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# Spectral characteristics of active medium for tunable dye laser

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Spectral and fluorescent characteristics of mixtures of two couples of laser dyes for the red region have been studied with the purpose of tuning range broadening. Energy transfer of the monochromatic pumping from donor to acceptor was used in the first pair. The second couple of the dyes had the absorption spectra in the close spectral regions near wavelength of pumping, but its fluorescence spectra were characterized by essentially different Stokes shifts. As a result, the fluorescent band of the dye mixture expanded. The appreciable influence of solvents on fluorescence and laser characteristics of the second couple of the dyes has been revealed. Measuring of quantum yield of the dyes showed for one of them — DCM this characteristic was the largest in aprotic bipolar dimethylsulfoxide and the smallest in proton-donating methanol. The continuous tuning of laser radiation from 575 nm to 734 nm has been fulfilled under laser pumping of the selected dyes and its mixtures.

С целью расширения диапазона перестройки лазера для красной области исследованы и проанализированы спектральные и флуоресцентные характеристики смесей двух пар лазерных красителей. В первой паре используется передача энергии монохроматического излучения накачки от донора к акцептору. Вторая пара красителей имеет спектры поглощения в соседних областях вблизи длины волны накачки, но их спектры флуоресценции имеют существенно различающийся Стоксов сдвиг. В результате, полоса флуоресценции смеси красителей расширяется. Выявлено существенное влияние растворителя на флуоресцентные и лазерные характеристики второй пары красителей. Измерение квантового выхода флуоресценции этих красителей показало, что для одного из них — DCM, этот параметр максимальный в апротонном биполярном диметилсульфоксиде и минимален в протонодонорном метаноле. При лазерной накачке выбранных красителей и их смесей осуществлена непрерывная перестройка лазера от 575 нм до 734 нм.

## 1. Introduction

During some decades dye lasers keep on the position of main source of continuously tunable radiation of optical range for a number of applications such as remote probing, isotope separation, and highly sensitive analytical spectroscopy. Currently in novel areas of quantum electronics namely in laser physics of micro- and nanostructures [1], molecules of laser dyes are frequently used as activators or light pulse converter [2]. Amount of publications devoted to medical and biological applications of lasers for red and near infrared (NIR) spectral ranges as well as sensitizing dyes for diagnostics in these regions of the spectrum is increased [3,4] since penetration depth in the living tissue for this range is a centimetre or more. Very frequently harmonics of yttrium aluminum garnet laser (YAGL) are employed for pumping of these lasers [5].

The goal of the present work was to fabricate active medium for dye laser tuned in the range overlapping the entire red and neighbouring NIR regions under excitation with the green monochromatic radiation near the line of frequency-doubled YAGL.

## 2. Tunable laser with energy transfer in active medium

The donor-acceptor couple of the laser dyes studied earlier [6, 7] has been selected. Benzopyrane derivative — LD1 dye [6] that has high quantum yield of fluorescence ($q$) and high laser efficiency under pumping near 530 nm was used as a donor. Its own tuning range is located in short-wave side of the actual spectral range. The laser dye LD703 synthesized at D.Mendeleyev Moscow Chemical Technological Institute [8] was employed as an acceptor. LD703 generates laser radiation in long-wave zone of this range under pumping near maximum of its absorption spectrum $\lambda_m^a = 620$ nm [7]. When LD703 solution was excited by radiation of the green spectrum, its laser action was absent because of low absorptance of LD703 in this spectral region. A solvent recommended by authors [8] — acetonitrile was used in all our examination. Our previous measurements of fluorescent characteristics of selected dyes [6, 7] have showed that they have high enough quantum yield of fluorescence in acetonitrile: $q_{\text{LD703}} = 0.61$, $q_{\text{LD1}} = 0.97$.

Measuring of tuning range for examined dyes and their mixtures was fulfilled in laser with diffraction grating (LDG). The diffraction grating of 1200 lines/mm and wideband dielectric mirror with reflection factor $R \geq 98$ % formed the laser cavity. Output of laser radiation was realized via zeroth order of the diffraction grating by means of a 90°-prism with total reflection. The experimental setup was described in detail in [7, 9]. The LDG was excited transversely to the axis of its cavity by radiation of flashlamp-pumped dye laser (FLPDL) with wavelength $\lambda_p = 530$ nm. Neutral ethanol solution of iminocoumarin G283 [6] was used as active media of the FLPDL. Output energy of the FLPDL was monitored with standard unit of IMO-2N type (Russia). The FLPDL radiation was focused in a strip of ~ 0.5 mm width on lateral surface of the LDG cell in parallel to its axis by cylindrical quartz lens with $F = 110$ mm. Laser spectra of LD1 dye and the mixtures of LD1 and LD703 dyes were registered by spectrograph with an UF-90 camera, a 1200 lines/mm gitter, and taking camera of EOS 400D DIGITAL type. Reciprocal dispersion of the spectrograph in the tuning range of the LDG was ~ 6.22 Å/mm.

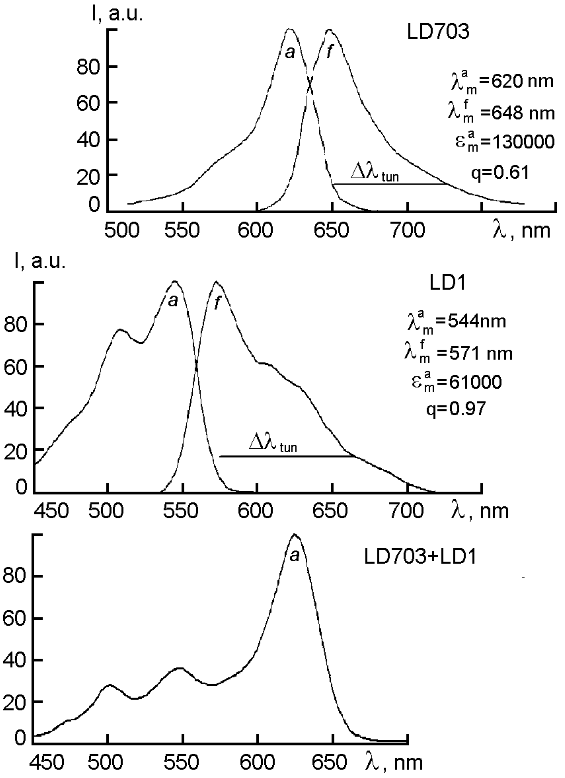
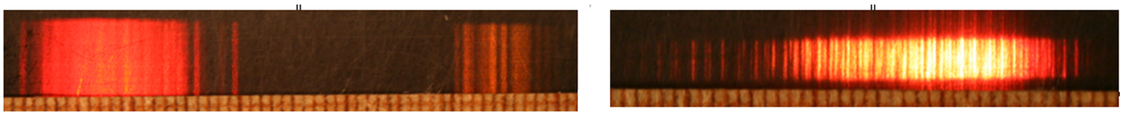


Fig. 1. Absorption ($a$), fluorescence ($f$) spectra, and laser tuning range ($\Delta\lambda_{tun}$) of the dyes in acetonitrile. Tuning range in the top spectra was obtained for mixture of LD703 and LD1 under pumping $\lambda_p = 530$ nm and that in the middle spectra — for LD1 taken separately. The bottom spectrum is absorption one of the laser working mixture.

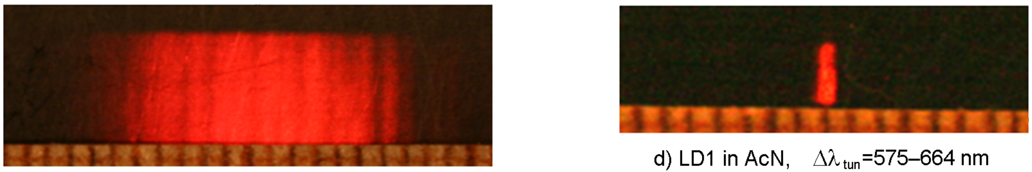
Fig. 1 shows the spectra of absorption and fluorescence of each of the dyes dissolved in acetonitrile separately (two upper spectra) and absorption spectrum of the working mixture that was used in the LDG (lower spectrum). The absorption spectra were recorded with a HITACHI-U-3210 spectrophotometer and fluorescence spectra and their quantum yields with a HITACHI-F-4010 fluorometer [7]. One can see that fluorescence spectrum of the donor (LD1) has a good overlapping with absorption spectrum of the acceptor (LD703).

For the purpose of expansion of continuous tuning range of the LDG some solutions with different concentrations of LD1 and LD703 dyes in mixture have been proved. We had previously determined [7] for used pumping system of laser with non-selective cavity (LNSC) that the optimal value of absorption coefficient of its active solution at pumping wavelength $\lambda_p$: $k_{opt}(\lambda_p) \approx 10$ cm$^{-1}$.



a) LD1 (0.167 mM in MeOH), $\lambda^{c}_{las1}$=616 nm, $\lambda^{c}_{las2}$=593 nm

c) LD1(0.134mM)+LD703(0.201mM) in AcN $\lambda^{c}_{las}$=679 nm



b) LD1(0.407 mM in AcN), $\lambda^{c}_{las}$=614 nm

d) LD1 in AcN, $\Delta\lambda_{tun}$=575–664 nm
LD1(0.134 mM)+LD703(0.201 mM)
in AcN: $\Delta\lambda_{tun}$=660–731 nm

Fig. 2. Spectrograms of LD1 and LD703 dyes lasing in the LNSC (a, b, c) and in the LDG (d): solvents — methanol (MeOH), acetonitrile (AcN), $\lambda^{c}_{las}$ — central laser wavelength in the LNSC, $\Delta\lambda_{tun}$ — tuning range of the LDG.

This value was reference since the optimal concentration of the solution $C_{opt} = k_{opt}/\varepsilon(\lambda_p)$, where $\varepsilon(\lambda_p)$ — the dye molar extinction at $\lambda_p$. In addition, we assumed that pumping wavelength for the donor dye: $\lambda_p^d$ = 530 nm, and one for acceptor LD703 conforms to maximum of the donor fluorescent band: $\lambda_p^a = \lambda_{fl}^d$ = 544 nm.

We have estimated the quantum efficiency of donor-acceptor energy transfer $\eta_{d\text{-}a}$ in the working laser dye mixture by metering of output energy of this mixture in the LNSC with two wideband dielectric mirrors ($R_1 \approx$ 99 %, $R_2 \approx$ 60 %). The dye mixture in LNSC was excited at $\lambda_p \approx$ 530 nm by the FLPDL transversely to the axis of this cavity. Then in the same conditions output laser energy of solution containing only donor LD1 dye with the same concentration as in the mixture have been measured. As a result of metering of the output energies and central laser wavelengths we have evaluated for selected couple of the dyes magnitude of $\eta_{d\text{-}a} \approx 0.9$.

Laser emission spectrograms of studied dyes in the LNSC and the LDG are shown in Fig. 2. Note, that two band lasing of LD1 dye in alcohol solutions (Fig. 2a) as it was earlier demonstrated in [6], is caused by presence of two forms of its molecule in the excited state. For acetonitrile solution of LD1 with concentration of 0.407 mmole/l laser spectrum is single-band (Fig. 2b), that is indicates presence of one form of LD1 molecule in aprotic polar acetonitrile only.

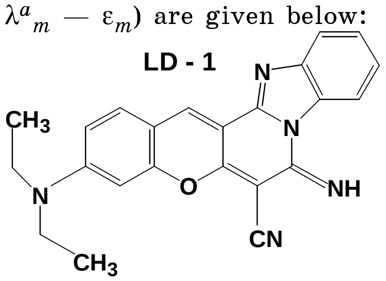
As measurements of the laser spectra of the dyes in the LDG have showed (Fig. 2d), acetonitrile solution of LD1 (0.41 mmole/l) generated radiation in the range of 575–664 nm ($\Delta\lambda_{tun}$ = 89 nm), and the dye mixture of LD1 (0.14 ÷ 0.24 mmole/l) + LD703 (0.13 ÷ 0.20 mmole/l) — in the range of 660–734 nm ($\Delta\lambda_{tun}$ = 74 nm). At the same time middle value of the width of the LDG emission spectrum at level 0.1 was $\Delta\lambda_{0.1}$ = 0.5 nm.

Thus continuous tuned laser radiation from yellow spectrum region to near IR one and covered the range of $\Delta\lambda_{tun}$ = 159 nm under pumping with 530 nm green line have been realized using two laser dyes with ability of radiation energy transfer between them in active media of tunable laser.

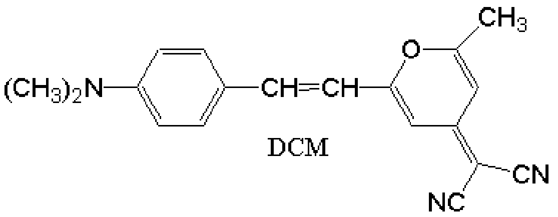
## 3. Solvent effect on characteristics of tunable dye-mixture laser

Utilization of the mixture of dyes with donor-acceptor mechanism of pump energy transfer results in expansion of laser tuning range in long-wavelength spectrum region. However, tuning spectrum of donor dye gets narrow in short-wave part of its fluorescence band because of self-absorption in the working mixture as a result of overlapping donor fluorescent spectrum and acceptor absorption one. Tuning range of the dye-mixture laser may be widen if one will match such couple of dyes that absorb in the close spectral regions near wavelength of pumping and their fluorescence spectra have essentially different Stokes shift. As a result, the fluorescent band of the dye mixture expands.

We used LD1 dye [6] and DCM (ALDRICH) [10] as such couple of the dyes for red range of the spectrum. At first methanol has been selected as a solvent since it was earlier employed for these laser dyes [6, 10]. Formulas of the dyes and characteristics of their methanol solutions that we have measured (the wavelengths of maxima of absorption $\lambda^a{}_m$, fluorescence $\lambda^f{}_m$, quantum yield of the last — $q$, and extinction at $\lambda^a{}_m$ — $\varepsilon_m$) are given below:



$\lambda^a_m$=547 nm, $\varepsilon_m$ = 61000 l·mole$^{-1}$·cm$^{-1}$,
$\lambda^f_m$ = 572 nm, $q$ = 0.96.



$\lambda^a_m$= 472 nm, $\varepsilon_m$ = 43000 l·mole$^{-1}$·cm$^{-1}$, $\lambda^f_m$ = 615 nm, $q$ = 0.39.

Output laser energy and spectral characteristics of these dyes and their mixtures have been measured in the setup described in the previous section. Excitation of solutions in the LNSC and the LDG was produced by the FLPDL with ethanol solution of coumarin C314 (concentration $C_{C314}$ ~ 0.2 mmole/l). Central wavelength of pumping was $\lambda_p$ = 507 nm and halfwidth of pump spectrum ~ $\Delta\lambda_{0.1}$ = 3 nm at the level of 0.1 of the maximum.

Energy of pumping the studied dyes and their mixture in the LNSC was monitored with an IMO-2N measurer and their output energy of lasing was measured by pulse photometer of the FOG type (Russia). For extension its dynamic range a set of calibrated neutral filters was used. The fulfilled measurements of dependence of laser energy of methanol solutions of the dyes in the LNSC on their concentrations showed that DCM yielded to LD1 essentially in laser efficiency under used pump duration $\tau_p$ ~ 1.5 μs. Though earlier under nanosecond duration of pump by copper vapor laser [11] or 2nd harmonic of $Nd^{3+}$:YAG laser [12] DCM have laser output comparable with Rhodamine 6G and yielded to the last 15–20 % only. Probably under pump of microsecond duration an influence of generating DCM molecule form "twisted" around its double or single C–C bonds [13] in the excited $S_1$ state on the non-radiating deactivation of $S_1$ state was increased. This *cis*-form quenches the fluorescence of DCM dye [13]. Nevertheless, laser emission of methanol solutions of DCM in the range of 605–670 nm ($\Delta\lambda_{tun}$ = 65 nm) and of the dyes mixture of DCM + LD1 in the range of 595–665 nm ($\Delta\lambda_{tun}$ = 70 nm) was obtained in the laser with diffraction grating (Fig. 3a).

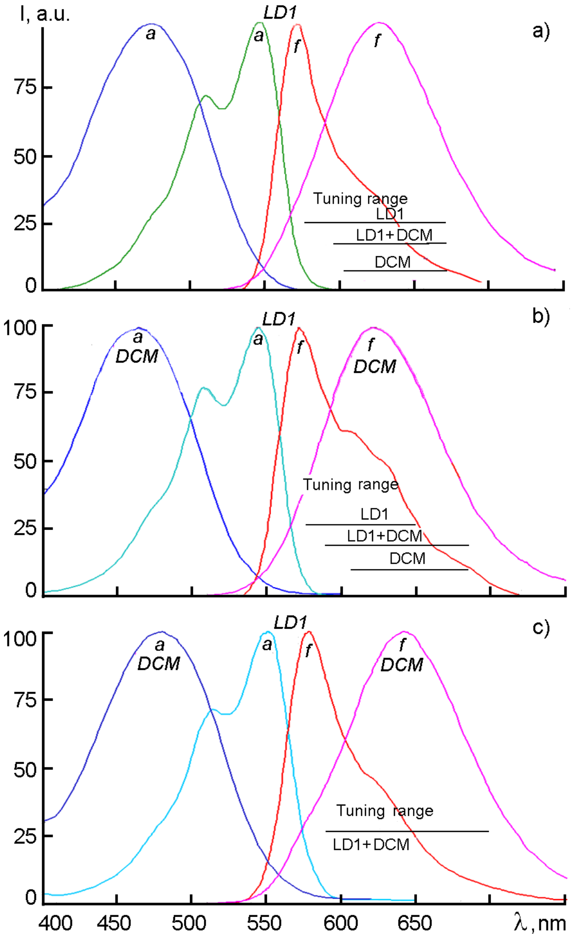


Fig. 3. Absorption (a), fluorescence (f) spectra, and laser tuning range ($\Delta\lambda_{tun}$) of DCM and LD1 dyes in methanol (a), acetonitrile (b), and dimethylsulfoxide (c).

Authors [14] showed that DCM quantum yield in solution increased when methanol was replaced by acetonitrile (AcN) and achieved the maximum in dimethylsulfoxide (DMSO). The last has a high polarity, and

Table 1. Spectroscopic features of the dyes

| Dye | LD1 | | | | | DCM | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | $\lambda^a_m$, nm | $\varepsilon_m \cdot 10^{-3}$ | $\lambda^f_m$, nm | $q$ | $\Delta\nu^{St}$, cm$^{-1}$ | $\lambda^a_m$, nm | $\varepsilon_m \cdot 10^{-3}$ | $\lambda^f_m$, nm | $q$ | $\Delta\nu^{St}$, cm$^{-1}$ |
| MeOH | 547 | 61 | 572 | 0.96 | 800 | 472 | 43 | 630 | 0.39 | 5300 |
| AcN | 544 | 60 | 571 | 0.97 | 870 | 463 | 43.5 | 622 | 0.45 | 5500 |
| DMSO | 552 | 55 | 578 | 1.0 | 810 | 480 | 45 | 643 | 0.50 | 5280 |

92 % of molecules of the DCM dye exist within DMSO in coplanar trans-form.

For optimization of operating solutions of the selected dyes in acetonitrile and dimethylsulfoxide for tunable laser we have at first measured their absorption and fluorescence spectra. Solvents that we used were "chemically pure" grade (CROWN) and were not additionally purified. Absorption spectra and value of extinction at the maximum of spectrum were measured with a VSU2-P spectrophotometer (Germany), fluorescence spectra and its quantum yield — with a FluoroMax-4 (USA) spectrofluorimeter. For measuring of absorptions characteristics we prepared solutions with optical density at maximum — $D_{max} \approx 1.0$ and fluorescence one — with optical density at extinction wavelength $D_{ex} \approx 0.02$. We used methanol solution of LD1 dye for that $q$ = 0.96 [15] as reference for calculation of value $q$.

The spectrofluorimeter being used allowed to record corrected spectra i.e. taking into account the compensation of spectral responsivity of the "monochromator-photodetector" system. Quantum yields (at room temperature) were calculated by formula:

$$q = q_0 \cdot \frac{D_0}{D} \cdot \frac{\Sigma}{\Sigma_0} \cdot \frac{n^2}{n_0^2}. \qquad (1)$$

Here $q$ and $q_0$ — fluorescence quantum yields of sample measured and reference, respectively; $D$ and $D_0$ — optical densities of solutions at wavelength of excitation; $\Sigma$ and $\Sigma_0$ — area under curves of corrected fluorescence spectra; $n$ and $n_0$ — the refractive indexes of solvents (the indices "0" refer to reference).

Spectral features of the dyes measured and calculated are adduced in the Table 1 and absorption and fluorescence spectra of DCM dye in methanol (MeOH), acetonitrile (AcN), and dimethylsulfoxide (DMSO) are shown in Fig. 4.

Comparing spectral characteristics of the dyes in the Table 1, we note that Stokes shift value $\Delta\nu^{St}$ between the absorption and fluorescence maxima for DCM is six times more than for LD1. This indicates that dipole moment $D_{S1}$ of DCM molecule in the first exited state $S_1$ increases essentially and one of LD1 changes weakly. According to [16] for DCM $D_{S1}$ = 20 D. Electrical parameters of used solvents are presented in Table 2.

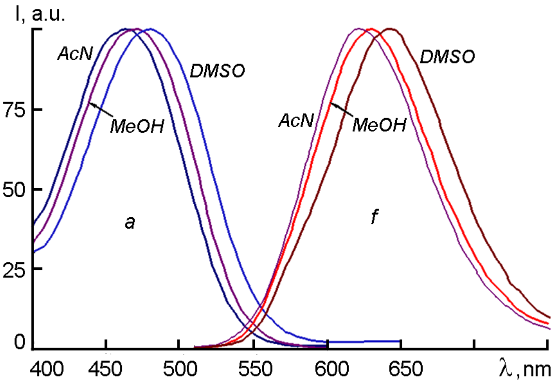


Fig. 4. Absorption (a), fluorescence (f) spectra of DCM dye in acetonitrile (AcN), methanol (MeOH), and dimethylsulfoxide (DMSO).

Fig. 4 shows that there is bathochromic shifts of DCM absorption and fluorescence spectra at change of acetonitrile to methanol and then to DMSO. In this connection these shifts for methanol is caused by "specific" intermolecular interactions [17] owing to its low values of $D$ and $\varepsilon$, and for DMSO the main role perform the "universal" interactions at the expense of Van der Waals forces.

Table 2. Electrical features of the solvents

| Solvent | $D$, D | $\varepsilon^*$ | Type |
|---|---|---|---|
| MeOH | 1.664 | 32.63 | Polar, protonic |
| AcN | 3.37 | 37.5 | Polar, aprotonic |
| DMSO | 3.96 | 45 | Bipolar, aprotonic |

* ε — dielectric permittivity at 20–25° C.

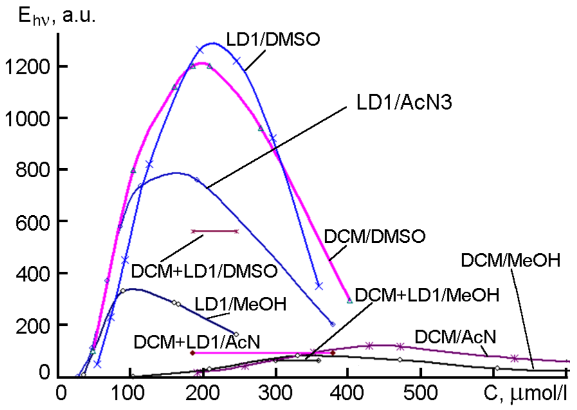


Fig. 5. Output laser energy of the dyes and its mixtures in methanol (MeOH), acetonitrile (AcN), and dimethylsulfoxide (DMSO) in non-selective cavity versus dye concentration.

It should be noted that if for LD1 the quantum yield in all used solvents does not practically change and near the unit then for DCM it has minimal value in protonic methanol (our measurement $q_{\mathrm{MeOH}} = 0.39$) and maximal — in aprotic bipolar DMSO ($q_{\mathrm{DMSO}} = 0.50$).

As mentioned above possibility of forming conformation of DCM molecule twisted around single C–C bond with intramolecular charge transfer — TICT-conformation causes fluorescence quenching as a result of non-radiating transitions. The "specific" interactions with forming hydrogen bounds [18] play an important role in this process.

On the grounds of the obtained spectroscopic data of LD1 and DCM dyes in various solvents we have prepared their solutions for laser measurements. For determination of the optimal dye concentration $C_{opt}$ in active solution of the tunable laser we have measured dependence of output laser energy of the LNSC on concentration of single-component dye solutions and their mixtures for three solvents (Fig. 5). During measurement of the LNSC output energy by the FOG unit the pump energy — the FLPDL output one was monitored with the IMO-2N meter and kept standing at 150 ± 5 mJ.

The measurement accuracy of dependences in Fig. 5 was equal about 15 % and it was estimated from statistical straggling of the LNSC output energy value measured. The main contribution for this fallibility has been given by jitter of the FLPDL output energy and the FOG aspect scatter. Results shown in Fig. 5 are well concordant with fluorescence measurements. Laser output energy of DCM dye and it mixtures with LD1 increases accordingly to rise of DCM quantum yield. Under using of optimal concentrations $C_{opt}$ for operating solutions of the LDG the next laser tuning ranges were realized in acetonitrile solution of LD1 — 580–660 nm ($\Delta\lambda_{tun} = 80$ nm), DCM — 606–678 nm ($\Delta\lambda_{tun} = 72$ nm), and their mixture — 591–677 nm ($\Delta\lambda_{tun} = 86$ nm) (Fig. 3b). The maximal tuning range for single solution has been accomplished with dye mixture of LD1 and DCM in dimethylsulfoxide — 592–687 nm, $\Delta\lambda_{tun} = 95$ nm (Fig. 3c).

## 4. Conclusion

Thus the exploration fulfilled have showed that for creation of source tuned throughout the red and NIR ranges of the spectrum one can use mixtures with pumping energy transfer between the active molecules as well as those with broadened fluorescence spectrum. In this connection the solvent surroundings have a considerable impact on spectral-energy characteristics of dye-mixture laser. The measurements of output laser energy performance of the dyes mixtures in non-selective cavity have displayed the high quantum efficiency of energy transfer for the first couple ~0.9 and permitted to determine the optimal concentration proportion for the second one. Continues tuning laser emission from the yellow region — 575 nm to NIR one — 734 nm has been fulfilled for selected dyes and their mixtures under laser pump of the green spectrum radiation. In conclusion author thanks Dr.Yu.A.Gurkalenko for help in measuring fluorescence spectra of laser dyes.

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# Спектральні характеристики активного середовища лазера на барвниках, що перестроюється

### *В.В.Маслов*

З метою розширення діапазону перестроювання лазера для червоної області досліджено і проаналізовано спектральні та флуоресцентні характеристики сумішей двох пар лазерних барвників. В першій парі використовується передача енергії монохроматичної накачки від донора до акцептора. Друга пара барвників має спектри поглинання в сусідніх областях, поблизу довжини хвилі накачування, але їх спектри флуоресценції мають суттєво різний Стоксів зсув. Результатом цього є розширення смуги флуоресценції суміші барвників. Суттєвий вплив розчинника на флуоресцентні та лазерні характеристики виявлено для другої пари барвників. Вимірювання квантового виходу флуоресценції цих барвників показало, що для одного з них — DCM, цій параметр найбільший в апротонному біполярному диметилсульфоксиді та найменший у протонодонорному метанолі. При лазерному накачуванні вибраних барвників та їх сумішей здійснено безперервне перестроювання лазера від 575 нм до 734 нм.