CHARACTERISTICS OF A MULTICOLOR DYE LASER

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An experimental investigation on the possibility of obtaining tunable, multiple wavelength output in mixture of dyes pumped by a nitrogen laser has been carried out. A great number of binary dye mixtures have been tested. Simultaneous two wavelength operation is generally possible provided the gain profiles of both dyes are neither strongly overlapped nor too widely separated. Three color emission is feasible in many mixtures, but the possible combinations are limited. A simple scheme for multiple, simultaneous wavelength tuning is presented.

This letter presents an experimental investigation on the possibility of achieving simultaneously tunable, multiple-frequency operation, of a mixture of dyes in a single cell, pumped by a nitrogen laser. The performance of several binary combinations is presented. Up to three widely separated, independently tunable frequencies can be obtained from ternary dye mixtures at adequate concentration. Four-dye mixtures can also exhibit multiple wavelength operation at the expense of a drastic drop of efficiency.

The mechanism responsible for multicolor emission is essentially based on energy transfer among the different molecules in the dye mixture. The subject has been treated in a number of papers for flashlamp pumping, as well as for nitrogen laser pumping [1–8] and it is well known that fluorescence conversion is commonly used, in commercial systems, to pump dyes which do not conveniently absorb at the wavelength emitted by the pumping source.

Simultaneously two wavelength operations from binary dye mixtures has been reported by Hilborn and Braynan [9]. They could successfully tune both outputs. However, they concluded that pumping two separated dye cells was the simplest and less expensive method to obtain multiwavelength output. Ahmed et

al. [10] also had reported three-color output from a mixture of three dyes while Marowsky and Zagara have operated a dual wavelength flashlamp pumped dye laser [11].

The above mentioned mechanism can be readily understood in terms of a "dye laser pumped dye laser". A primary dye (D_1) is transversely pumped by a N_2 laser. As the dye cell is introduced into an optical resonator, a strong radiation flux is created in the pumped region, at the wavelength corresponding to the fluorescent emission band of the dye. A secondary dye, (D_2) whose absorption spectrum overlaps more or less the fluorescent spectrum of D_1, can be pumped by laser radiation of the primary dye, inside the cavity. The concentration of D_2 must be adjusted so that the emission from D_1 will not be quenched. The same effect occurs without the presence of the resonator, provided the concentration of D_1 is high enough so that strong superradiance occurs along the pumped region. The secondary dye radiation can pump a tertiary dye D_3, and so forth. When this above mentioned mechanism is responsible for pumping of the dyes, the laser emission of the last dye in the chain is, in any case, subject to the presence of laser oscillation or superradiance in all the preceding dyes.

The experimental set up consisted in a dye cell with slightly tilted windows, in which the solution could be flown. The molecular nitrogen laser used was Blumlein excited, constructed in our laboratory, and

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could provide pulses of about 1 mJ in 10 ns fwhm. The uv emission was focused onto the dye cell by means of a cilindrical quartz lens, 15 cm focal length. The pumped region was about 10 mm long and approximately 0.2 mm depth and 0.1 mm width. The broad-band resonator consisted of a totally reflecting planar aluminum mirror, and a parallel glass plate as output reflector. Mirror separation was approximately 6 cm. Two dye cells, 10 and 20 mm long respectively, with rear-mirror incorporated, were also used. Tuning experiments were performed by using the arrangement suggested by Shoshan et al. [12] in which a grating was mounted at an incidence angle approaching 90° (grazing incidence), as can be seen in fig. 1. Two mirrors M_2 and M_3, could be independently tilted, in order to tune over two separate wavelengths. In case of three frequency output, a third mirror could be introduced. It is the introduction of this extremely simple tuning system, by means of which a narrow line output could be obtained, that justifies the tentative to reduce to a single dye cell the attainment of multiple frequency operation. The output was monitored by means of a Tropel photodiode and a Tektronix 535A oscilloscope. Corrections were made for the sensitivity response of the photodiode versus wavelength. All the dyes used were Lambda-Physik, laser grade; all solutions were made with ethyl alcohol as solvent.

Binary mixtures of dyes in broad-band regime were first investigated. It was noticed that short cavities gave better performances. Primary dye solutions were generally overconcentrated with respect of optimum output, so that superradiance was always observed
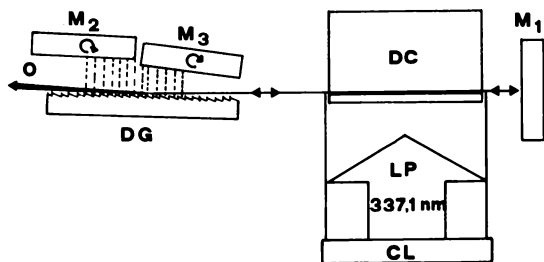
when the resonator was removed or misaligned. The secondary dye concentration was increased step by step. Usually, the D_1 output power decreased slowly at the beginning, up to the point where D_2 started lasing. The D_1 output decreases much faster beyond this point. The D_2 emission increased with increasing concentration up to a maximum and then decreased when the D_1 radiation flux was almost totally quenched. At concentrations where D_2 began to lase, its output was critically dependent on cavity alignment. Further increase of output power of D_2 at high concentrations is either due to a direct energy transfer by fluorescence reabsorption, by a resonant energy transfer due to a longrange dipole-dipole interaction [4] or, in some cases (Coumarin 102 + Rhodamine 6G), due to direct pumping of the second species by the pump source.

Fig. 2 presents the above described behavior for two combinations of dyes, namely Rhodamine 6G (R6G) + Cresyl Violet (CV) (fig. 2a), and Coumarin 102 (C 102) + R6G (fig. 2b). The first is a well-known combination in which the absorption and fluorescence
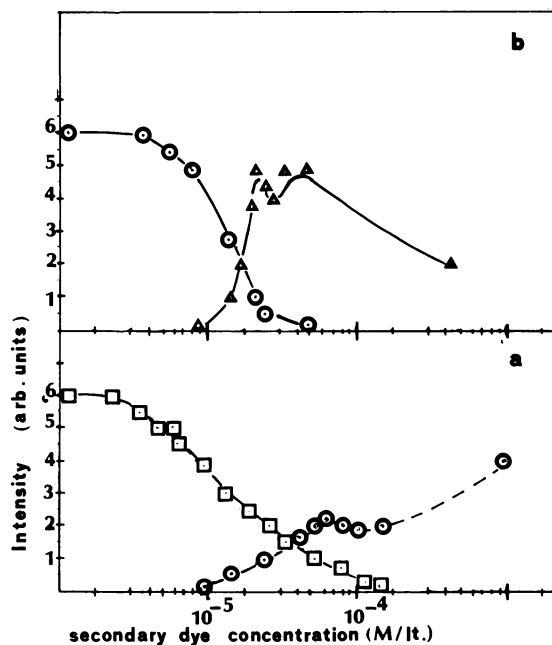
Fig. 1. Schematic diagram not in scale of experimental set-up: CL, cilindrical quartz lens, 15 cm focal length; LP, nitrogen laser pulse; DC, dye cell; DG, diffraction grating; $M_1M_2M_3$, silvered plane mirrors; O, output.

Fig. 2. Output from a binary dye cell versus concentration of secondary dye (C_{D2}). Selected experimental data. a) D_1: Coumarin 102; D_2: Rhodamine 6G. b) D_1: Rhodamine 6G; D_2: Cresyl Violet.

spectra of both components closely overlap. Tunability curves of the two dyes are also partially superimposed. In this case the peak of the fluorescence spectrum of CV, approximately at 630 nm, is in the region where the R6G molecules may substantially contribute to laser emission at both frequencies and the D_2 radiation helps in increasing the 630 nm emission band at the expenses of the D_1 570 nm band. This competition effect is reported in a number of papers and it is well described by Friesem et al. [13].

Referring to the R6G + CF mixture, it has to be noted that the absorption length of CV at the concentration corresponding to the onset of oscillation, and in the spectral region where R6G exhibits the maximum of fluorescence, is approximately 0.4 cm, the absorption length at 337.1 nm (emission band of N_2 laser) is of the order of 3.3 cm. These lengths are much longer than the transverse dimension of the pumped region, which is only a few tenths of a millimeter. The concentration is also too low for taking into account far resonant transfer excitation [3]. It has to be concluded that laser action in CV is due to longitudinal pumping by the R6G laser emission.

The combination C102 + R6G described in fig. 2b, exhibits substantially the same behaviour, differing only quantitatively from the R6G + CV one. The decay of the C102 emission is less abrupt, and output versus concentration curves appear to be smoother. This is due to the fact that the emission spectra of the components are widely separated and no competition effects occurs.

Two more cases have to be considered:

a) Extremely separated, D_1 and D_2 emission spectra. In this case no double frequency output is to be expected by means of the described mechanism, and in fact double wavelength emission was not observed (see C102 + CV, table 1).

b) Close overlap of D_1 and D_2 emission spectra. When the gain curves superimpose so that a single maximum results, laser emission occurs in a single band. Both dyes are forced to radiate by a spectral narrowing effect at the peak of the gain curve, resulting in a frequency pulling of the two emission bands towards an intermediate value. A typical case with the described behaviour is the mixture C102 + Coumarin 6 (C6). Although the separation of their spectra is comparable to the R6G + CV case, only a single emission band was observed. By increasing the C6 concentration, the blue emission of C102 peak peaked at 475 nm, was green-shifted towards 512 nm

Table 1
Experimental data on binary dye mixtures, output characteristics

D_1 Primary dye	D_2 Secondary dye	D_1 Concentration (M)	D_2 Concentration (M)	D_1 (a) λ_{01}	D_1 Wavelength range (nm)	D_2 (b) λ_{02}	D_2 Wavelength range (nm)	Energy ratio (c)
Coumarin 102	Uranine	2.7×10^{-3}	1.7×10^{-4}	482	— (t)	516	— (t)	0.3
Couramin 102	Couramin 6	3×10^{-2}	7×10^{-5}	481	— (t)	500	— (t)	0.6
Coumarin 102	Rhodamine 110	3×10^{-3}	3×10^{-5}	475	468–489	529	528–530	0.55
Coumarin 102	Rhodamine B	4.8×10^{-3}	2×10^{-4}	472	468–477	585	582–592	0.08
Coumarin 102	Rhodamine 6G	5×10^{-3}	3×10^{-5}	470	468–472	550	547–552	0.5
Rhodamine 110	Rhodamine B	5×10^{-3}	2.2×10^{-5}	555	554–557	575	569–586	1
Rhodamine 110	Cresyl Violet	3.5×10^{-3}	10^{-4}	552	546–554	635	626–643	0.33
Rhodamine 110	Nile Blau	2.8×10^{-3}	8.5×10^{-4}	560	— (d)	692	— (d)	0.04
Coumarin 102 + Couramin 6	Rhodamine 6G	4×10^{-3} 2×10^{-3}	2.4×10^{-4}	512	496–517	553	549–557	0.67
Rhodamine 6G	Cresyl Violet 2.3	2.3×10^{-3}	1.8×10^{-4}	573	562–589	638	629–659	0.67
Rhodamine 6G	Nile Blau	2.3×10^{-3}	1.5×10^{-4}	589	563–590	686	677–695	0.13

D_1, primary dye; D_2, secondary dye; (a), peak emission wavelength, primary dye; (b), peak emission wavelength, secondary dye; (c), Energy ratio. Ratio of total output energy, when output on both colours are equal, to the output energy of pure D_1; (d), not measurable with the same experiments; (t), spectral overlapping is present. The columns, wavelength range indicate the width of superradiant output. Ethyl alcohol was used as solvent in all solutions.

(peak of the C6 emission), but a double frequency operation was never observed.

Table 1 shows the results obtained with several binary combinations of dyes. The concentrations listed in the table are given for the points where D_1 and D_2 are equal. In order to give an indication of the efficiency when the laser is operating with binary mixture, we also report the ratio between the total energy of double wavelength emission and the emission of the pure primary dye.

The analysis was performed on the basis of the available dyes at our laboratory, and it is reasonable to state that many other combinations may exhibit double frequency output, provided that: a) gain curves do not closely overlap; b) fluorescence emission of D_1 reasonably fits with absorption spectrum of D_2, and c) the two dyes can conveniently dissolve in the same solvent.

Three color operations in combinations of three dyes appears possible over a limited number of cases. The tertiary dye (D_3) should in fact absorb some of the D_2 fluorescence. In many cases, attempts to introduce D_3 in a binary mixture, reduces output at D_1 and D_2 simultaneously. D_2 can therefore be quenched before D_3 starts lasing. D_1 and D_2 concentrations have to be somewhat higher than for binary mixtures. Three color output has been achieved in mixtures of C102 + Rhodamine 110 (R110) + Rhodamine B (RB); Coumarin 2 (C2) + RB + CV; C2 + C6 + R6G; R6G + CV + Nile blue (NB), and some others. The most spectacular was a white output (blue + yellow + red) obtained with a C102 + R6G + CV mixture, the ratio of total energy to energy of pure D_1 before adding the other dyes was 0.25. The dye concentrations were (C102) 10^{-2} M; (R6G) 1.8×10^{-4} M; (CV) 1.4×10^{-4} M.

Independent tuning over the emission spectrum of each dye has been demonstrated in the arrangement shown in fig. 1 for the combinations which exhibit double color output. In some cases, the concentration of the primary dye had to be increased. The high concentration of D_1 causes a tendency to superradiant output. Superradiance can be quenched by the laser narrow band oscillation, when tuning is performed in the vicinity of the peak of the gain curve. This reduces the tunability range in a narrow interval of the order of 20 nm. Ternary dye mixture can also be independently tuned over three spectral regions with the limitations due to superradiance. However,

the tuning mechanism became in this case somewhat cumbersome.

In conclusion, we have demonstrated that multiple frequency operation is possible in a single dye cell by using mixtures of adequate dyes at the appropriate concentration. It is evident that the longer wavelength dyes are pumped successively by the longitudinal laser field or superradiance at the shorter wavelength. Almost any binary combination of laser dyes can give tunable emission over their tunability spectra, provided that the above mentioned conditions are fulfilled. Three color emission is possible in a limited number of combinations.

Emission of two widely separated frequencies, independently tunable, is useful in a number of applications like the coherent anti-Stokes Raman scattering, sum frequency mixing and difference-frequency generation.

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