SOVIET PHYSICS JETP VOLUME 35, NUMBER 6 DECEMBER, 1972

# Luminescence of Liquid Organic Solutions Excited by Electron-Beam Bombardment

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Submitted August 18, 1971
Zh. Eksp. Teor. Fiz. 62, 2019–2025 (June, 1972)

An investigation was made of the dependence of the intensity of luminescence of binary organic solutions on the electron-beam current density ($j_{max} = 1.2$ A/cm$^2$, $E_0 = 1$ MeV). The luminescence efficiency was determined for several compounds. Possible utilization of these compounds in lasers pumped with fast-electron beams is considered.

## 1. INTRODUCTION

EXPERIMENTAL investigations have recently been made of the pumping of laser media with hard ionizing radiations. The interest in such radiations stems from the fact that they may provide the most effective means of pumping of lasers emitting in the ultraviolet range[1] and from the fact that one would be able to use powerful excitation sources such as nuclear reactors.[2] Laser action in mixtures of inert gases,[3] in liquid xenon,[1] and $Y_3Al_3O_{12}:Nd^{3+}$[4] has been achieved by pumping with a beam of electrons of $E_0 \leq 1$ MeV energy. On the other hand, the rapid progress made with liquid organic-dye lasers has led to the development of coherent light sources emitting in the near ultraviolet (up to 340 nm).[5] Since many of the dye solutions used in such lasers are also employed as scintillators, pumping with a beam of charged particles may have advantages over optical pumping.

In contrast to light, the energy of ionizing radiations is absorbed nonselectively and, therefore, pumping with such radiations can be efficient only when the energy absorbed in the solvent is transferred to the molecules of the luminescent dye. This can be achieved, for example, in aromatic solvents. Since the fraction of the energy of a charged particle dissipated in the primary excitation of the $\pi$ shells of the organic solvent molecules amounts to ~10%,[6] the efficiency of a dye laser excited in this way should be of the order of several percent if the transfer of energy to the luminescent substance is efficient and the quenching is weak.

The most efficient pumping source and active medium can be selected partly on the basis of the results of investigations of scintillation counters. However, since powerful charged-particle fluxes are used in laser pumping, an allowance must be made for the effects which increase with increasing radiation dose rate because this increase enhances the importance of the second-order reactions[7] and thus increases the quenching of the excited states.

We investigated the luminescence generated by bombardment of some dyes and scintillators with an electron beam. Experimental results reported below were obtained for derivatives of ceramidonine (C), synthesized at the Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences[8] (Fig. 1), and n-terphenyl. These dyes were selected because of their relatively high radiation stability, good solubility in aromatic solvents, and low laser thresholds[9]. The dyes investigated will be denoted by Roman numbers: I) 2-methyl-C; II) N-oxide-2-methyl-C; III) 2-methyl-8-methylamino-C; IV) 2-methyl-6-dimethylamino-C; V) 2-methyl-6-anilino-C; VI) 2-methyl-6, 8-methylamino-C.

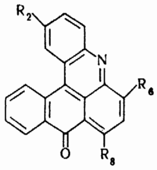

FIG. 1. Structural formula of the derivatives of ceramidonine: $R_i$ are the various possible substituents.

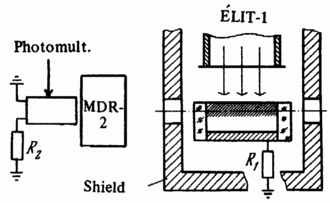

FIG. 2. Schematic diagram of the apparatus.

## 2. EXPERIMENTAL INVESTIGATIONS

We determined the following characteristics of the luminescence excited by electron bombardment: 1) the dependence of the luminescence intensity on the electron current density and the distribution of this intensity with depth in the sample; 2) the absolute efficiency of the luminescence at high current densities; 3) the fall in the luminescence intensity with increasing absorbed dose.

2.1. The dependence of the luminescence intensity I on the current density j was determined using the apparatus shown schematically in Fig. 2. This apparatus consisted of a cuvette with quartz windows, which was placed close to the exit from an ÉLIT-1 accelerator, an MDR-2 monochromator, and an FÉU-14B photomultiplier. The voltage drop across a resistor $R_1$, connected to the metal bottom of the cuvette, was used to study the parameters of the incident electron current pulse ($\tau = 2\ \mu$sec). The solution was protected from the atmosphere by a 10-$\mu$ polyethylene terephthalate film (the solution was not outgassed before the measurements). Figure 3 shows the results of measurements obtained in the range $j \leq 0.25$ A/cm$^2$ for the dyes II and IV, which exhibited the strongest luminescence, for n-terphenyl, and for rhodamine 6G dissolved in various solvents (the curves in Fig. 3 are not all to the same scale because the intensity of the luminescence emitted from alcohol solutions was considerably

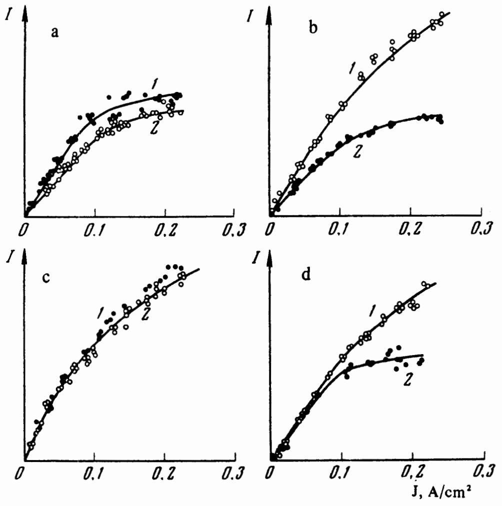

FIG. 3. Dependence of the luminescence intensity of various solutions on the density of the current of $E_0$ = 540 keV electrons. a—Rhodamine 6G in ethanol (λ = 570 nm): 1) c = 0.4 g/liter, 2) c = 0.03 g/liter; b—n-terphenyl in benzene (λ = 350 nm): 1) c = 5.0 g/liter, 2) c = 0.05 g/liter; c—dye IV (λ = 620 nm): 1) c = 0.04 g/liter in toluene, 2) c = 0.03 g/liter in ethanol; d—dye II (λ = 610 nm): 1) c = 0.18 g/liter in benzene, 2) c = 0.15 g/liter in ethanol.

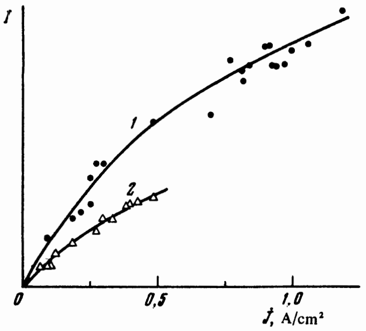

FIG. 4. Dependence of the luminescence intensity of a solution of n-terphenyl in n-xylene on the electron current density (λ = 350 nm): 1) $E_0$ = 900 keV; 2) $E_0$ = 685 keV.

lower than that emitted from solutions in aromatic compounds).

Figure 4 shows the dependence I(j) for a solution of n-terphenyl in n-xylene for values of j up to 1.2 A/cm$^2$ and for two values of the electron energy $E_0$. If the curves in Fig. 4 are replotted using the coordinates I = I(j$E_0$), i.e., if the luminescence intensity is plotted as a function of the absorbed energy and not the current density, it is found that curve 2 lies a little below curve 1. This shows that at lower electron energies the quenching is stronger and the density of secondary products along particle tracks is higher. The ratio of the measured intensities I(j, 900 keV) × /I(j, 685 keV) = 1.3 is identical with the corresponding ratio for the luminescence generated by single electrons (compare with Fig. 6-1 in[6]).

The distribution of the luminescence intensity along the direction of propagation of the electron beam, recorded with a PIM-3 image converter, was found to coincide almost completely with the known distribution of the electron energy losses.[10] The luminescence intensity reached its maximum value at a depth of 0.8 mm for electrons of $E_0$ = 0.9 MeV energy and it fell to zero when the depth reached 2.7 mm.

Table I

| Substance | $\lambda_{max}$, nm | Δλ, nm | $\tau^0$, nsec | $c_0 \cdot 10^{-16}$, cm$^{-3}$ | η, % |
|---|---|---|---|---|---|
| n-terphenyl | 340 | 26 | | 7,8 | 100 |
| I | 550 | — | 22 | 4.1 | — |
| II | 600 | 72 | 42 | 5.8 | 79 |
| III | 560 | — | 59 | 3.7 | — |
| IV | 625 | 88 | 23 | 3.5 | 46 |
| V | 625 | 106 | 40 | 3.2 | 13 |
| VI | 570 | 70 | 49 | 3.4 | 38 |

Table II

| Solute | Solvent | $c_0 \cdot 10^{-16}$, cm$^{-3}$ | η, % | $\varphi c^* \cdot 10^{-12}$, cm$^{-3}$ |
|---|---|---|---|---|
| n-terphenyl | benzene | 1320 | 0.22 | 4.4 |
| » | toluene | 1320 | 0.25 | 5.0 |
| IV | toluene | 6.4 | 0.016 | 6.5 |
| » | ethanol | 6.4 | 0.00016 | 0.065 |

2.2. We used the same apparatus (Fig. 2) to measure the relative energy efficiency of the luminescence of the solutions. We kept the current density constant (j = 0.25 A/cm$^2$, $E_0$ = 540 keV) and used the MDR-2 monochromator and the FÉU-14B photomultiplier to determine the spectral density of the luminescence:

$$dI/d\lambda = i(\lambda)\mu(\lambda)\xi(\lambda).$$

Here, i(λ) is the measured amplitude of the photomultiplier current pulse; μ(λ) is the measured spectral sensitivity of the photomultiplier in kA/W; ξ(λ) is the measured transmission of the monochromator. The area under the curve

$$I = \int_0^\infty \frac{dI}{d\lambda} d\lambda$$

is proportional to the total luminescence power. Table I lists the relative energy efficiency of the luminescence η obtained in this way (we assumed that the efficiency of n-terphenyl was 100%). The relative quantum efficiency was found by dividing the values of η obtained in this way by the average energy of the luminescence quanta. In some cases (denoted by dashes in Table I) the luminescence was not observed right up to excitation levels at which the solvent and the cuvette windows emitted radiation. Table I gives also the wavelength of the luminescence peak and the width of the luminescence band as well as the lifetime of the excited state $\tau^0$ calculated from the parameters of the first absorption band.[11]

The absolute energy efficiency was determined for n-terphenyl and for the solution IV. The results are given in Table II for j = 0.25 A/cm$^2$ and $E_0$ = 540 keV. In this table $c_0$ denotes the concentration of the solution and $\varphi c^*$ is the concentration of the excited molecules participating in the luminescence. The latter quantity was calculated from the expression

$$\varphi c^* \approx jS_k E_0 \eta \tau^0 / h\bar{\nu};$$

here, $h\bar{\nu}$ is the average energy of a fluorescence quantum; $\tau^0 = 2.2 \times 10^{-9}$ sec for n-terphenyl;[12] φ is the quantum efficiency of the fluorescence; $c^*$ is the total concentration of the excited states.

2.3. Since the radiation flux used in laser pumping could be high, we investigated the dependence of the luminescence intensity on the absorbed dose. For nonoutgassed solutions of n-terphenyl and of the dyes I-VI in benzene, n-xylene, and hexafluorobenzene this dependence was nearly logarithmic in the dose range 1–100 Mrad. The concentration of the dye due to radiolysis also decreased logarithmically falling by a factor of 4.5 at 100 Mrad compared with an unirradiated sample. It was interesting to note that the rate of fall of the concentration of the same dye due to radiolysis in a solution in ethanol was much faster than logarithmic; it fell by a factor of 75 when the dose of 100 Mrad was reached.

## 3. DISCUSSION OF RESULTS

It is known[6] that aromatic solvents can transfer efficiently the excitation energy to the molecules of a scintillator, whereas most of the other solvents do not have this property. Our experiments have shown that ceramidonines are good acceptors of the energy transferred in this way and the quantum efficiency of the luminescence $\eta/\bar{\nu}$ of the solutions of the dyes II, IV, and VI is not inferior to that of n-terphenyl (Table I). Since the first excited states of the solvents and ceramidonines are separated by a large gap, it follows that the energy is transferred through higher excited states. The large variations in the luminescence efficiency from one ceramidonine to another are primarily due to differences in the probability of the intramolecular nonradiative degradation of the energy, associated with different positions of the substituents in the dye molecules,[9] rather than due to different rates of the transfer of energy from the solvent.

It is evident from Table I that the dyes II, IV, and VI have, like n-terphenyl, a fairly high quantum efficiency and they are promising materials for lasers pumped with powerful electron beams. The threshold concentration of the excited molecules corresponding to $c_0 = 5 \times 10^{16}\ \text{cm}^{-3}$ is $2.8 \times 10^{14}\ \text{cm}^{-3}$ for the dye IV[14] if the calculations are made in accordance with[13]. It is evident from Table II that very powerful electron currents would be required to reach this concentration and it follows from Figs. 3 and 4 that linear extrapolation would be invalid at current densities exceeding 0.1 A/cm$^2$.

The reduction in the observed luminescence efficiency may be due to the appearance of short-lived intermediate products of radiolysis of the solvent which have high extinction coefficients at the laser wavelength (these may be radicals, triplet-excited molecules, etc.). The reduction may also be due to the formation of short-lived products which quench the excitation directly. Since the nature of the dependences I(j) is the same for n-terphenyl and for ceramidonines and the luminescence emitted differs considerably in respect of the wavelength, it is more likely that the second factor predominates. Therefore, the inflections in the curves may be explained by an increase in the local concentration of particles because of overlap of the excitation regions within separate particle tracks.

When a single fast particle is slowed down in a medium, it forms "spurs" of 50–100 eV energy around its track[7,10] and the distance between these spurs is a function of the energy, mass, and charge of the particle. The "primary" quenching of the excited states depends only on the distance between such spurs, which is about 2000 Å for electrons of $E_0 = 1$ MeV energy. When the electron current density is increased, the distance between tracks decreases and when it falls below 2000 Å the local density of excited states rises and the quenching becomes stronger. The "cross section" of a track $S_{tr}$ can be deduced from inflections of the curves in Figs. 3a, 3c, and 3d by assuming that at the point of influenction the ratio $\sigma$ of the total area of the tracks per unit area in the medium is equal to that unit area:

$$\sigma_{\text{infl}} = \frac{j\tau S_{\text{tr}}}{e} \approx 1,$$

where the lifetime of the excited dye molecules is $\tau \sim 10^{-8}$ sec and j = 0.1 A/cm$^2$. Then, $S_{tr} \approx \sqrt{1400}$ Å, i.e., it is close to the distance between the spurs.

It is also evident from Figs. 3b, 3c, and 3d that the linear regions in the dependences are less pronounced for the solutions in aromatic solvents and that these regions terminate at lower values of j. Since the Coulomb sphere diameter in hydrocarbons is 300 Å,[10] the hypothesis of multistage migration of the energy can account for the increase in the effective diameter of a track by a factor of 2–3.

If the system of rate equations is solved for the concentration of the excited acceptor molecules in the presence of molecules of the donor and the quenching agent (the concentration of the latter increases with rising j), we find that under steady-state conditions[14] the functional dependence I(j) in the case of overlap of tracks is of the form

$$I(j) \propto j\,/\,(C_1 + C_2 j), \tag{1}$$

where $C_1$ and $C_2$ are constants related to the rates of elementary processes and to the concentration of the solution. Since the luminescence intensity I is proportional to the concentration, we can extrapolate curves denoted by 1 in Figs. 3 and 4 to find the threshold concentration of the excited molecules. If this extrapolation is valid, the threshold concentration is achieved wh when the current density is $j \sim 50$ A/cm$^2$. However, at the current densities employed in our study the overlap between cracks is important only in the quenching process because the excitation is transferred over long distances. The yield of radicals, triplets, etc. is still linear because their diffusion during the lifetime in benzene can carry them over distances of ~100 Å.[7] This means that when the distance between the spurs decreases below 100–200 Å because of the overlap of the tracks, the short-lived products may interact, the quenching of the excited molecules may become different, and the nature of the function I(j) can change at current densities of the order of 10 A/cm$^2$.

The present authors cooperated with R. V. Khokhlov and V. V. Fadeev (Moscow State University) and G. A. Abakumov (L. Ya. Karpov Physicochemical Institute) in an investigation of the possibility of laser action when an electron beam produced in an RIUS-5 accelerator ($E_0 = 2$ MeV, $\tau = 50$ nsec) was used to excite the solutions of n-terphenyl, ceramidonines, and POPOP in various solvents. The laser action was not observed at current densities up to several hundreds of amperes per square centimeter. This demonstrated the need for further detailed investigations of the processes occurring in solutions at higher excitation levels.

The authors are deeply grateful to R. V. Khokhlov, G. V. Abakumov, and V. V. Fadeev for valuable discussions of our experimental results.

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Translated by A. Tybulewicz
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