Energy transfer in solid-state dye lasers based on methyl methacrylate co-doped with sulforhodamine B and crystal violet

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Laser action in methyl methacrylate (MMA) co-doped with sulforhodamine B and crystal violet dyes was investigated. The dye mixture was incorporated into a solid polymeric matrix and was pumped by a 532-nm Nd:YAG laser. Distributed feedback dye laser (DFDL) action was induced in the dye mixture using a prism arrangement both in the donor and acceptor regions by an energy transfer mechanism. Theoretically, the characteristics of acceptor and donor DFDLs, and the dependence of their pulse widths and output powers on acceptor–donor concentrations and pump power, were studied. Experimentally, the output energy of DFDL was measured at the emission peaks of donor and acceptor dyes for different pump powers and different acceptor–donor concentrations. Tuning of the output wavelength was achieved by varying the period of the gain modulation of the laser medium. The laser wavelength showed continuous tunability from 563 nm to 648 nm.

Keywords: sulforhodamine B, crystal violet, distributed feedback dye laser, solid state distributed feedback dye laser

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1. Introduction

Solid-state dye lasers (SSDLs) have attracted much attention during the past few decades because of their technical and economical advantages over the classical liquid dye lasers. The advantages include low cost, high efficiency, and a wide spectrum range compared with other tunable laser sources. Consequently, SSDLs based on polymeric materials,[1–4] sol–gel derived glasses,[5,6] and composite materials[7–9] have generated extensive research interest. Great progress in the performance of SSDLs has been made in recent years by using different host matrices such as fluorinated polymers,[10,11] organic–inorganic hybrid materials,[12–14] and nano-particle dispersed polymers,[15–17] especially in longevity. The studies of the photodegradation mechanisms[18,19] and other research, such as miniaturized cavity designs and surface emitting lasers[20–23] also contribute to the efforts for generating highly efficient, long lasting, and broadly tunable organic lasers for practical applications. Among these, distributed-feedback (DFB) lasers based on sol–gel and polymeric thin films have been extensively investigated.[24–30] Instead of a conventional resonator cavity, the optical feedback is provided via backward Bragg scattering from periodic perturbations of the refractive index and the gain of the laser medium.[24–30] This mechanism results in the generation of short pulses with a narrow linewidth, thus the DFB lasers become attractive compact coherent light sources. When a nanosecond or sub-nanosecond pulse of laser is pumped into a DFB structure, sequences of laser pulses in picoseconds are generated by the phenomenon of relaxation oscillation. Using nanosecond and/or sub-nanosecond pulses as the pump source, a DFB structure could generate pulses 20 to 100 times shorter than the pump pulse.[31,32] This significant pulse shortening is caused by self Q-switching, which is due to the spatial gain modulation dependence of the feedback.

Although a number of long-wavelength-emitting commercial dyes are available, which have reasonable efficiencies, these dyes have two important drawbacks: low absorption at the pumping wavelength and/or rather poor photostability. One approach to overcome these drawbacks is to use a mixture of dyes in a system based on an energy transfer process between the dye molecules.[33–35] This system needs two dyes: one (donor) efficiently absorbs the pump radiation at 532 nm and transfers the excitation energy to the second (acceptor) dye, which emits at long wavelengths. This energy transfer dye laser system has the advantage of being tunable to any desired wavelength by means of only one pumping source. For a particular donor–acceptor (D–A) pair, it is possible to make both the donor and the acceptor lase at their respective gain regions due to the energy transfer mechanism. If such a dye mixture is taken as the active medium in DFDLs, ultra-short pulses tunable over the entire gain spectrum of donor and acceptor dyes are generated.[36–39] Yang *et al.*[30] have reported that by using the optimized dye pair combinations, improved DFB laser performance can be achieved. Since little work has been done on solid-state dye lasers based on dye mixtures for reasonable lasing tunability, an attempt has been made to im-

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prove the lasing performance. Hence it is proposed to study energy transfer solid-state dye lasers using dye mixtures for extended tunability and photostability.

In the present work, laser action in methyl methacrylate (MMA) co-doped with sulforhodamine B and crystal violet dyes is investigated. The laser dye co-doped thin films are fabricated by dip-coating, and their waveguiding parameters, such as the refractive index and film thickness, are studied. The energy transfer between the co-doped laser dyes and DFB laser action are observed under the excitation of a 532 nm Nd:YAG pump laser source. The characteristics of donor and acceptor DFDLs as well as the dependence of their pulse widths and output powers on various pump powers and donor–acceptor concentrations are studied by theoretical simulations. Experimentally, the output energy of the DFDL has been measured at the emission peaks of donor and acceptor dyes for different pump powers and different acceptor concentrations, and tunability is observed in the 563–648 nm range using a prism arrangement.

2. Theoretical studies

The active medium of energy-transfer DFDLs is a mixture of two dyes (sulforhodamine B or SRB, the donor; crystal violet or CV, the acceptor). Upon optical pumping, the donor dye molecules absorb the pump energy, get excited, and then relax by transferring the energy to the acceptor dye molecules. Thus through the energy transfer, the acceptor dye molecules are excited indirectly.

The main mechanisms for intermolecular singlet–singlet electronic energy transfer in D–A pairs may be radiative or non-radiative (Forster type). Thus, the two types of energy transfer mechanisms are (i) radiative energy transfer, involving the emission of a photon by the donor molecule and its subsequent absorption by the acceptor molecule, and (ii) radiationless (Forster type) energy transfer, due to the interactions between the donor and acceptor molecules during the excitation lifetime of the donor prior to the emission of a photon. The radiationless energy transfer occurs by one of the following two mechanisms: 1) diffusion-controlled collision and transfer, which occurs over intermolecular distances of the order of molecular distances; this mechanism is dependent on the solvent viscosity and temperature;[40] 2) resonance transfer due to long-range dipole interactions, in which the energy transfer occurs at much greater donor–acceptor distances than the collisional diameters. A good overlap of donor emission spectrum and acceptor absorption spectrum is required for the radiative transfer and resonance transfer due to the long-range dipole interactions. The radiative energy transfer mechanism is common in dilute solutions, and its occurrence cannot be ignored in the studies of radiationless energy transfer. By measuring the donor fluorescence lifetime as a function of the acceptor concentration, it is possible to predict which of the two energy transfer mechanisms has occurred; if the donor lifetime is slightly affected by the concentration of the acceptor molecules, the radiative energy transfer mechanism is dominant.[41]

2.1. Results and discussion

A rate equations model described in Refs. [36]–[38] has been used to study the behavior of the dye mixture doped with MMA. The model uses both the radiative and Forster types of energy transfer. The fourth-order Runge–Kutta method has been used to solve the rate equations model. The spectral parameters of SRB and CV have been determined from the observed absorption and fluorescence spectra. The spectral parameters used in the rate equations model are shown in Table 1.

Table 1. Spectral parameters of SRB and CV used in the rate equations model.

Symbol	Definition	Value
τ_d	donor lifetime	2.9 ns
τ_a	acceptor lifetime	2.5 ns
R_0	critical transfer radius	33.71 Å
C_0	critical concentration	6.23×10^{18} cm^{-3}
$C_{1/2}$	half quenching concentration	3.06×10^{18} cm^{-3}
k_F	Forster type transfer rate	1.126×10^{-10} cm^3/s
σ_{pd}	absorption cross-section of donor dye at pumping wavelength 532 nm	2.237×10^{-16} cm^2
σ_{pa}	absorption cross-section of acceptor dye at pumping wavelength 532 nm	0.335×10^{-16} cm^2
σ_{edl}	emission cross-section of donor dye molecules at lasing wavelength $\lambda_l = 591.2$ nm of donor	9.564×10^{-16} cm^2
σ_{aal}	ground-state absorption cross-section of acceptor dye molecules at lasing wavelength $\lambda_l = 591.2$ nm of donor	0.465×10^{-16} cm^2
σ_{eal}	emission cross-section of acceptor dye molecules at lasing wavelength $\lambda_l = 591.2$ nm of donor	2.93×10^{-16} cm^2
σ_{eaa}	emission cross-section of acceptor dye molecules at lasing wavelength $\lambda_a = 612$ nm	5.47×10^{-16} cm^2
L	length of the transversely excited region	0.9 cm
b	height of the transversely excited region	0.02 cm
c	speed of light	3×10^{10} cm^{-1}
n	refractive index of the solvent	1.328
n_p	refractive index of the prism	1.52
V	visibility of the interference pattern	0.4
S	spectral factor contributing spontaneous emission	10^4
Ω_d	factor determining the fraction of the spontaneously emitted photons by excited donor dye molecules	1.95×10^{-9}
Ω_a	factor determining the fraction of the spontaneously emitted photons by acceptor dye molecules	0.39×10^{-7}

The donor dye (SRB) molecules emit laser radiation in the range of 563–598 nm with the emission peak at 591.2 nm. Similarly, the acceptor dye (CV) molecules emit laser radiation in the range of 590–648 nm with the emission peak at 612 nm.

The DFDL output as a function of pump power and donor and acceptor concentrations at lasing peak wavelengths have been studied using computer simulations. Just above the threshold pump power, a single DFDL pulse is emitted. With increasing pump power/donor concentration, the output power of the single DFDL pulse increases and the pulse width decreases. At the same time, the DFDL pulse is found to emerge earlier than the DFDL pulse emitted with low pump power/donor concentration.[42,43] This is due to a faster inversion of population with the increase of pump rate. Above a certain pump power/donor concentration, the second DFDL pulse emerges. Calculations show that for higher pump power/donor concentration, the DFDL pulse appears earlier with respect to the peak of the pump pulse, as illustrated in Figs. 1–4. As the concentration of the donor molecules increases, the effective distance between the donor molecules decreases, leading to the energy transfer within the donor system itself.[44]

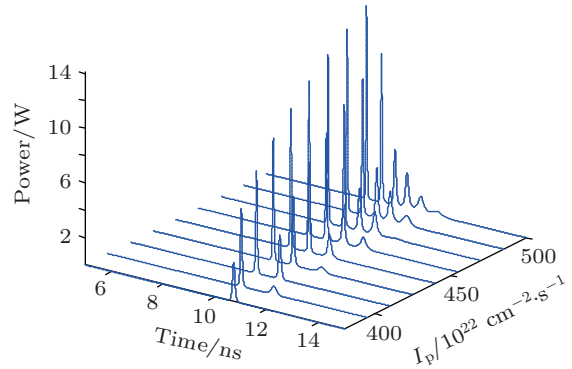


Fig. 1. (color online) Variation in pulse width and peak output power of donor DFDL at fixed concentrations of donor ($N_d = 1.8 \times 10^{18}$ cm^{-3}) and acceptor ($N_a = 0.6 \times 10^{18}$ cm^{-3}) for different pump intensities.

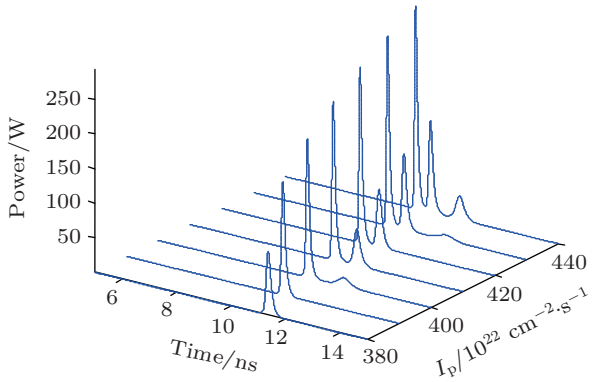


Fig. 2. (color online) Variation in pulse width and peak output power of acceptor DFDL at fixed concentrations of donor ($N_d = 1.8 \times 10^{18}$ cm^{-3}) and acceptor ($N_a = 0.6 \times 10^{18}$ cm^{-3}) for different pump intensities.

Nevertheless, the DFDL emission at the donor wavelength depends on the acceptor concentration. With an increase in the acceptor concentration, the number of DFDL pulses at the donor wavelength decreases, and the output power of a single pulse decreases with an increase in the pulse width (Fig. 5). As a result, the DFDL pulse emerges late. But, in the case of DFDL emission at the acceptor wavelength, as the acceptor concentration increases, both the number of DFDL pulses and the peak power are found to increase with a decrease in the pulse width due to the reabsorption occurring in the acceptor system (Fig. 6).

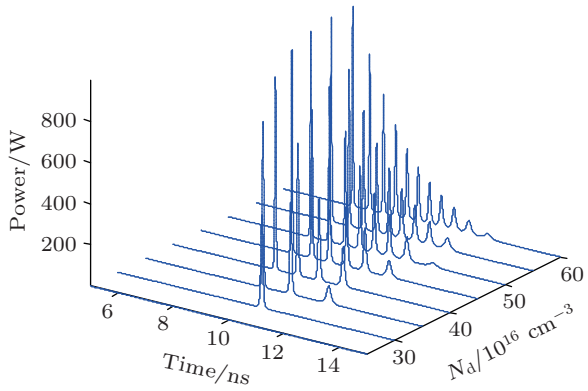


Fig. 3. (color online) Variation in pulse width and peak output power of donor DFDL at fixed acceptor concentration $N_a = 0.6 \times 10^{18}$ cm^{-3} and pump intensity $I_p = 0.8 \times 10^{22}$ cm^{-2}·s^{-1} for different donor concentrations.

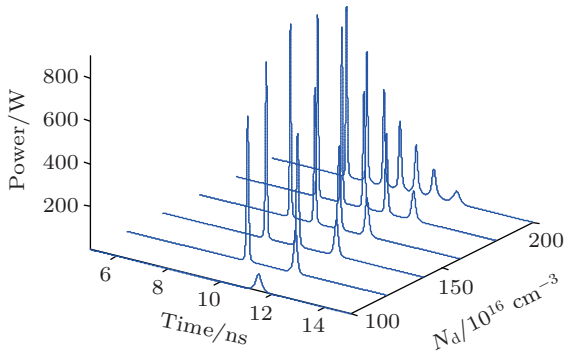


Fig. 4. (color online) Variation in pulse width and peak output power of acceptor DFDL at fixed acceptor concentration $N_a = 0.6 \times 10^{18}$ cm^{-3} and pump intensity $I_p = 0.8 \times 10^{22}$ cm^{-2}·s^{-1} for different donor concentrations.

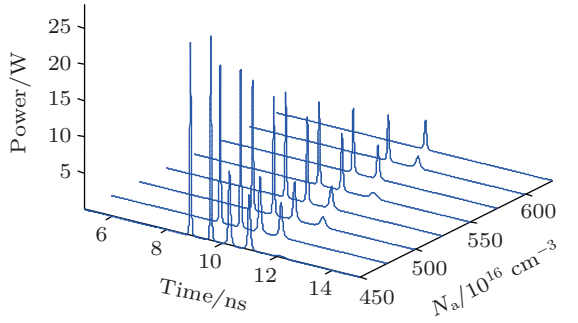


Fig. 5. (color online) Variation in pulse width and peak output power of donor DFDL at fixed donor concentration $N_d = 1.8 \times 10^{18}$ cm^{-3} and pump intensity $I_p = 0.4 \times 10^{22}$ cm^{-2}·s^{-1} for different acceptor concentrations.

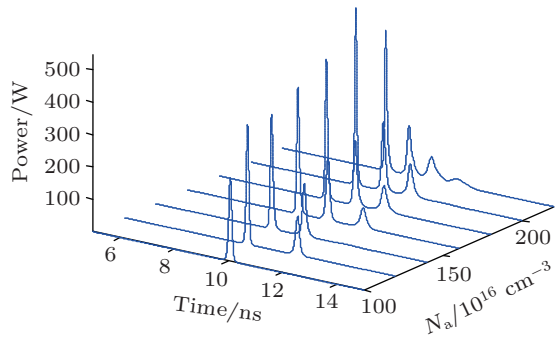


Fig. 6. (color online) Variation in pulse width and peak output power of acceptor DFDL at fixed donor concentration $N_d = 1.8 \times 10^{18}$ cm^{-3} and pump intensity $I_p = 0.4 \times 10^{22}$ cm^{-2}·s^{-1} for different acceptor concentrations.

From the data generated, the output energy has been calculated by multiplying the peak power with its pulse duration (FWHM) for a single pulse. For a chain of pulses, the total output energy has been found by summing up individual pulse energies. From our results, it is found that the output energy increases with increasing pump power/donor concentration but decreases with increasing acceptor concentration.

3. Experimental studies

3.1. Materials

Dyes SRB and CV of laser grade and MMA were purchased from Sigma-Aldrich, and the ethanol used was of spectroscopic grade. General formulae and structures of SRB (C.I 45100), CV (C.I 45010), and MMA are shown in Fig. 7. A *Q*-switched Nd-YAG laser (Spectra Physics, USA) with a pulse width of 6 ns and a repetition rate of 10 Hz was used to pump the DFDL. The absorption and emission spectra of the dyes at

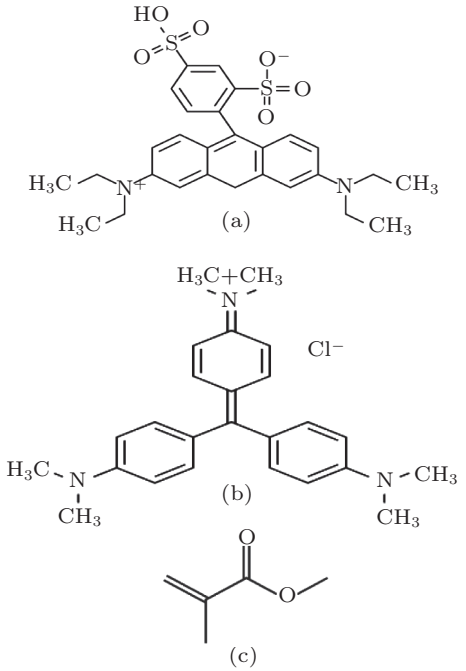


Fig. 7. (color online) Molecular formulae and chemical structures of (a) SRB ($C_{27}H_{29}N_2NaO_7S_2$), (b) CV ($C_{25}H_{30}N_3Cl$), and (c) MMA ($C_5H_8O_2$).

0.01 mM concentration were measured by using a spectrophotometer (ELCO, India) and a spectrofluorometer (Fluoromax II, USA), respectively.

3.2. Absorption and fluorescence spectra

Dyes SRB and CV in ethanol show wide absorption and fluorescence emission bands (Fig. 8). The fluorescence spectra of SRB overlap with the absorption spectra of CV, allowing electronic energy to transfer from one dye to the other.

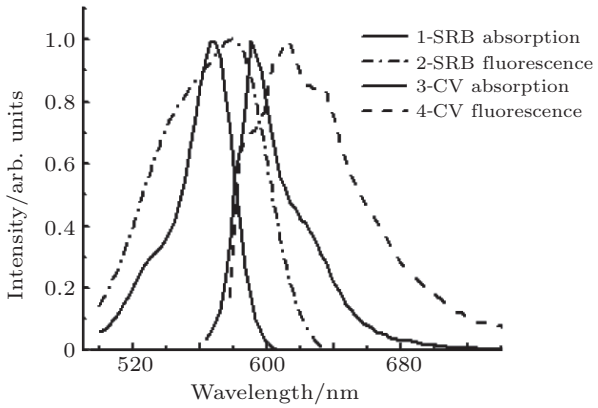


Fig. 8. Absorption and fluorescence spectra of SRB and CV.

3.3. Preparation of dye-doped polymer

The dye-doped polymer was prepared by thermal polymerization. A mixture of MMA and ethanol (4:1) in a solution of SRB (3 mM) and CV (1 mM) was prepared. Benzoyl peroxide (3 mg per 100 ml of the solution) was added to initiate polymerization. The solution was kept inside a thermostat-controlled water bath maintained at 80 °C. A polymer in gel form was obtained within 2 h. By a dip-coating method, the gel was coated on one side of a prism and dry fixed. The thickness and refractive index of the film were found to be 180 μm and 1.40, respectively.

3.4. Experimental set-up

The experimental set-up comprising the thin-film dye-coated prism and the frequency-doubled Nd:YAG laser is shown in Fig. 9(a). An isosceles right-angled quartz prism, to obtain a distributed feedback for the dye laser, is seen in this configuration. A cylindrical quartz lens (focal length 5 cm) will focus the pumped beam into a line image incident on the hypotenuse *AB* of the prism. The light transmitted by the hypotenuse is totally reflected from side *AC* of the prism, interfering with the dye film and forming fringes (Fig. 9(b)), resulting in the periodic modulation of the refractive index and gain of the active medium. The feedback thus will be obtained by the means of reflection (Braggs scattering) from the periodic structure incorporated throughout the active medium. With this arrangement, a transversely excited pumped region of width 0.02 cm will be generated in the dye-coated prism.

When pumped by the light of wavelength λ_p incident at an angle θ on the active medium, the DFDL wavelength[45] is given by

$$\lambda_{DFDL} = n\lambda_p / n_p \sin\theta.$$

Here n and n_p are the refractive indices of the dye solution and the prism material, respectively.

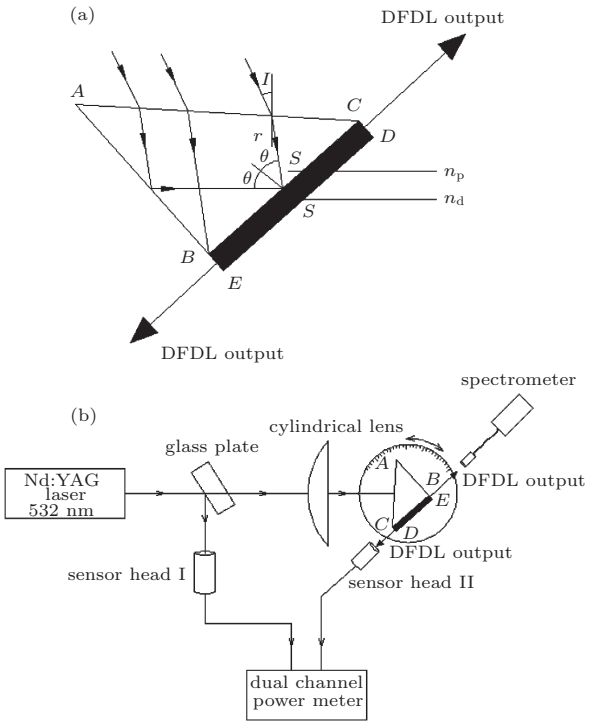


Fig. 9. (a) Thin-film coated dye prism. (b) Experimental set-up for prism DFDL.

3.5. Output measurements

3.5.1. Energy characteristics

Using a dual-channel power meter (EPM 2000; Coherent Molectron, USA), the output energy of the solid-state DFD laser was measured for different input pump powers and donor and acceptor concentrations at one end of the dye-coated prism.[36–38] The measured values and computed results are shown in Figs. 10–12. Our results show that the experimental values are in close agreement with the theoretical ones.

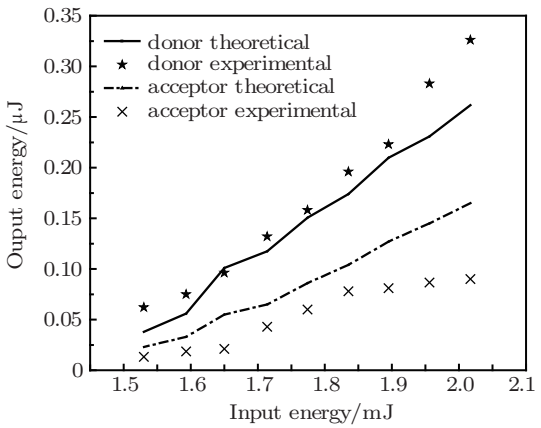


Fig. 10. Donor and acceptor DFDL output energies as a function of pump energy for fixed donor $N_d = 1.8 \times 10^{18}$ cm^{-3} and acceptor $N_a = 0.6 \times 10^{18}$ cm^{-3} concentrations.

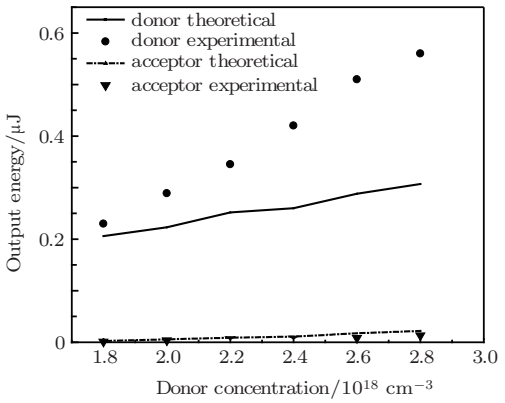


Fig. 11. Donor and acceptor DFDL output energies as a function of donor concentration for fixed pump power $I_p = 0.8 \times 10^{22}$ cm^{-2}·s^{-1} and acceptor concentration $N_a = 0.6 \times 10^{18}$ cm^{-3}.

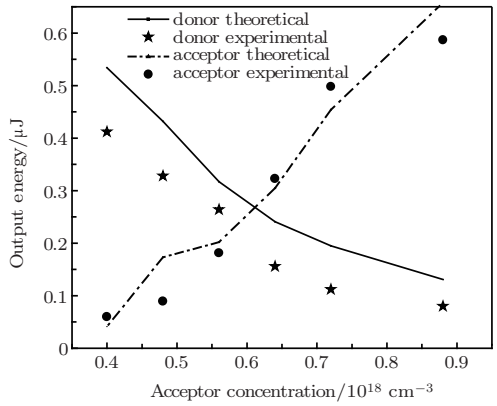


Fig. 12. Donor and acceptor DFDL output energies as a function of acceptor concentration for fixed pump power $I_p = 0.4 \times 10^{22}$ cm^{-2}·s^{-1} and donor concentration $N_d = 1.8 \times 10^{18}$ cm^{-3}.

3.5.2. Wavelength tuning

In a separate experiment, MMA co-doped with SRB (3 mM) and CV (1 mM) was coated on the prism. The emission peak of the donor (SRB) was to be read by varying the angle of interference (θ) of the pump beam. The tunability of the donor region was studied by varying the angle of interference between 53° and 58°, with its peak found at 54°. Next, the prism was tuned to the acceptor region by varying the angle of interference between 47° and 52°, and its peak was found at 51°. The wavelength output was measured using a spectrometer (OSM2, USA). The tunability range studied for the donor DFDL was 563–598 nm, and it was extended up to 648 nm for the acceptor DFDL. In Figs. 13 and 14, the experimental values of tuning are compared against the theoretical values, according to which the angular tuning of both donor and acceptor is nearly linear.

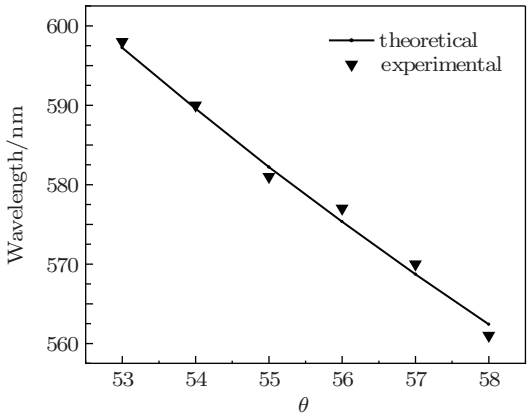


Fig. 13. Donor (SRB) DFDL as a function of angle of interference θ.

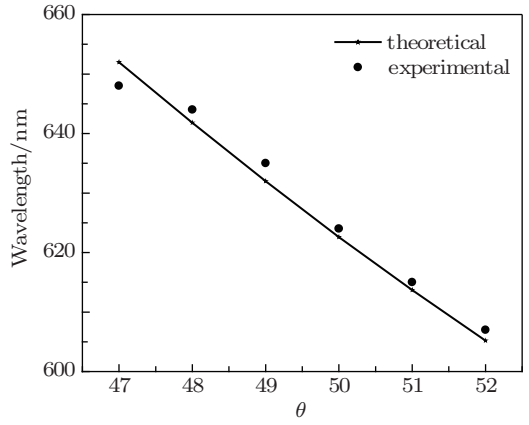


Fig. 14. Acceptor (CV) DFDL as a function of angle of interference θ.

4. Conclusion

Solid-state dye samples based on MMA co-doped with SRB and CV were prepared. The characteristics of the energy-transfer DFDL, incorporated into a solid polymeric matrix, were investigated in both the donor and acceptor regions. Dependencies of the pulse width and output power on the pump power and acceptor concentrations of the energy-transfer DFDL were studied both theoretically and experimentally. While the energy transfer from SRB to CV was clearly evident, the concentrations of SRB and CV molecules in the dye mixture incorporated in the solid polymeric matrix appeared to control the lasing properties. The results of energy measurements were in good agreement with the theoretical values, and the wavelength tunability of the DFDL across the yellow and red regions (563–648 nm) was well demonstrated.

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