\lambda_p = 530$ nm, $P = +1$.^[47]

B. Laser Action in Dyes Excited by Pulsed Lamps

Laser action of this type has been obtained independently in^[23,24]. In^[24], they developed a pulsed lamp of a special design. Figure 13 shows the construction of the laser head using this lamp. The cuvette (a quartz tube with polished ends) was placed in a quartz cylinder. The space between them was filled with an air-argon mixture, and served as the discharge region of the lamp. Tungsten electrodes were placed at the edges of the gap. The disk of the pulse capacitor was coaxial with the cuvette. This design made it possible to reduce the inductance of the discharge circuit, and to shorten the rise time of the flash pulse to 300 nsec. Laser action was obtained in solutions of three dyes in this head (Table III). The electrical energy for threshold pumping amounted to 15–30 joules.

Standard pulse lamps of the type IFP-1200 were used in^[20,23,26,40] to obtain laser action. The emission time for two lamps connected in series was ~ 60 μ sec, the capacitance of the supply capacitor being ~ 100 μ F. The dye solution was poured into a cylindrical cuvette made of molybdenum or quartz glass. The cuvette length was varied from 20 to 100 mm, and the diameter from 3 to 5 mm. The resonator was made of two plane mirrors of reflectivities of 65–99.5%.

With this method of excitation, laser action was obtained from six different compounds (see Table III). The most efficient were rhodamine B, rhodamine 6G, and pyronine G. Isoamyl alcohol was used as the solvent. The concentration of active particles was varied over the range $10^{16}-10^{17}$ cm^{-3} .

The minimum electrical threshold for laser action (250 Joules) was shown by a solution of rhodamine 6G in a quartz cuvette 20 mm long. The threshold rose

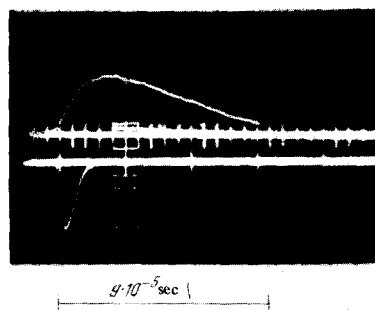
*This happens even when the degree of polarization of the luminescence of the solution is extremely small.

*Increase in the length of the resonator while keeping the cuvette length constant increases the coefficient of harmful losses, and thus affects the position of the laser spectrum.

*Using interferometers as the reflectors of the resonator apparently proves even more effective for this purpose.

Table III. Dyes used in lasers excited by pulsed lamps

Dye	Solvent	λ_g , nm	$\Delta\lambda_g$, nm
Rhodamine B ^[23,26]	Isoamyl alcohol	610	12
Rhodamine 3B ^[26]	Isoamyl alcohol	610	8
Rhodamine 6G ^[24,26,48]	Isoamyl alcohol, water	580	15
Pyronine G ^[26]	Isoamyl alcohol	585	13
Rapid-filter gelt ^[26]	Isoamyl alcohol	610	5
Violetrot ^[26]	Isoamyl alcohol	610	5
Acridine red ^[24,48]	Ethanol	610	
Fluorescein ^[24]	Ethanol	550	
	Water	550	
Fluorescein Na ^[24,43]	Ethanol, water	550	
	Heavy water	550	


FIG. 14. Oscillograms of pumping (above) and laser action (below) in rhodamine 6G.^[26]

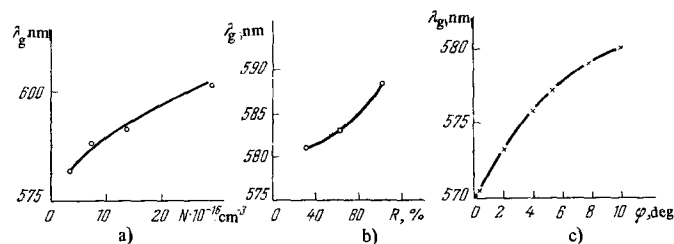
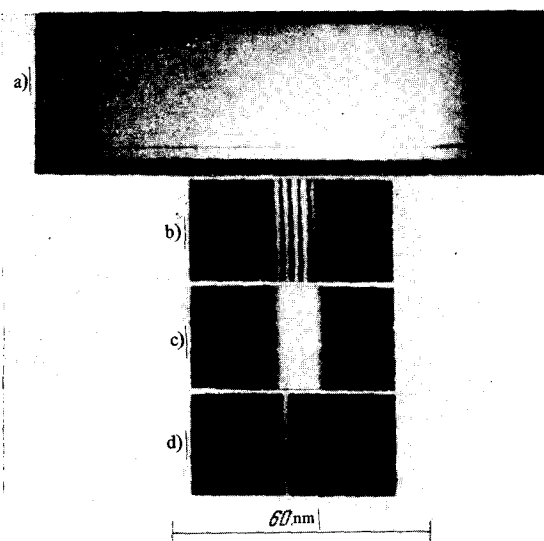
somewhat with increasing cuvette length, and amounted to 280 Joules for $l = 100$ mm. The rise in the threshold with increasing length of the active layer involves an increase in the losses at a rate faster than linear. The latter is due to thermal inhomogeneity of the refractive index of the solution. The relatively high value of the threshold pumping energy was due in this case to the long duration of the flash applied.

Figure 14 shows oscillograms of the time course of laser action and pumping for a cuvette 10 cm long. The lasing is free from spikes in all the dyes. As was mentioned in the previous section, this involves the extremely high cross-section for limiting amplification and the low population of the labile level during the lasing process ($\sim 10^{14}$ particles/cm³).*

We see from Fig. 14 that the laser process begins almost simultaneously with the pumping pulse. This indicates the low value of u_p^{thr} . However, laser action ceases even before the peak pumping intensity is reached. This feature involves thermal distortions of the resonator in the pumping process. They are considerably worse in liquid media than in solids. The duration of laser action is in the range 5–15 μsec for a cuvette length of 10 cm. The losses due to thermal distortions decrease with decreasing l . Hence the duration of laser action increases, and approaches the flash duration. For certain substances, the duration of laser action may be limited by accumulation of particles in the metastable level.

The emission energy generated by a solution of rhodamine 6G (of volume ~ 0.6 cm³) amounts to 0.03–0.07 Joule. This corresponds to a power at the

*For this reason, lasers based on dye solutions are not suitable for use in a system of pulsed Q value Q-switched lasers.


FIG. 15. Relation of the laser wavelength to the particle concentration (a), the reflectivity of the mirrors (b), and the rotation angle of the interferometer (c) for rhodamine 6G.^[26]

FIG. 16. Spectra of luminescence (a) and laser action (b – d) in rhodamine 6G excited by pulsed lamps. b – c) Without an interferometer, in different resonators; d) with a Fabry-Perot interferometer inside the resonator.^[26]

peak of the laser pulse of about 7–10 kW.

The angular divergence of the beam of the discussed lasers does not exceed 4×10^{-3} radians.

The laser spectrum of dyes pumped by pulsed lamps is analogous to that obtained with laser excitation. It also shifts as a function of the reflectivities of the mirrors and the concentration (Fig. 15). If the reflective coatings of the external mirrors are deposited on plan-parallel substrates, the spectrum shows a distinct line structure (Fig. 16b). Introducing an inclined Fabry-Perot interferometer of small spacing into the resonator narrows the laser spectrum to 1–2 Å, as in the previous case (Fig. 16d). Tipping the interferometer permits to regulate smoothly the value of ν_g (Fig. 15c).

All taken together, use of an interferometer and substitution of different working substances make it possible to get laser lines of width 1–2 Å at any wavelength from 550 to 650 nm.

CONCLUSION

Thus, the theoretical and experimental data cur-existing show that lasers based on solutions of organic dyes have an entire set of new, interesting properties and are an especial class of laser systems. They used either as efficient frequency-converters for

tion from other lasers, or as independent generators.

The radiation frequencies of ruby and neodymium lasers have already been converted with dyes at practically all frequencies of the visible and near infrared. Here one can attain very high energy conversions. The wide choice and smooth tuning of coherent-radiation frequencies characteristic of dye lasers open up new possibilities in studying non-linear interaction between light and matter. The recently-observed doubling and shifting of laser frequencies in dyes* make it possible to extend substantially the coherent-radiation spectrum, and to possess a selection of tunable frequencies in the ultraviolet. In the longitudinal system of exciting solutions, one can easily get combined fluxes of ruby and dye laser radiation at the output. This is very convenient for studying two-photon absorption spectra.

Use of dyes as independent light generators shows great promise. The fact that one can get any tunable frequency of coherent radiation within the visible makes them the perfect instrument for spectral-luminescence studies, and permits one to use them in color holography, photochemistry, etc. We must consider a useful property of these lasers to be their lag-free operation and freedom from pulsations of emission. The studies that have been conducted show that dye lasers can operate at a high frequency of flash repetition, the heat of the active material being removed by flow of the solution through the cuvette.

The large amplification coefficients and modest threshold pumping powers make it possible to use dyes in developing wide-band light amplifiers and compact lasers.

It is essential to note that the number of dyes that can be used in lasers is practically unlimited, while their cost is small.

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