

Bleaching wave lasers utilizing complex organic compounds

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1. INTRODUCTION

Tunable lasers utilizing solutions of complex organic compounds (dyes) are well known as practical sources of visible radiation.^{1,2} The distinction between these lasers and other types is that the active particles are organic molecules, i.e., compounds consisting mainly of carbon and hydrogen atoms. The organic molecules employed for this purpose usually emit a strong fluorescence, i.e., they are capable of absorbing light in one spectral range and reemitting it rapidly in another range at longer wavelengths. The chemical structure of these molecules usually containing tens of atoms, such as coumarin 6 (C6) (Fig. 1), consists of chains of alternate single and double (i.e., unsaturated) bonds. The chains are important because it is the length of the chains, i.e., the number of alternate bonds, that determines largely the color of a given organic compound and the range of its fluorescence. This is due to the fact that electrons and unsaturated bonds can be regarded approximately as moving freely along chains of single and double bonds throughout the molecule. These are known as the π electrons and they are easiest to excite and it is these electrons that determine the color of organic compounds. The longer the chains the longer the absorption and fluorescence wavelength. A typical energy level scheme of such molecules is shown in Fig. 2: it consists of singlet and triplet levels with vibrational and rotational sublevels forming continuous bands in the spectra.

If a molecule of this kind is excited with light of test photon energy higher than the energy of the S_1-S_3 transition, the absorption of a photon is followed by nonradiative relaxation of the molecule in a time of the order of 10^{-12} s to the lower excited level S_3 , and this is followed by a radiative transition from S_3 to the ground state in a time of the order of 10^{-9} s. The cross section of such a transition is of the order of 10^{-16} cm². Such allowed transitions are used in lasers. The lower active level is depopulated in picoseconds and lasing occurs effectively in a four-level scheme.

Dye lasers have been under development since 1966 and about 1000 different substances are now available, which makes dye lasers the most convenient sources of tunable ra-

diation covering the wavelength range 308–1850 nm with efficiencies from 10 to 30% when short-wavelength optical pumping is used, and in some spectral regions the efficiency can be as high as 40–70% with a specific output energy of 1–10 J/cm³. These tunable lasers are used in the cw and pulsed modifications, including those generating the shortest available (femtosecond) pulses providing a convenient means for the investigation of both slow and fast processes. The average output powers of flashlamp-pumped pulse-periodic lasers can reach several hundreds of watts³ and energies in excess of 100 J can be obtained for single pulses.⁶ There is a strong demand for high-power tunable lasers (with an average output power in excess of 1 kW) also in industry for the purpose of isotope separation,^{7,8} processing of materials, and laser chemistry.⁸

However, in recent years the rate of development of these lasers and of improvement in their characteristics (increase in the output energy, efficiency, and directionality) has slowed down greatly because of a number of serious difficulties relating primarily to changes in the properties of the amplifying medium under the influence of high-intensity pump radiation. The problem of improvement and development of dye lasers is being tackled by many specialists, because tunable lasers emitting visible light are having a major influence on the development of practically all optical branches of science and technology and improvements in these lasers open up new avenues of important applications.

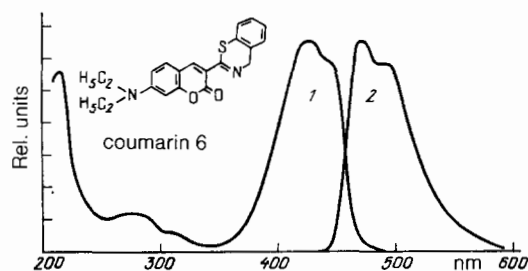


FIG. 1. Absorption (1) and fluorescence (2) spectra of a solution of coumarin 6 (C6) in diethyl ether.

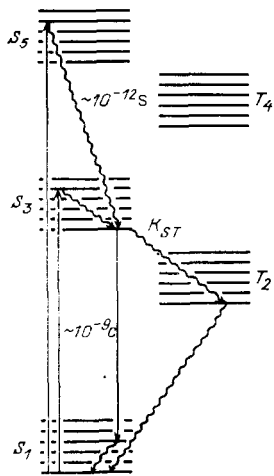


FIG. 2. Energy level scheme of complex organic molecules. Here, S_i represents systems of singlet levels, T_i are systems of triplet levels, k_{ST} is the rate constant of the singlet-triplet conversion. The wavy lines represent nonradiative transitions.

We shall consider the possibility and ways of constructing high-power lasers emitting visible light and utilizing solutions of complex organic compounds.

2. PROBLEMS IN THE DEVELOPMENT OF LASERS UTILIZING COMPLEX ORGANIC COMPOUNDS

In the development of dye lasers it is necessary to carry out a number of important tasks,^{1,2} which can be formulated as follows:

- 1) increase the lasing efficiency of active media in the course of prolonged noncoherent pumping right up to rates used in short-duration laser pumping,
- 2) increase the volume of the pumped active medium and extend the spectral range of excitation so as to utilize more rationally the light from the existing high-power pump sources,
- 3) reduce angular divergence of the laser radiation; 4) develop a method for fast angular and spectral tuning of laser radiation.

The importance and complexity of each of these tasks are well known.^{1,2} The main difficulty is that all these tasks are mutually related, so that a solution found in one case is often at the expense of deterioration in some other respect. For example, in attempts to increase the efficiency it is necessary to eliminate or greatly reduce the influence of thermooptic distortions of the active medium, distortions due to accidental acoustic waves, triplet losses (due to the absorption of laser radiation by long-lived triplet molecules formed during the process of lasing), and optical instability of laser dyes. Thermooptic distortions can be reduced by employing solutions with a low thermal coefficient of the refractive index and by circulating the active medium through a laser cell at a velocity of about 10 m/s. An increase in the circulation velocity improves the laser characteristics considerably, but it is not possible to increase this velocity too much because cavitation appears in solutions² and this reduces the Q factor of the laser and can result in mechanical damage to the system.

The interrelationships between the various loss mechanisms means that the efficiency of noncoherently pumped lasers is much inferior to the efficiency achieved as a result of short-duration laser pumping. Laser pumping (by pulses of $\sim 0.1 \mu\text{s}$ duration) makes it possible to reach frequently las-

ing efficiencies in the range 40–60%, whereas in the case of noncoherent pumping (50–500 μs) the efficiency normally does not exceed 1%. The divergence of laser radiation during prolonged pumping can reach 10^{-2} – 10^{-1} . The growth of the losses with time means that a large group of dyes, working effectively in the case of pumping with short laser pulses, cannot operate during prolonged excitation.

The current status of dye lasers is as follows: effective active media are available and these are capable of operating at high efficiencies for $\sim 1 \mu\text{s}$, but there are no simple (non-laser) pump sources generating pulses of such duration, although there are inexpensive high-energy noncoherent pump sources but these are characterized by an emission time of $\sim 100 \mu\text{s}$ which is too long for efficient lasing of complex molecules in solutions. It is this serious mismatch of the time intervals for efficient operation of active media and pump sources that is the main difficulty hindering the development of dye lasers.

What is the solution to this problem?

If we increase the efficiency and directionality of dye laser radiation by means other than reducing the duration of operation of pump sources (and usually lowering the input energy), we can still shorten the time during which an active medium is exposed to pump radiation. This method has been used successfully in cw dye lasers in which a solution is circulated at a velocity of $\sim 10 \text{ m/s}$, so that the active medium spends only microseconds in an excitation zone of width $\sim 100 \mu\text{m}$, which makes it possible to achieve efficiencies of $\sim 30\%$ in the case of cw operation.² However, the mechanical replacement of an active medium in $\sim 1 \mu\text{s}$ in a cell of $\sim 1 \text{ cm}$ diameter requires velocities of 10^6 – 10^7 cm/s , which is one or two orders of magnitude higher than the velocity of sound in solutions. Such velocities are unrealistic in the case of liquid systems and they have been considered only in the design of future vapor and aerosol dye lasers.⁹

The problem in circulating a medium is related also to the problem of rapid removal of heat, which interferes with lasing, and is the key problem in all high-power high-energy lasers.^{10,11} This has been tackled on many occasions and the investigators have reached a clear and fairly firm conclusion that an output power of the order of 1 kW can be achieved, irrespective of the pumping method, only by the use of gaseous active media because it is possible to circulate such media rapidly.

However, the results reported below demonstrate that high rates of replacement of an active medium needed in high-power high-energy laser systems can be achieved also using dye solutions, which modifies the current view that condensed media cannot be used in lasers with a high average output power.

3. FEASIBILITY OF CONSTRUCTION OF HIGH-ENERGY LASERS UTILIZING SOLUTIONS OF COMPLEX ORGANIC COMPOUNDS AND OPERATING IN THE BLEACHING WAVE REGIME. CHARACTERISTICS OF BLEACHING WAVE LASERS

The required rates of replacement of an active medium can be achieved and the problems discussed above can be solved by a new approach to dye lasers which involves utilization of a bleaching wave.¹²

In contrast to conventional lasers, bleaching wave (BW) lasers utilize optically thin layers of the active medi-

um in which dye molecules are excited optically and participate in lasing, and after several conventional absorption-emission cycles they experience photochemical or photo-physical changes (for example, they react chemically or exhibit photoisomerization) and become completely bleached, opening up deeper layers of active molecules to the action of pump photons. The concept of a BW laser is thus based on the feasibility of altering the absorption spectra of complex organic dye (molecules) in solutions (as a result of chemical reactions or changes in the structure), so that these spectra shift by tens of nanometers in the ultraviolet direction. Molecules then lose their color (they become bleached) and become invisible to the incident pump radiation. Consequently, the excitation (and lasing) zone penetrates to a new layer of the active substance which in turn becomes bleached, i.e., lasing occurs at the front of a bleaching wave where the excited substance is replaced rapidly in the course of operation of the laser. The motion of the bleaching front then resembles the melting of snow by strong sunshine.

Ways of realizing the concept of BW lasers will be discussed later and at this stage we shall simply consider some features of the proposed lasing regime. In rough estimates it is permissible to use a simple mathematical model in which a semiinfinite active medium has a plane boundary and is characterized by a concentration of active molecules N_0 ; it is subjected to a directional pump light flux of intensity I_0 and lasing takes place in a transverse direction. Conditions favorable for photochemical reactions of bleaching of excited singlet molecules (or triplet molecules immediately after their formation) are established in the active medium. We shall assume that in the case of excited singlet molecules the probability to undergo a photochemical change during a radiative lifetime τ and to become completely bleached (to pump radiation) is $1 - \eta$, where η is the quantum efficiency of fluorescence or the probability that during this time a spontaneous photon is emitted and a molecule returns to the ground state. A calculation of the total number of bleached particles then gives the velocity of a bleaching wave in the absence of lasing¹³:

$$v_c = \frac{(1-\eta)I_0}{N_0}. \quad (1)$$

We can show that this formula is suitable for the description of the wave velocity irrespective of the mechanism responsible for the bleaching of singlet or triplet molecules if the factor occurring in this formula $(1 - \eta)$ is replaced with the probability of bleaching of a particle, typical of a given mechanism, due to absorption of one pump photon. For example, when molecules in a medium in which the special conditions for rapid bleaching have not yet been established are characterized by the fluorescence quantum efficiency η_0 and the selected mechanism of bleaching of quantum molecules reduces their fluorescence quantum efficiency to η , the probability of bleaching per one photon is $(\eta_0 - \eta)/\eta_0$ and in Eq. (1)—as well as in all the subsequent expressions—we can replace η with η/η_0 .

If we establish conditions under which the probability of bleaching of excited molecules of a dye in a solution is 10^{-1} instead of the usual value 10^{-4} – 10^{-6} , i.e., if we ensure such conditions that ten pump photons are needed to bleach one molecule, then, for the usual concentration of the particles $N_0 = 10^{16}$ – 10^{17} cm⁻³ and the pumping rate $I_0 = 10^{23}$

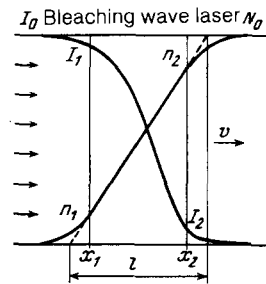


FIG. 3. Profile of a bleaching wave showing a lasing region $x_2 - x_1$.

cm⁻²s⁻¹ we can expect velocities of the order of 10^5 – 10^6 cm/s in solutions.

When lasing takes place, the wave velocity decreases because of a reduction in the concentration of excited particles in the solution. The threshold concentration of excited particles n_{th}^* for lasing is determined by the losses in the mirrors, i.e.,

$$n_{th}^* = -\frac{\ln(R_1 R_2)}{2\sigma_a L}, \quad (2)$$

where R_1 and R_2 are the reflection coefficients of the mirrors; L is the length of the active medium; σ_a is the amplification cross section of the stimulated radiation emitted by excited particles. The velocity of the wave in the presence of a lasing region $x_1 - x_2 \approx l$ (Fig. 3) is determined by the fact that the concentration of excited particles in the lasing zone capable of participating in the bleaching reaction is maintained at the threshold value. We then have

$$v = \frac{n_{th}^* k M l}{N_0}, \quad (3)$$

$$l = \frac{1}{\sigma_0 N_0} \left[1 + 2 \ln \frac{(1-\eta) \sigma_0 N_0 I_0}{n_{th}^* k M} \right], \quad (4)$$

where k is the rate constant of the bleaching reaction; M is the concentration of the particles which react and cause bleaching; σ_0 is the pump absorption cross section. The quantity l (Fig. 3) represents the width of the bleaching front. At the threshold (needed for lasing in the bleaching wave) pump intensity

$$I_0^{th} = \frac{(\tau^{-1} + kM) 4 n_{th}^*}{\sigma_0 (N_0 - \eta n_{th}^*)} \quad (5)$$

Eq. (3) reduces to Eq. (1).

The time taken to establish a steady wave profile after activation of a pump source is governed by the number of particles which must be bleached to form a bleaching front, i.e., the time t_{st} lies within the limits

$$\frac{l}{2v_c} < t_{st} \leq \frac{l}{2v}, \quad (6)$$

since lasing appears after some delay relative to the moment at which pumping is started.

Slowing down of the bleaching wave as a result of lasing is due to a reduction in the concentration of excited particles. The efficiency of conversion of the pump photons into laser radiation is given by the expression

$$\text{conversion efficiency} = \frac{v_c - v}{v_c} \quad (7)$$

and may reach 90%.

Estimates indicate that among the characteristic and most important features of BW lasers are those listed below.

1) The replacement of the working layer of the active medium in a BW laser can occur at a high velocity ($> 10^5$ cm/s), so that the lasing efficiency should be comparable with that achieved as a result of pumping with laser radiation (40–60%). The rapid replacement of the working layer in a BW laser means that dye lasers are not subject to constraints relating to the steepness of the edges and duration of the pump pulses, so that it is possible to excite BW lasers using the existing high-power high-energy light sources emitting pulses of $\sim 100 \mu\text{s}$ duration.

2) The transverse dimensions of the active medium are governed by the wave velocity and the duration of operation of the source, so that in principle these dimensions can be tens of centimeters. According to the calculations reported in Ref. 14, the lengths of active media can reach several meters. When working layers are replaced at velocities higher than that of sound, lasing occurs effectively in a medium at rest so that the output radiation is highly directional.

3) The motion of the lasing zone in the active medium can be utilized¹⁵ for rapid angular and spectral tuning of laser radiation at rates higher than in mechanical systems.

4) When several dyes with shifted absorption bands are positioned in series (layer by layer) in a BW laser, it should be possible to utilize up to 40–50% of the pump radiation in the excitation of lasing.

It thus follows that using the currently available pump sources it should be possible to increase the efficiency of conversion of the stored energy into light (values in excess of 50% are reported in Refs. 31 and 32), so that pulse-periodic BW lasers with an overall efficiency of 15–30% become feasible and the output energy would then be limited by the capabilities of the available pump sources.

4. ACTIVE MEDIA FOR BLEACHING WAVE LASERS

The active media for BW lasers must be molecules which after several absorption--emission cycles undergo a photochemical transformation in an excited state and become completely bleached within the pump band. We shall consider several media that do have such properties.¹²

Bleaching or discoloration are the properties shared normally by all dyes. Changes in the color of organic compounds are observed by us regularly in the surrounding plant kingdom and the process of bleaching of an organic compound such as rhodopsin can be seen with the naked eye and is in fact the basis of vision itself. Plants utilize bleaching of some of the organic molecules (phytochromes) to control their growth.¹⁶ Shifts of the spectra of organic substances as a result of photophysical or photochemical changes of their structure are utilized to burn dips ("holes") in the absorption profiles of complex organic molecules at low temperatures in solid matrices^{17,18} and in the development of new photosensitive materials of the Reoksan type.¹⁹

The nature of photochemical transformations in organic molecules (and particularly in the case of laser-active compounds) has not yet been investigated sufficiently thoroughly. The attention has been concentrated so far on the selection of the compounds with the highest optical stability, including those used in dye lasers (see, for example, Refs. 20–22), whereas bleaching has been regarded as an undesirable property of these substances.

Terenin²³ demonstrated that photochemical transformations of the majority of dye molecules occur in a long-

TABLE I. Values of $k\tau$ (10^{-21} cm^3) for bleaching reactions in ether.

Reagent	Substance		
	DPB	ST	DSB
C6	7.3 ± 0.7	0.43	6.3
C2	—	3.3	—
C7	5.0	1.0	12.5
C30	1.5	0.24	—
C47	—	6.7 ± 0.6	—
C102	3.3	1.24 ± 0.4	—
C120	—	1.6	—
C153	—	0.025	—
C307	—	0.032	—
C314	32 ± 2.5	0.7	25
Imitrine 21	0.9	0.012	—
Oxazine 17	0.12	0.05	8.8
Pyrylium salt	—	1.5	—

lived triplet state (Fig. 2) which some of them reach from an excited singlet level. However, in the case of BW lasers, where bleaching of excited molecules should occur in a time of the order of 10^{-8} s, we can utilize also direct reactions of singlet excited molecules with molecules of a reagent. We shall consider several such bleaching reactions in the case of laser dyes for the visible range, i.e., dyes which are of practical interest in BW lasers.

It has been suggested that the reactions used in BW lasers should be those between excited molecules of dyes with different chemical structures: coumarins, imitrines, and other compounds listed in Table I, on the one hand, and unexcited molecules of diphenylpolyene reagents, such as stilbene (ST), 1,4-diphenylbutadiene (DPB), and 1,4-disubstituted benzene (DSB), on the other.

The bleaching reactions have been investigated in solutions and the solvent has been usually diethyl ether, in which the saturation values of the concentrations of the reagents (M_0) are high at room temperature: $M_0(\text{DPB}) = 5 \times 10^{19} \text{ cm}^{-3}$, $M_0(\text{ST}) = 2 \times 10^{20} \text{ cm}^{-3}$, and $M_0(\text{DSB}) = 1.6 \times 10^{18} \text{ cm}^{-3}$.

Mixtures of dyes and reagents were prepared in darkness and placed in quartz cells of the type used in spectroscopy, so that in the course of the experiments it was possible to monitor at regular intervals the changes in the optical density of solutions under the influence of illumination. The light source is either scattered daylight transmitted by a room window or light from an incandescent lamp. The exposure time necessary for significant bleaching of a solution is found by trial and error.

Figures 4 and 5 demonstrate the changes in the optical density as a result of bleaching reactions. Optical filters have been used to establish that the bleaching rate (rate of reduction of the optical density of a solution in an absorption band of a dye) is a linear function of the intensity of the light flux reaching the cell. Bleaching reactions do not occur in darkness.

Bleaching of coumarin 6 (C6) is demonstrated in Fig. 6 for different concentrations of DPB. Pumping out of oxygen (which can quench the triplet states) from a solution does not alter the bleaching reaction rate, indicating that short-lived singlet molecules participate in the reaction. For any initial dye concentration (and even when the initial saturated solution of a diphenylpolyene contains a certain number of undissolved dye crystals) exposure to light at room

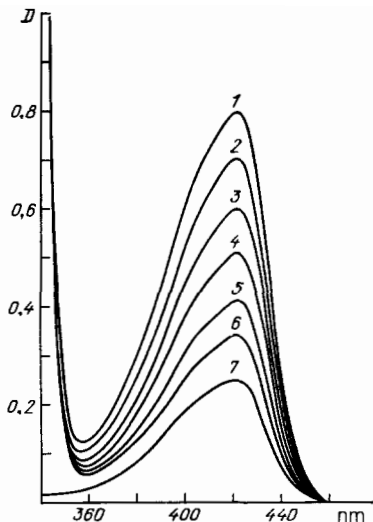


FIG. 4. Reduction in the optical density D of a solution of coumarin C314 in ether mixed with stilbene ($M = 0.85 \times 10^{20} \text{ cm}^{-3}$) and subjected to scattered daylight. The duration of exposure between curves 1-6 was 1 min; curve 7 represents the absorption spectrum of C314 in ether without stilbene. The cell thickness was 1 cm.

temperature results in complete bleaching of the solutions; the crystals are dissolved and the solutions lose their bright-green fluorescent color and become completely colorless. At the same time the concentration of the reagent molecules decreases.

Storage of a bleached solution in darkness (for several days) creates a small number ($< 1\%$) of the original molecules which are bleached again by light. Bleached solutions retain their transparency for several months when stored in the presence of light. The nature of the solvent is not important from the point of view of bleaching because similar bleaching reactions are observed in pentane, ethanol, and dimethylsulfoxide (DMSO), although at a lower rate. Detection of changes in the absorption by solutions in the ultraviolet range in the course of bleaching reactions made it possible to identify the absorption spectrum of the resultant

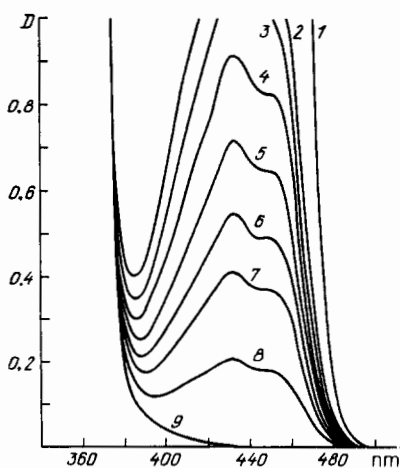


FIG. 5. Reduction in the optical density D of a solution of coumarin C6 in ether mixed with diphenylbutadiene ($M = 5 \times 10^{19} \text{ cm}^{-3}$) and exposed to scattered daylight. The exposure time between curves 1 and 2 was 1.5 min and between curves 2-7 was 15 s; between curves 7 and 8 it was 30 s, and between curves 8 and 9 it was 30 min.

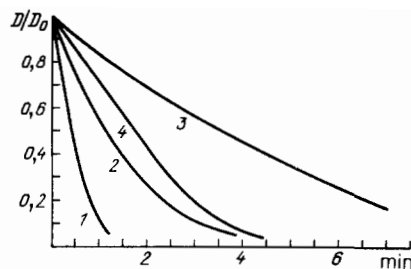


FIG. 6. Reduction in the normalized optical density (measured at the wavelength of 436 nm) of a solution of coumarin C6 in ether mixed with diphenylbutadiene with the duration of action of scattered daylight: 1) $M = 5 \times 10^{19} \text{ cm}^{-3}$; 2), 4) $M = 1.72 \times 10^{19} \text{ cm}^{-3}$; 3) $M = 5.75 \times 10^{18} \text{ cm}^{-3}$. The initial densities were $D_0 = 0.8$ for curves 1-3 and 1.6 for curve 4.

product, which in the case of C6 is shown in Fig. 7. The product is completely transparent to the pump radiation in the long-wavelength absorption band of the dye. Its spectrum resembles the spectrum of the reagent, but is shifted toward shorter wavelengths. The observed bleaching reactions are partly reversible, as demonstrated in experiments involving interaction of bleached solutions with hard ultraviolet radiation in the wavelength range 255-275 nm, where the absorption by the new products is particularly strong. This produces dye molecules in the solution and increases the concentration of the reagent. A similar recovery of the dye can be induced by heating a bleached solution to 70-100°C. Cooling of the solutions in the presence of light bleaches them again.

It has been established that the rates of bleaching reactions involving dyes are proportional to a reduction in the quantum efficiency η of their fluorescence in the solution when a diphenylpolyene is added (Fig. 8). This is a demonstration of the participation of excited singlet molecules in the bleaching reaction and makes it possible to estimate the rate constants of the observed bleaching reactions on the assumption that the reduction in η is due to such a reaction.

In determination of the absolute values of the rate constants we need the lifetime of the excited particles, which is not known accurately, but in estimates we can assume that it is of the same order of magnitude as in the case of C6 ($\sim 3.3 \text{ ns}$).

The rate of bleaching of C6 by interaction with DPB dissolved in DMSO is, for the same concentration of the reagent, approximately 250 times less than in ether, which demonstrates an inverse relationship between the rates of interaction and viscosity, typical of diffusion-controlled reactions.²⁴

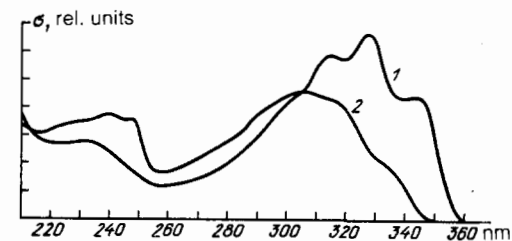


FIG. 7. Absorption spectra of diphenylbutadiene in ether (1) and the product (2) formed as a result of a bleaching reaction between coumarin C6 and diphenylbutadiene in ether under the action of scattered daylight.

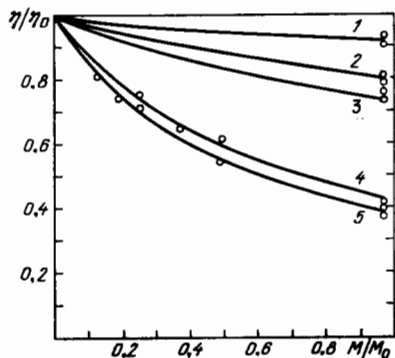


FIG. 8. Experimental results (points) representing the reduction in the relative value of the quantum efficiency of fluorescence η/η_0 of dyes in ether on increase of the concentration of the reagent M/M_0 in the solution, where M_0 is the saturation value of the concentration in ether at 20 °C. The continuous curves represent calculations carried out using a formula $\eta/\eta_0 = (1 + k\tau M)^{-1}$, where the values of the product $k\tau$ are listed in Table I. 1) Coumarin C6 with stilbene; 2) coumarin C102 with stilbene; 3) coumarin C6 with diphenylbutadiene 4) coumarin C47 with stilbene; 5) coumarin C314 with diphenylbutadiene.

Experiments on oxazine 17 mixed with DPB, ST, and DSB have revealed apparently two bleaching stages. In the first stage the bleaching reaction produces products which absorb in the pump and fluorescence bands and then the absorption decreases, i.e., the new products in turn become bleached (Fig. 9). A mixture of several dyes with a reagent has demonstrated bleaching in accordance with the individual rates of the bleaching reactions of the dyes, as demonstrated in Fig. 10.

Low rates of the bleaching reactions have been reported for coumarins C153 and C307 interacting with ST, and also for some other compounds (Nile blue, POPOP, imitrine 3) mixed with ST. High bleaching rates are typical of a wide range of laser compounds and reagents, so that bleaching reactions can be regarded as a common property of these substances.

The simultaneous reduction in the concentration of the dye and reagent in the course of a bleaching reaction and their increase due to heating or ultraviolet irradiation are in agreement with a model in which a bleaching reaction of an excited dye molecule with an unexcited reagent molecule produces an exciplex and then a fairly strong, at room tem-

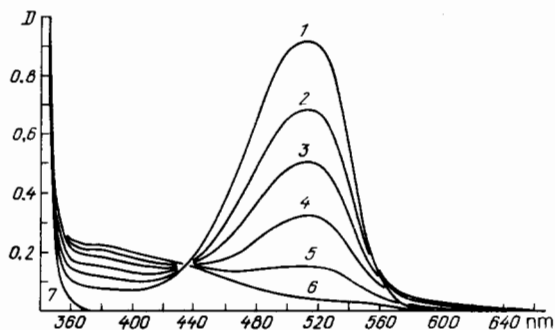


FIG. 9. Reduction in the optical density D of a solution of oxazine 17 in ether mixed with stilbene ($M = 2 \times 10^{20} \text{ cm}^{-3}$) and exposed to scattered daylight. Exposures lasted 12 min (between curves 1-3), 18 min (3-4), 20 min (4-5), 45 min (5-6), and 10 h (6-7). Absorption was observed in the region of 580-660 nm and then it disappeared.

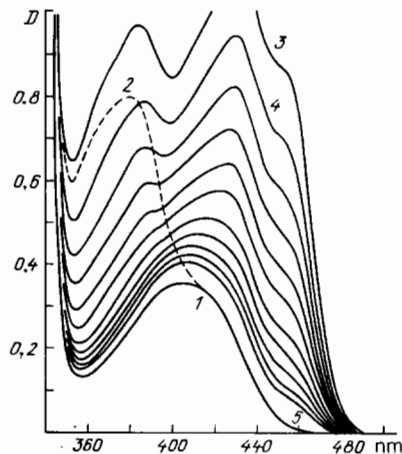


FIG. 10. Reduction in the optical density D of a mixture of coumarin dyes C153 (initial density represented by curve 1), C102 (initial density is the difference between curves 2 and 1), and C6 (initial density is the difference between curves 3 and 2) dissolved in ether and mixed with stilbene ($M = 2 \times 10^{20} \text{ cm}^{-3}$), exposed to scattered daylight. Exposure lasted 1.5 min between curves 3 and 4 and 1 min for each curve between curves 4 and 5.

perature (but not so strong when heated to 100 °C), chemical complex with a binding energy of the order of $\sim 0.5 \text{ eV}$. It is very likely that the stereochemistry of these photochemical reactions is similar to the familiar reactions of photoattachment of alkenes²⁵ and dienes to simpler organic compounds, such as benzene and its derivatives, and to condensed hydrocarbons²⁶ (naphthalene and anthracene) in accordance with reactions of the type shown in Fig. 11, involving formation of singlet exciplexes. This allows us to draw the conclusion that the observed bleaching of dyes is due to breaking of the π chains of molecules in a complex, responsible for the bleaching, and that such chain breaking can be induced in practically all the organic compounds by a suitable selection of the reagents (because they all contain π chains of unsaturated bonds, which can be saturated chemically).

The low rates of bleaching in the case of coumarin molecule C153 and C307 reacting with ST can be linked reliably to the influence of the CF_3 group, because replacement of this group with CH_3 (C102 and C2) increases the rate of bleaching by almost two orders of magnitude. The number of dyes and reagents suitable for BW lasers will undoubtedly

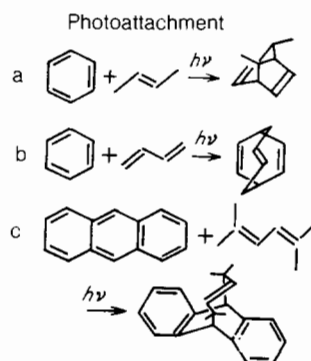


FIG. 11. Known reactions of photoattachment to benzene (a, b) and to anthracene (c).²⁶

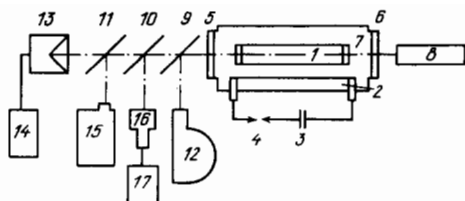


FIG. 12. Schematic diagram of the apparatus: 1) cell made of quartz of the KLZh grade, 1.8 cm in diameter and 40 cm long, containing the active medium; 2) open electric discharge initiated by an exploding wire; 3) bank of capacitors representing $C = 48 \mu\text{F}$ charged to $U = 30\text{--}45 \text{ kV}$; 4) controlled spark gap; 5), 6) adjustable plane mirrors of a laser resonator; 7) electric-discharge chamber; 8) laser used for alignment; 9)–11) light-deflecting quartz plates; 12) image-converter camera operating in the streak mode; 13) calorimeter; 14) automatic plotter; 15) spectrograph; 16) photodiode; 17) oscilloscope.

increase in future because of utilization of a wide range of known²⁶ and new photochemical reactions of excited organic compounds. The advantages of the reagents selected by us here are the high rates of bleaching reactions, sufficient for the use in BW lasers, and their known ability²⁷ to quench triplet molecules that interfere with efficient lasing of dyes. Moreover, their absorption bands lie in the ultraviolet range²⁸ and overlap only slightly absorption bands used to pump the dyes. In the case of BW lasers it would be of interest to search also for laser compounds of the photochrome type²⁹ in which bleaching reactions accompanied by a change in the structure are of internal molecular type and are accompanied by the required shift of the absorption spectrum.

The ability of some substances to become "invisible" as a result of a bleaching reaction may be useful in the removal of laser photoproducts interfering with lasing by converting them to the colorless form (as demonstrated, for example, in Fig. 9).

5. FIRST BLEACHING WAVE LASERS

Construction of the first BW lasers was reported in Ref. 30. The experiments were carried out using a high-power source of light flux, which was an open electric discharge initiated in air (or in some other gas) by a thin exploding wire. Such a source is characterized by a high brightness temperature ($35\,000\text{--}50\,000 \text{ K}$)^{31,32} and can be used to pump many gaseous laser-active media.^{33–36} Use was made of the apparatus shown schematically in Fig. 12.

The active medium was an ether solution of coumarin C6 with DPB, characterized by sufficient bleaching rate (Table I). Measures were taken to protect the solution from

light during preparation, i.e., the formation of a mixture, pouring into a cell, placing in a chamber, and alignment were all carried out in the presence of red light which did not affect bleaching of C6 or this was done in darkness. After several hours of storage of the cell in the chamber, when the solution became highly homogeneous in the optical sense, the resonator mirrors were aligned. One mirror (6) had a reflection coefficient of 98% and another mirror (5) was usually semitransparent. A tungsten wire 0.01 cm in diameter and 40 cm long was stretched parallel to the cell axis at a distance of 1–1.5 cm from its outer surface. The radial velocity of expansion of the discharge channel was $\sim 1 \text{ km/s}$ in an SF_6 atmosphere, which ensured that this light source acted for $10\text{--}15 \mu\text{s}$ until the discharge plasma came in contact with the cell. Light reflectors were not used and pumping was provided by light which reached the cell directly (which represented $\sim 1/6$ of the total flux from the source). An image-converter camera was operated in the streak mode and it recorded both the pump source and the motion of the fluorescence or lasing zone across the cell diameter.

A typical streak record of the motion of a bleaching wave in the active medium in the absence of lasing is shown in Fig. 13. The motion of the wave along the solution was readily recorded because of a strong fluorescence emerging from the optical excitation zone, which under the influence of pumping traveled due to bleaching of the particles. In this experiment the concentration of C6 molecules was $N_0 = 7.5 \times 10^{16} \text{ cm}^{-3}$ [$\sigma_0 N_0(433 \text{ nm}) = 11.3 \text{ cm}^{-1}$] and the concentration of DPB was $M = 4.5 \times 10^{19} \text{ cm}^{-3}$. The exit mirror was a quartz plate with a reflection coefficient of $\sim 4\%$. The rate of expansion of the discharge channel in SF_6 (at 1 atm) in Fig. 13 was 1 km/s and the velocity of the bleaching wave varied with time and reached 3 km/s. The width of the wavefront was $\sim 0.9 \text{ cm}$.

According to Eq. (1) under these conditions for $(1 - \eta) = 0.27$ (Fig. 8) and $I_0 \approx 6 \times 10^{22} \text{ cm}^{-2} \cdot \text{s}^{-1}$ the average velocity of the wave was estimated to be $v \approx 2 \text{ km/s}$, in good agreement with the observed velocity of the excitation zone. This confirmed the correctness of the proposed and theoretically demonstrated feasibility of motion of an optical excitation zone in a liquid medium at high velocities, i.e., at velocities exceeding the speed of sound, when the replacement of excited particles could occur practically without disturbance of the initial optical homogeneity of the medium.

Lasing was observed when the threshold conditions were reached in the bleaching wave. Figure 14 shows a streak record obtained for the first BW laser characterized by $N_0 = 13.3 \times 10^{16} \text{ cm}^{-1}$ ($\sigma_0 N_0 = 20 \text{ cm}^{-1}$) and



FIG. 13. Streak record of the motion of a bleaching wave in a solution of coumarin C6 in ether mixed with diphenylbutadiene in the absence of lasing (the pump source is shown below the cell).

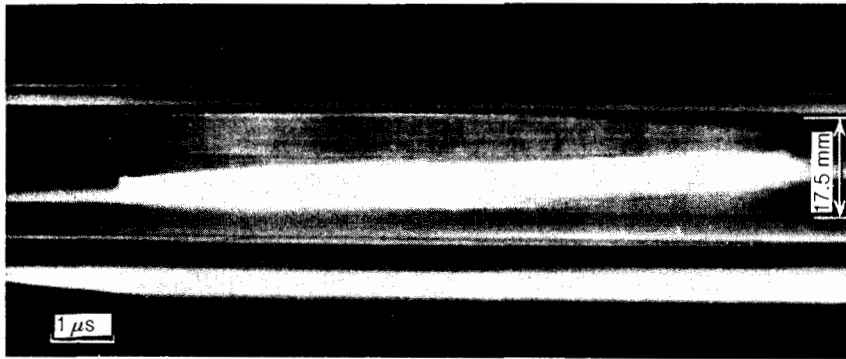


FIG. 14. Streak record obtained for a bleaching wave laser utilizing a solution of coumarin C6 dissolved in ether and mixed with diphenylbutadiene ($U = 30$ kV).

$M = 4.1 \times 10^{19} \text{ cm}^{-3}$, employing a quartz plate as an exit mirror. The velocity of the lasing wave was 1 km/s and the width of the lasing zone was ~ 0.6 cm. The profile of a laser radiation pulse was determined in the wavelength range 517 ± 3 nm; it is shown in Fig. 15 for the case when the voltage across a battery was $U = 30$ kV.

When the voltage across the discharge capacitor bank was increased to $U = 44$ kV (Fig. 16), the laser radiation energy was 0.5 J and when the quartz plate was replaced with an exit mirror characterized by $R_2 = 67\%$ (Fig. 17) this energy became 2.5 J, corresponding to a specific output energy of 0.05 J/cm^3 (in the range 518 ± 3 nm) and an average power of 0.17 MW (for a pulse duration of $15 \mu\text{s}$).

In another experiment the reagent participating in the bleaching reaction with C6 in the BW laser was ST ($M = 1.7 \times 10^{20} \text{ cm}^{-3}$). When the reflection coefficient of the exit mirror was $R_2 = 67\%$, the output energy was 1.5 J for a pulse of $14 \mu\text{s}$ duration. These results demonstrate that both ST and DPB were effective in quenching the triplet states, thus ensuring prolonged lasing. In the case of ST the velocity of the bleaching wave was approximately 5 times less than in the case of DPB, which was due to the lower rate constant of the bleaching reaction (Table I).

When in one of the experiments carried out using ST the distance between the exploding wire and the cell was increased to 20 mm, the duration of the output pulse increased to $28 \mu\text{s}$, confirming the steady-state quasi-cw nature of the emitted laser radiation and the fact that the lasing ceased when the plasma reached the cell wall.

An analysis of a streak record in Fig. 17 showed that, in contrast to conventional laser systems, the investigated BW laser exhibited automatic rapid bleaching and deactivation of the parts of the active medium with a low Q factor (be-

cause of the corresponding high concentration of the excited particles in these regions). A perturbation created in the active medium by a shock wave of an expanding plasma resulted in rapid suppression of lasing in the wall layer of the cell and shifted the lasing zone to deeper layers. This feature could be used to increase the general efficiency of lasing by switching the pumping to parts of the active medium with higher values of the Q factor.

Since ultraviolet radiation interacting with such a medium induced a process which was the reverse of bleaching, screening from such radiation was ensured by making laser cells of quartz of the KLZh grade (characterized by a transmission of less than 10% at wavelengths shorter than 340 nm) or of glass (in the experiments involving ST). An estimate of the influence of ultraviolet radiation was obtained from experiments in which the laser cells were made of transparent quartz of the KU grade. A streak record of lasing obtained for this case for a mixture of C6 ($N_0 = 2.5 \times 10^{17} \text{ cm}^{-3}$ and DPB ($M = 3.4 \times 10^{19} \text{ cm}^{-3}$) is shown in Fig. 18. There was clear pulsating switching of the lasing zone from the wall layer to deeper layers in the medium, but although there were some indications of lasing, complete bleaching of the front pump layer did not occur. These results demonstrated that infrared radiation of the pump sources must be transformed into longer wavelengths before such radiation could be used to excite substances with absorption bands at shorter wavelengths (such as $\text{C}_3\text{F}_7\text{I}$).³³

6. FUTURE OF BLEACHING WAVE LASERS

At high concentrations of diphenylpolyenes in the active solutions used in BW lasers (10^{19} – 10^{20} cm^{-3}) the lifetime of triplet molecules is estimated not to exceed several nanoseconds, so that the accumulation of triplet losses and the influence of triplet states on the parameters of BW lasers can

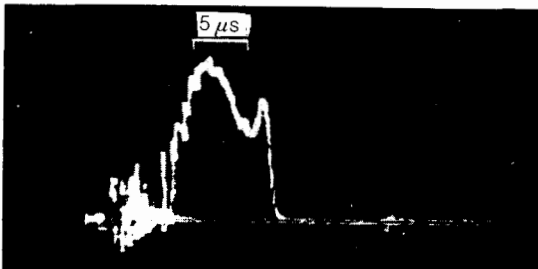


FIG. 15. Oscillogram of an output pulse from a bleaching wave laser obtained in the wavelength range 517 ± 3 nm. The horizontal scale is $5 \mu\text{s/div}$.

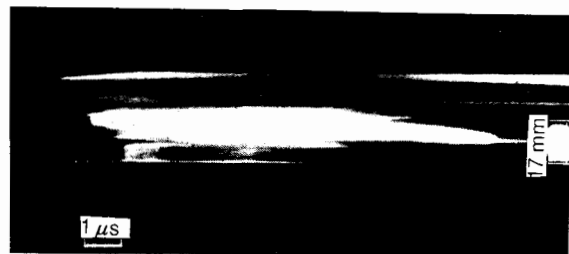


FIG. 16. Streak record obtained for a bleaching wave laser utilizing a solution of coumarin C6 and a mirror with $R_2 = 4\%$. The pump source is shown below the cell. $U = 44$ kV, $E_{\text{las}} = 0.5$ J.

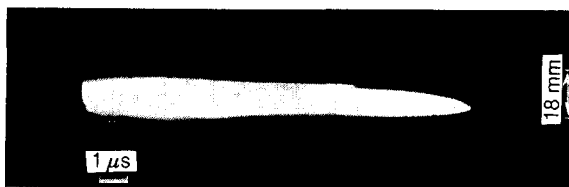


FIG. 17. Streak record of a BW laser utilizing a solution of coumarin C6 and a mirror with a reflection coefficient $R_2 = 67\%$. $U = 45$ kV, $E_{\text{in}} = 2.5$ J.

be ignored. The longitudinal dimensions of the active medium can therefore reach several meters.¹⁴ The transverse dimensions of the active medium of a BW laser when the pump source operates for, for example, $100 \mu\text{s}$ and the wave velocity is 1.5 km/s, can amount to ~ 15 cm.

If we wish to achieve efficiencies in BW lasers comparable with those attainable for dye lasers pumped with laser radiation, it is necessary to ensure that the excitation zone travels in the active medium at a velocity higher than that of sound, i.e., that the velocity in solutions is $v \gg 10^5$ cm/s. At this velocity an input energy of $1-2$ J/cm³ requires pump light fluxes of intensity $I_0 \gg 3 \times 10^{23}$ cm⁻²·s⁻¹. In an excitation band of width 0.5 eV such fluxes can be provided by pump sources¹⁾ characterized by a temperature of $3-4$ eV, so that in the case of complete utilization of the light fluxes and for lasing efficiencies of $30-50\%$ shown to apply to complex organic compounds we can count on an output energy of $0.3-1$ J/cm³. In the case of mechanical replacement of a bleached solution between pump pulses (for the purpose of cooling and regeneration) the repetition frequency of the output pulses of a BW laser with a chamber of volume $0.1-1$ m³ can be in excess of 10 Hz.

Bleaching wave lasers with a high output energy can themselves be used as pump sources in other BW lasers. Naturally, these principles of BW lasers can be realized also in other condensed media (such as those containing F color centers, etc.) and products other forms of high-intensity optical and nonoptical pump sources capable of converting active substances (reversibly or irreversibly) into transparent to the pump radiation. There should be no special difficulties in selecting such substances and creating the necessary conditions for their excitation, but it should be pointed out that up to now the majority of condensed media used in lasers have been distinguished by exactly opposite properties of a high stability and resistance to external changes, so that their stability must be lowered if they are to be used in BW lasers.

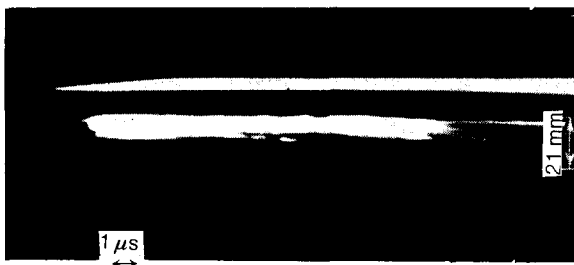


FIG. 18. Streak record of laser emission from coumarin C6 dissolved in ether and mixed with diphenylbutadiene without screening the ultraviolet component of the pump radiation ($U = 30$ kV).

The search for optimal variants in BW lasers is only beginning and much coordinated effort of physicists, chemists, mathematicians, and power engineers will be necessary before the high potentialities of BW lasers are utilized in the form of increased efficiencies, directionalities, and output energies and average powers.

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¹⁾Pump sources with a lower temperature are also of interest in BW lasers, because attainment of velocities in excess of 10 m/s in the replacement of the active medium and self-termination of low-Q modes can again improve the lasing characteristics of the active medium, but because thermo-optic distortions develop in a solution after several microseconds from the beginning of excitation,¹⁷ the replacement of an excited volume after a longer time will increase the divergence of the resultant laser radiation, i.e., full potentialities of BW lasers will not be utilized.

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