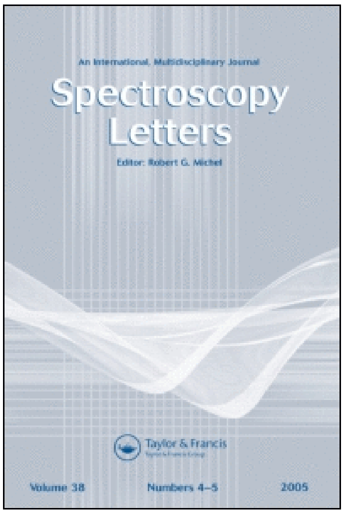

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ELECTROCHEMICAL REACTIONS IN DYE LASERS

Key words: ECL, Dye Laser.

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INTRODUCTION.

In recent years a considerable success has been achieved in the development of tunable dye-lasers and their applications. The information on this topic is presented in a series of the review articles.[1-3]

Further expansion of the dye lasers is essentially dependent on the prospects of their efficiency increase, construction simplification and miniaturization. In this respect the problem of dye laser pumping with electrochemical reactions in solution is of great interest.

In this paper the possibility of the stimulated emission of dye molecules in solutions under electrochemical pumping using ultrasonic stimulation and oncoming flows of radicals is discussed. In addition experimental results on the electrochemical frequency tuning in the conventional optically pumped dye lasers are presented.

ELECTROCHEMICAL PUMPING OF THE MOLECULES IN SOLUTIONS

1. Principal processes.

Prospects of dye laser development with electrochemical pumping of the molecules in solutions have been discussed recently in the papers[4-7].

The pumping mechanism is considered to be the same as that of the electrochemiluminescence (ECL). ECL is usually observed (see[4-5]) when bipolar low voltage is supplied to the electrodes inserted into the cell with dye solution. The voltage produces the anion (R^-) and the cation (R^+) radicals (see Fig. 1) the recombination of which may lead to the production of the excited singlet R^* and triplet R_T states of the molecules or the excited singlet R^*_{ex} states of the eximer complex. Emission takes place as a result of spontaneous transitions from the excited singlet states of monomer or eximer molecules. The excited triplet states contribute to the luminescence by means of the T-T annihilation.

2. Quantum efficiency of the ECL.

A number of ECL solutions as well as the electric regimes of their excitation were found in previous

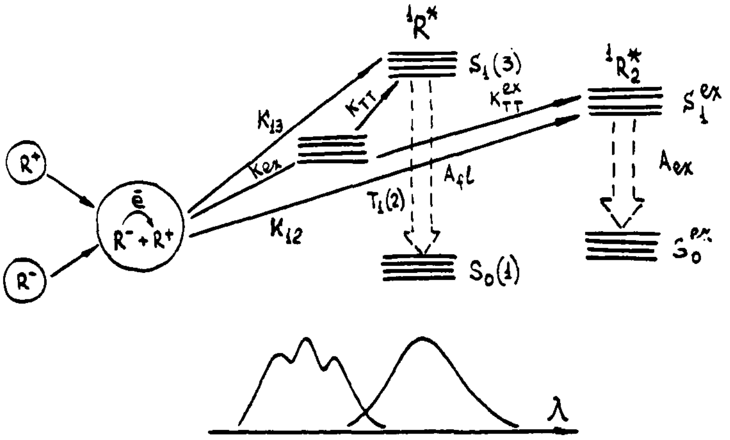

Fig. 1 . The main reactions leading to the ECL.

works[4,8,9]. One of the most efficient ECL system is 9,10-diphenylantracene (DPA) in dimethylformamide (DMF) for the blue region of the visible spectrum and some derivatives of styrylpyrazolines for the green region.

The quantum efficiency of the majority of the systems is lower than 1 %. The higher values were reported in[8,13] but the authors have made some assumptions when evaluating the reabsorption and the reflection of the ECL light from the electrode.

Most probably the low output of the ECL can be attributed to the multiple energy transfer between the singlet states of R^* and R molecules, which for a while continue to stay at a short distance from each other after the electron transfer reaction between the corresponding radical. Such multiple transfer is usually accompanied by nonradiative energy losses similar to the photoluminescence quenching at high concentration of molecules.

According to[3,8] ECL power as much as several mWt per cm^2 of the electrode surface is achieved experimentally. The ECL is known to take place only within a very thin layer of the solution near the electrode, but the accurate measurements of the layer thickness ΔX haven t been carried out up to date. The calculations in[5] and our experimental observation by means of the microscope show that ΔX doesn't exceed 10^{-4}cm. Using this maximum value and taking into account the thickness of the layer ΔX mentioned above one can conclude that at present the excited molecules concentrations of the order of 10^{12} cm^{-3} are obtained experimentally near the working electrode of the cell. Even if this value is several times as large (which apparently may be done by chemical means) it is still an order of magnitude less than required for laser action. So the problem of the ECL intensity increase is the crucial one for the successful electrochemical laser pumping.

3. Stimulation of ECL with ultrasonics.

We suggest applying an acoustic field , to the solution to increase the ECL intensity and efficiency under the bipolar excitation. For the series of molecules (DPA, diphenylstyrylpyrazolines, rubrene, perylene and others) the application of acoustic field allowed the ECL intensity to be increased considerably. It should be noted that the ultrasonics increases also the ECL quantum efficiency (e.g. with ultrasonics intensity of 10^{-2} Wt·m^{-2} the quantum efficiency of rubren in DMF at the concentration of $5 \cdot 10^{3}$ M is increased by an order of magnitude). The ECL intensity of DPA solution in DMF as a function of the electrode potentials is given in Fig.2.

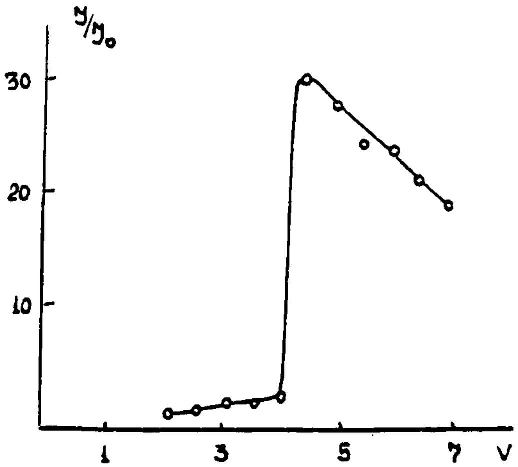

Fig.2. Relative increase of the ECL intensity (quasi-stationary regime) of the rubrene solution under the influence of ultrasonics versus the applied voltage (intensity of ultrasonic field 10^{-2}Wt·m^{-2}. Frequency 20 KC per sec).

As is seen from the figure the application of acoustic field greatly increases the ECL power by a factor of 30 at U=4,5v and consequently the excited singlet state population R.

Two main reasons responsible for the ECL power growth in the acoustic field must be considered: the strong acoustic mixing of the solution resulting in the increase of the ion-radical production on electrodes and the alteration of the energetics of the electron-transfer reaction caused by the redox-potential change.

As is known the energetics of the electron transfer reaction is determined by its enthalpy

$$-\Delta H = E_{pa} - E_{pc} - T\Delta S^{\circ}$$

where E_{pa} and E_{pc} -potentials of the oxidation and reduction, $T\Delta S$ -entropy factor. Our experiments revealed that ultrasonics affects the increase of the absolute value of the measured redox potentials (e.g. in rubrene solution the oxidation potential E_{pa} is changed by I50 mV and the potential of the reduction E_{pc} by 2I0 mV). Thus the increase of the absolute magnitudes of E_{pc} and E_{pa} values causes the increase of the system enthalpy. This might be enough for the conversion of the energy deficient reaction into energy sufficient one and consequently for the enlargement of the ECL intensity so far as sufficient reactions possess higher quantum efficiency.

4. ECL in the radical oncoming flows.

Unfortunately, the electrochemical pumping with bipolar pulses produces excited singlet molecules only within an extremely thin layer of 10^{-4}cm. It is difficult to use such a layer as an active zone of a laser. We consider here the possibility of the zone extension as well as the further ECL intensity increase by means of the ion-radical oncoming flows[7] which can be created when additional electrical field pulses $\tau \sim \frac{\ell}{uE}$ (where ℓ is interelectrode pulse distance, u - ion-radical mobility, E - intensity of electrical field) are applied to interelectrode space with the help of appropriate electrodes insulated from the solution. Taking into account the ion-radical oncoming flows the quantitative descripition of the reactions represented in Fig.I in one dimensional space is given by the following system of nonlinear differential equations

$$(\partial R^-/\partial t) = \mathcal{D}_1(\partial^2 R^-/\partial x^2) - K_R R^- R^+ + v_1(\partial R^-/\partial x) \qquad (1)$$

$$(\partial R^+/\partial t) = \mathcal{D}_2(\partial^2 R^+/\partial x^2) - K_R R^- R^+ + v_2(\partial R^+/\partial x) \qquad (2)$$

$$(\partial R^*/\partial t) = \mathcal{D}^*(\partial^2 R^*/\partial x^2) + K_{13} R^- R^+ + K_{TT} R_T^2 - (A_{31} + P_{32}) R^* \qquad (3)$$

$$(\partial R_{ex}^*/\partial t) = \mathcal{D}_e(\partial^2 R_{ex}^*/\partial x^2) + K_e R^- R^+ + P_{e1} R_{ex}^* \qquad (4)$$

$$(\partial R_T/\partial t) = \mathcal{D}_T(\partial^2 R_T/\partial x^2) + K_{12} R^- R^+ + P_{32} R^* - P_{21} R_T \qquad (5)$$

$$(\partial R/\partial t) = \mathcal{D}(\partial^2 R/\partial x^2) + K_R R^- R^+ + A_{31} R^* + K_{TT} R_T^2 \qquad (6)$$

where R^-, R^+, R^*, R^*_{ex}, R_T and R are concentrations, $\mathcal{D}_1$, $\mathcal{D}_2$, $\mathcal{D}^*$, $\mathcal{D}_e$, $\mathcal{D}_T$ and $\mathcal{D}$ are the diffusion coefficients for anion-radicals, cation-radicals, excited singlet molecules, eximer, triplet and neutral molecules respectively, v_1 and v_2 - the velocities of radicals, $v_1 = v_2$. The functions $R^-(x,t)$, $R^+(x,t)$, $R^*(x,t)$, $R^*_{ex}(x,t)$, $R_T(x,t)$ and $R\,(x,t)$ are the solutions of the system (1)-(6), which should satisfy (1-6) and the following initial conditions:

$$R(x) = N\,,\ R^-(x) = R^+(x) = R^*_{ex}(x) = R_T(x) = 0 \qquad (7)$$

This means that at t=0 there are only neutral molecules in the solution.

The boundary conditions for the determined functions are obvious from the physical considerations:

$$x = -\ell + \delta,\ R^* = R_{ex} = R_T = R^- = 0 \quad \Big| \quad x = \ell - \delta,\ R^* = R^*_{ex} = R_T = R^+ = 0 \qquad (8)$$

$$(\partial R/\partial x) = \frac{2N}{\ell}\exp\left(-\frac{\pi^2\mathcal{D}t}{4\ell^2}\right) \quad \Big| \quad (\partial R/\partial x) = -\left(\frac{2N}{\ell}\right)\exp\left(-\frac{\pi^2\mathcal{D}t}{4\ell^2}\right) \qquad (9)$$

$$\mathcal{D}(\partial R^+/\partial x) + vR^+ = \mathcal{D}(\partial R/\partial x) \quad \Big| \quad \mathcal{D}(\partial R^-/\partial x) - vR^- = \mathcal{D}(\partial R/\partial x) \qquad (10)$$

One seeks for the solution of the system (1) - (6) in the region $[-\ell+\delta,\ \ell-\delta]$, where δ is a very small value. The expression (9) is the solution of the equation (6) with regard for (7) and the initial condition t=0 R(x)=N. The equation (10) is a typical condition for the reflection, which takes into account the change of the molecular charge after the interaction with the electrodes.

This system describes both the diffusive recombinative, radiative, nonradiative prosesses and the ion-radical flux. The solution of the system (1) - - (6) at the chosen initial and boundary conditions gives data on the distribution and kinetics of the population of all initial, intermediate and final products represented in the reactions of Fig.1 . The solution of analogous systems in a general form is too much complicated to be obtained analytically.

We have made the numerical integration of the system (1) - (6) assuming that the concentration of neutral molecules is constant in the space between the electrodes R(x)=R and that the diffusive members are small in comparison with the other terms in the right sides of equations. The first assumption is valid when the extensive mixing of the solution near the electrodes is used the other one comes from the approximated evalution of the values in the equations taking into account that the diffusive members are by 4-6 orders less than the rest ones. The system (1) - (6) with the appropriate boundary and initial conditions as well as the simplifications made above were calculated using "Minsk-32" computer for the following parameters : $\frac{K_{13}}{K_R} = 10^{-2}$, $\frac{K_{1\ell}}{K_R} = 10^{-2}$, $K_{12} = K_R - K_{13} - K_{1\ell}$, $K_R = 3.10^{-11}$ sec^{-1}cm^3, $K_{TT} = 10^{-11}$ sec^{-1} cm^3, $v_1 = v_2 = v = 0{,}1$; 0,02 cm.sec^{-1}, $A_{31} = 10^8$ sec^{-1}, $\ell = \frac{1}{3}10^{-4}$ cm, $p_{32} = 10^7$ sec^{-1}, $p_{21} = 10^7$ sec^{-1}, $N = 10^{18}$ cm^{-3}, $\delta = 5.10^{-8}$ cm, $\mathcal{D} = 10^{-6}$ cm^{2}sec^{-1}, $p_{\ell 1} = 10^8$ sec^{-1}.

The time dependence of the population of molecules in the excited singlet state in the middle of the interelectrode space is represented in Fig. 3. As is seen from the Figure the population R increases at the first stage of the process and then becomes practically unchangeable. The saturation of R is obtained faster at larger flow speeds ($t = 6.10^{-5}$ sec for $v = 0{,}02$ cm sec^{-1} and $t = 5.10^{-5}$ sec for $v = 0{,}1$ cm sec^{-1}) and is proportional to the recombination coefficient K_R . This coefficient depends on v in the following way

$$K_R = K_{\mathcal{D}} + 6 \cdot 10^{-10} v \qquad (11)$$

where $K_{\mathcal{D}}$ is the diffusive recombination constant. As mobility of organic radicals in organic solutions is 10^{-4} cm.sec^{-1}.v^{-1}, the rate of radicals of the order of 0,1-1 cm.sec^{-1} is quite real at the electric field intensity of 10^3-10^4 v.cm^{-1}.

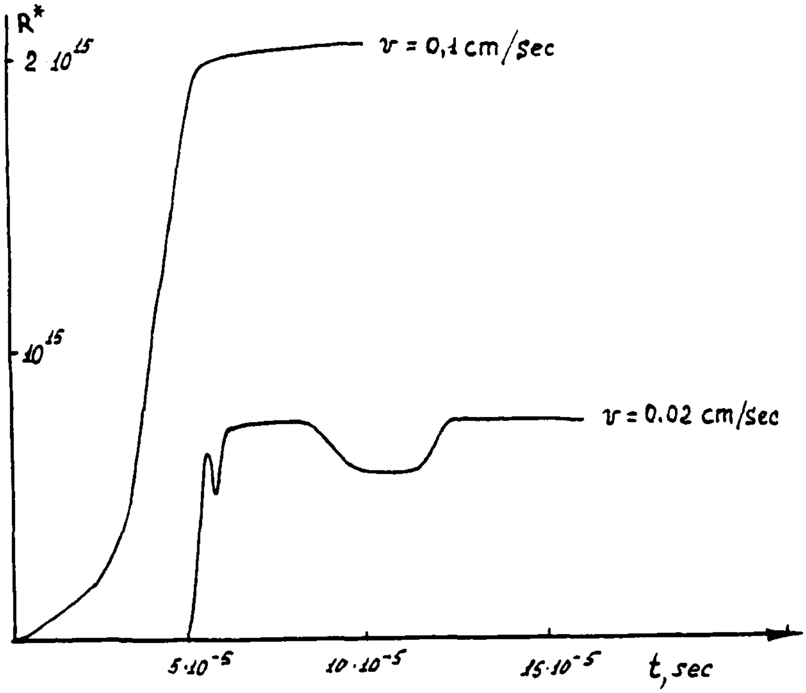

Fig.3. Time dependence of the excited molecule concentrations R^* in solution between electrodes after the voltage was switched on.

The represented results of calculations show the great influence of the ion-radical motion on the excited singlet state concentration of molecules R and as well as on the duration of the transient period.

According to the calculations the use of the oncoming flows increases the excited state population by a factor of $7,5.10^{2}$ i.e. up to $7,5.10^{14}$ at $v =$ $= 0,02$ $cm.sec^{-1}$ which is a sufficient value for the laser action. At the same time the size of an active zone now is limited only by the distance between the electrodes.

ELECTROCHEMICAL WAY OF FREQUENCY TUNING IN DYE LASERS

1. Physical principles.

The electrochemical reaction may be useful not only as a way of dye molecules pumping but also for frequency tuning in conventional dye lasers. The experimental realization of the electrochemical method of broad-band tuning has been reported in[12]. When the electric current is transmitted through the solution the anion and cation forms of the molecules appear near the electrodes. For instance, the near-cathode processes in the neutral solution of -methylumbelliferone in alcohol can be described as follows:

$$ROH + \bar{e} \rightleftharpoons H^{+} + RO^{-} + \bar{e} \rightarrow H + RO^{-}$$
$$2H \rightarrow H_2$$

where ROH - the dye molecule (maximum luminescence of 385 nm), $\bar{e}$ - the electron, RO^{-} the anion (maximum luminescence of 455 nm), H - the hydrogen atom, H^{+} -the proton.

The anions formed in the double layer near the electrode diffuse into the bulk of the solution,i.e. to the active zone of the laser. We have found out experimentally that the electric current transmission through the dye solution results in the formation of the products with efficient luminescence in the majority of the dye solutions having the stable ion forms[2]. The most of the cumarin, xanthene dyes, some anthracene derivatives and others are attributed to them.

2. Experimental results.

The dye lasers with an electrochemical active medium have some advantages in comparision with conventional dye lasers. In particular they allow to widen the spectrum range of the stimulated emission if selective cavity is used. In nonselective cavities the electric current transmission through the active medium leads to the strong tuning of broad-band generation. The electrochemical tuning of the laser emission spectra of esculin in ethanol (EtOH) is illustrated in Fig.4. Pumping was made by the N_2-laser with the 200 kWt peak power and the duration of pulses $\tau = 4 \cdot 10^{-9}$sec. The transverse geometry of dye laser was used. The active volume was situated near the electrode and had dimensions of 1x1x 15 mm. As is seen from the Figure 4 the

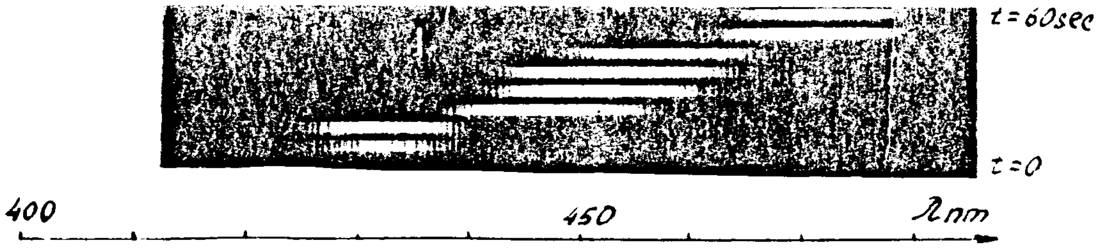

Fig.4. Stimulated emission of esculin in ethanol at different moments of time with the voltage switched on.

electric current transmission through the esculin for 60 sec produces laser spectra tuning from 430 to 465 nm i.e. over 35 nm. At shorter durations of the current transmission the laser spectra are in the intermediate positions. The electrochemical reactions on the electrode are usually under the difrusion control and the laser tuning time equals to several seconds. This time, however, can be decreased by a factor of 10^{-2}-10^{3} if a resonator with the sufficiently small active volume is used (for instance a confocal one).

It is interesting to notice that sometimes the nonlasing solution starts to laze when the current being transmitted through (for example, solution of 4-methylumbelliferone in acetone[12]). In this paper we do not intend to give a more detailed consideration concerning the properties of lasers with the electrochemical active medium. It should be mentioned, however that the electrochemical method of tuning is reversable. By changing the voltage polarity the initial characteristics of the active medium are restored.

By means of electrochemical reactions it is possible nearly to double the spectral interval of dye laser tuning without changing the dye solution.

The results given in the present paper show that the electrochemical phenomena may be successfully used for the dye laser improvement.

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