Characteristics of a Cresyl Violet Laser

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The properties of flashlamp- and laser-pumped cresyl violet lasers emitting between 620 and 710 nm were studied. In mixed cresyl violet-rhodamine 6G solutions, the excitation efficiency was found to be enhanced by more than a factor of two, the major part of the excitation energy being supplied by the rhodamine 6G fluorescence radiation.

Self-modelocking in a 3-component solution, containing cresyl violet, rhodamine 6G and a saturable absorber dye, was observed.

1. Introduction

Recently, flashlamp-pumped cresyl violet (CV) was reported to exhibit laser emission between 646 and 701 nm [1]. The CV laser is worth further studies because it extends the spectral range attainable by flashlamp-pumped dye lasers: in the red region it continues the emission range of the rhodamine lasers, while in the ultraviolet its frequency-doubled output closes the gap between direct emission from scintillator dyes (shortest wavelength 340 nm) and the 2nd harmonic emission from rhodamines (longest wavelength about 315 nm).

To enhance the efficiency of flashlamp-pumped CV lasers we added to the CV solution rhodamine 6 G (R6G), which absorbs at shorter wavelengths than CV (Figure 1). Its fluorescence band overlaps the CV absorption band, thus the R6G-fluorescence additionally pumps the CV. This technique of excitation by energy transfer from a "pumping dye" to the "laser dye", by which a broader range of the flashlamp spectrum is utilized, was previously applied to several other laser dyes [2]. Addition of a pumping dye may also be advantageous if the dye laser is excited by a laser light source. This is the case if the laser dye has very low absorption at the pumping laser wavelength or if a low concentration of the laser solution is used in order to reduce the self-absorption losses. While our work was in progress, a nitrogen-laser-pumped CV laser was described, the output power of which was also increased by the addition of R6G [3].

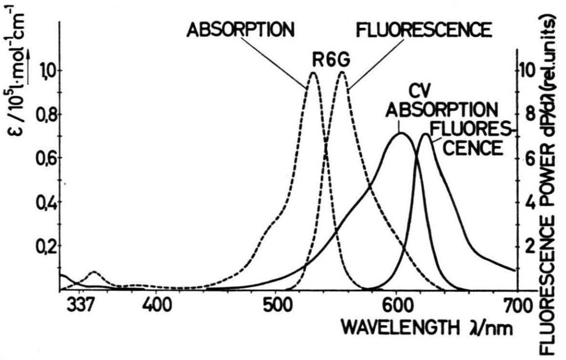

Fig. 1. Absorption and fluorescence bands of rhodamic 6G and cresyl violet dissolved in methanol.

Apart from comparative measurements with laser pumping, the work to be reported in this paper is primarily concerned with flashlamp-pumping. With the CV, output powers comparable to those obtained with R6G as well as extremely broad tunability ranges were achieved. The CV laser was found to be readily mode-locked using as a saturable absorber 3,3′-diethylthiadicarbocyanine-iodide (DTDC), a dye which is frequently used for *Q*-switching of ruby lasers [4].

2. Experiments and Discussions

a) Flashlamp Pumping

The dye laser consisted of an elliptical cylinder reflector containinig a linear flashtube (ILC) and a 50 mm-long dye cuvette [5]. The cuvette had Brewster-angle windows and a 3.5 mm inner diameter. In most cases the cavity was 115 mm long. The reflectivity product of the cavity mirrors was 25% between 450 nm and 710 nm. The flashlamp pulse duration was 700 nsec. If not otherwise stated, a pumping energy of 12.8 joule (0.1 μF, 16 kV) was applied. With a $7 \cdot 10^{-4}$ molar methanolic solution of R6G, an output power of 125 kW was achieved in this setup.

With $8 \cdot 10^{-5}$ molar methanolic solutions of CV, the output power was 17 kW. When R6G was added while the concentration of CV was kept constant, the output power increased as shown in Figure 2. The emission band was 5 to 10 nm broad and centered at 660 nm. This wavelength was independent of the R6G concentration. No triplet quenching agents[6] were added. The duration of the laser pulse obtained from the mixed R6G-CV solution was 250 nsec, whereas with pure R6G solutions pulses of 600 nsec duration were obtained in the same setup. Both dyes were purified by recrystallisation. To obtain from commercial grade CV output powers as high as from purified CV, the pumping power had to be increased twofold.

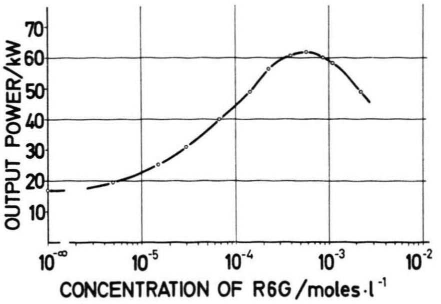

Fig. 2. Output power vs. R6G concentration of a mixed R6G-CV solution. CV concentration $8\cdot10^{-5}$ molar, pumping energy 12.8 joules. The ratio of the maximum output power to the output power of pure CV is not a criterion of the efficiency of the energy transfer (see text).

In a second series of measurements we stepwise increased the content of CV in a methanolic $1\cdot10^{-3}$ molar R6G solution. Figure 3 shows power and wavelength of both R6G and CV emissions as a function of the CV concentration. The R6G concentration was kept constant. With CV concentrations between 10^{-6} and 10^{-5} molar, both dyes emitted simultaneously. Also entered in the diagram are powers and wavelengths obtained with pure CV solutions. The observed wavelength shifts correspond to the theoretical expectation: the R6G emission is shifted towards blue with increasing losses introduced by the CV. CV exhibits the usual red shift with increasing concentration. In this latter respect the mixture behaves even quantitatively like a pure CV solution. The wavelengths obtained from pure CV coincide reasonably well with those obtained from the mixtures. The shape of the CV power curve at low concentration (Fig. 3) indicates that the transfer of excitation energy from R6G to CV is enhanced when R6G lases too. When the R6G laser action was suppressed, the CV power decreased by about 35%. To suppress the R6G laser, an absorption edge filter (RG610) fully transparent at the CV emission wavelength was inserted into the cavity. For the comparative measurement with both dyes lasing, the filter was replaced by a glass plate to make sure that the reflection losses were equal to those introduced by the RG 610 filter. The CV content in the solution was $6\cdot10^{-6}$ molar. This seems to indicate that the CV power will approximately follow the dashed line when only spontaneous emission from R6G is present. This result is quite reasonable, for in the case of laser action in R6G the portion of spontaneous R6G emission which escapes through the side walls of the cuvette is reduced. The concentration tuning curve of CV extends beyond 620 nm towards blue, whereas the CV fluorescence band has its maximum at 624 nm (Fig. 1). A free-running pure CV laser will never lase at the blue side slope of the fluorescence curve because there the reabsorption losses are higher than on the red side slope[5]. In an R6G-mixture, however, the fluorescence from the wing of the R6G band adds to the CV fluorescence. With a CV concentration that is sufficiently low the maximum gain may therefore occur on the blue side of the CV fluorescence band.

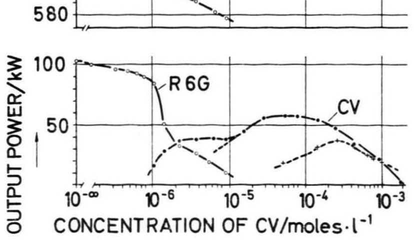

Fig. 3. Emission wavelength and output power vs. CV concentration of a mixed R6G-CV solution containing 10^{-3} moles/l of R6G (solid curves) and of a pure CV soluiton (dashed curves). Pumping energy 12.8 joules.

It should be pointed out that the optimum concentration for pure CV solutions is higher by a factor of 6 than for the CV content in the optimum compound solution. The pumping power required to obtain 25 kW of output power is higher by a factor of 1.6 for the optimum pure CV solution than for the optimum R6G-CV solution (see Figure 4). Due to the increased absorption and the reduced overall quantum efficiency in the compound solution, more heat energy and thus more schlieren are produced. Pure CV solutions may therefore be preferable whenever optical homogeneity is demanded.

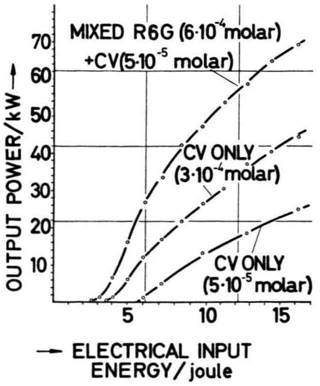

Fig. 4. Output power vs. pumping energy of mixed R6G-CV solutions and of pure CV solutions. $3 \cdot 10^{-4}$ moles/l is the optimum concentration to attain maximum efficiency with pure CV solutions.

Figure 3 shows that also at very high CV concentrations the addition of R6G is not very advantageous. However, for operating points at very low CV concentrations, i. e. at short wavelengths, the efficiency is drastically enhanced by the pumping dye.

The gap between the spectral regions occupied by the emission from the two components of the R6G-CV solution (Fig. 3) may be closed by using intracavity tuning elements. Even with unpurified CV ($2.5 \cdot 10^{-5}$ molar) together with R6G ($2.5 \cdot 10^{-4}$ molar), dissolved in water with 1.5% Ammonix LO[7], a continuous tuning range from 580 nm to 670 nm was achieved. A 3-prism frequency selector was used[5]. The power-vs-wavelength curve exhibited two equally high maxima at 590 and 638 nm. At 617 nm there was a relative minimum with about half the maximum power. This result may be considerably improved by optimizing the dye concentrations and the cavity mirror reflectivity, and by using purified CV in methanol rather than soap water. With soap water as a solvent the output power was usually reduced by a factor of approximately 2.5 in comparison with methanolic solution. The very longest wavelength obtained from CV ($5 \cdot 10^{-5}$ molar with $6 \cdot 10^{-4}$ molar R6G in methanol), tuned by an internal interference filter, was 710 nm.

Narrow tunable emission lines were obtained by a simple low-loss frequency selector consisting of an interference filter and a Fabry-Perot interferometer[5]. A methanolic solution containing $6 \cdot 10^{-4}$ molar R6G and $5 \cdot 10^{-5}$ molar CV was used for this experiment. The resonator was 280 mm long. The output mirror had dielectric coatings with 40% reflectivity. The free-running laser emitted 24.4 kW peak power within a bandwidth of 6 nm, centered at 652 nm. Inserting a dielectric interference filter (bandwidth FWHM 4 nm, maximum transmission 88%) reduced the bandwidth to 0.3 nm and the output power to 17.9 kW. The power per wavelength interval was thus increased from 4 kW/nm to 60 kW/nm. For further narrowing a solid Fabry-Perot interferometer was inserted. It consisted of a quartz plate of 0.25 mm thickness whose surfaces were parallel within $\lambda/200$; they were coated with dielectric mirrors having 78% reflectivity. The free spectral range of this etalon was about 0.58 nm at 660 nm. With both the etalon and the interference filter inserted, the laser emitted a single line ($\lambda = 660$ nm) of less than $5 \cdot 10^{-3}$ nm width with 15.8 kW peak power, corresponding to more than $3.2 \cdot 10^{3}$ kW/nm[7a]. The pumping energy was always 12.8 joules.

The ratio of the output powers from R6G-CV and pure CV solutions is not a criterion of the efficiency of excitation-energy transfer from the R6G pumping dye to the CV laser dye. This ratio critically depends on the cavity Q, on the pumping power and on the concentrations, tending toward infinity at the laser threshold of pure CV. However, reasonable estimates may be based on comparisons of the input powers necessary to produce equal output powers from pure CV and R6G-CV. An evaluation of Fig. 4 shows that the pumping energy required for 10 kW of output power is lower by a factor of 2 for an optimum R6G-CV solution than for pure CV of the same concentration as in the compound solution. This factor increases to 2.7 for an output power of 25 kW. These ratios approximately also hold for the peak power of the flashlamp radiation, which – as a consequence of the short lifetimes of the excited molecular states of the laser dye – is more directly related to the laser peak power than the electrical pumping energy. We found that the pumping light power increased almost linearly with increasing electrical input energy.

A comparison of the areas occupied by the respective absorption curves clearly shows that the major part of the excitation power is contributed by the R6G content of the compound solution. The absorption $A(\lambda)$ may be obtained by direct measurement or from Fig. 1, using the relation

$$A(\lambda) = 1 - 10^{-(\varepsilon_{R6G}\, c_{R6G} + \varepsilon_{CV}\, c_{CV})\, d}$$

where ε_{R6G} and ε_{CV} are the molar decadic absorption coefficients of the two dyes, c_{R6G} and c_{CV} are their concentrations and d is the path length. For $d = 1$ mm, $\int A(\lambda)\, d\lambda$ is found to be higher by a factor of 2.7 for the compound solution ($c_{R6G} = 6 \cdot 10^{-4}$ m/l, $c_{CV} = 5 \cdot 10^{-5}$ m/l) than for the pure CV solution ($c_{CV} = 5 \cdot 10^{-5}$ m/l). A still higher factor is valid if the absorbed flashlamp light power is considered, for the spectral power density of the pumping light rises toward shorter wavelengths. On the other hand, the power absorbed in the R6G is only partly transferred to the CV, due to (a) the lower energy of the emitted light quanta; (b) the fact that the R6G fluorescence band overlaps only partly with the CV absorption band; and (c) to the non-unity – though high – quantum efficiency of the R6G fluorescence. This will not be quantitatively discussed here. Neither will be discussed here the detailed mechanism of the energy transfer, for the experiments described above do not allow to distinguish between two possible mechanisms: apart from transfer by photons, the process of radiationless energy transfer studied extensively by FÖRSTER[8], may play an important role.

Some general considerations concerning the choice of suitable pumping dyes may be based on the results described above. Figure 1 shows that the R6G absorption overlaps the CV absorption. In the optimum compound solution, about one third of the CV absorption band is shielded by the R6G absorption. These conditions are similar with other pumping dye – laser dye mixtures. The reduction of direct pumping into the absorption band of the laser dye may be overcompensated by the manyfold increase of the overall absorption, provided that the quantum efficiency of the pumping dye is sufficiently high compared with the quantum efficiency of the laser dye. This is the case with R6G as a pumping dye for CV. Rhodamine B (RB) however, proved to be a far less efficient pumping dye than R6G, though the RB fluorescence is better matched to the CV absorption. The lower efficiency of RB-CV as compared with R6G-CV is primarily due to the broader overlap of the absorption bands of the two dyes. Adding a pumping dye may even have a negative effect, if it has a substantially poorer quantum efficiency than the laser dye. This we learned from our attempts to increase the efficiency of R6G, which is the most efficient of the laser dyes. Several dyes (fluoresceines, coumarines, brilliant sulphaflavine, trypaflavine) which were promising because of the spectral position of their absorption and emission bands, were tried as pumping dyes for R6G. If there was any effect at all, it was a reduction of the R6G output. The brilliantly fluorescing dye trypaflavine[8], which exhibited laser action neither with flashlamp nor with nitrogen laser pumping, totally suppressed the R6G laser emission even when added in low concentrations. This may be due to a triplet-triplet absorption band rapidly built up in the trypaflavine and extending to the spectral region where R6G lases. Triplet-triplet bands are known to be very broad. Therefore, a fluorescing dye which does not lase is most probably not suited for use as a pumping dye.

b) Mode Locking

When the CV laser described above, was operated in the free-runninig mode, its emission wavelength coincided exactly with the DTDC absorption maximum. When we placed a 1-mm cuvette containing a DTDC solution with 40% small-signal absorption in front of one cavity mirror, the pulse rise time was shortened to about 3 nsec. The pulse exhibited a narrow initial *Q*-switch peak about 5 nsec wide which protruded over the 150-nsec-broad tail of the pulse. A slight increase in the DTDC concentration resulted in a mode lock in the pulse tail. When the DTDC was added to the laser solution and the separate mode lock cell was removed, the modulation depth was drastically enhanced and the initiation of the mode lock was shifted to the very beginning of the pulse. Pulse forms, similar to those previously obtained from an R6G laser[9] were observed. This effect is being investigated at the present.

c) Laser Pumping

Pure superradiant laser emission was obtained when CV solutions were transversely pumped by laser radiation. A cylindrical lens was used to focus the laser beam into a narrow line parallel to the axes of the dye cell. The dye cell was 25 mm long.

Its windows were tilted in order to prevent feedback reflection. The various results obtained are shown in Figure 5. Curve A_1 shows output power vs. pumping power for a $4 \cdot 10^{-3}$ molar pure CV solution, pumped by a nitrogen laser[10]. The concentration was optimized for maximum output power. Curve A_2 was obtained from an R6G-CV solution which contained the dyes in the respective molar proportions of 5 : 1 and which had the same absorption as the pure CV solution at the excitation wavelength 337 nm. The ratio of the pumping powers required to obtain equal output powers from both solutions was 2. As stated in [3], the increased efficiency of the mixture may primarily be ascribed to reduced self-absorption.

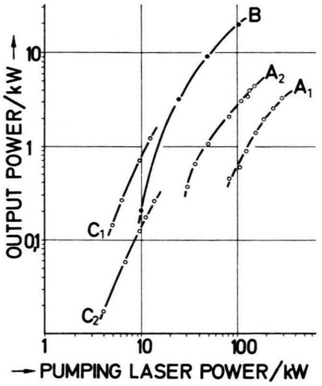

Fig. 5. Superradiance power vs. exciting laser power for different dye solutions and exciting lasers. A_1: pure CV solution excited by a nitrogen laser, A_2: R6G-CV solution excited by a nitrogen laser, B: pure CV solution excited by an R6G laser, C_1: pure R6G solution excited by a BSF laser, C_2: R6G-CV solution excited by a BSF laser.

The nitrogen laser was then replaced by a flashlamp-pumped R6G laser with an emission wavelength of 595 nm. Thus it was well matched to the strongest absorption band of CV. Predictably, this long-wavelength excitation proved to be more efficient than the UV excitation (Figure 5, curve B). The CV concentration of $6 \cdot 10^{-4}$ moles/l was optimum for maximum output.

Furthermore, a brilliant-sulphaflavine (BSF) laser[11] was used to pump an R6G-CV mixture, containing $4.5 \cdot 10^{-4}$ moles /l of CV and $2.5 \cdot 10^{-3}$ moles/l of R6G. The emission wavelength of the BSF laser, which was 530 nm, nearly coincided with the maximum of the R6G absorption band. Under these conditions, practically all of the excitation power is supplied by the R6G fluorescence (see Figure 1). Curve C_2 in Fig. 5 gives the results. For comparison a $2.5 \cdot 10^{-3}$ molar solution of R6G was excited by the BSF laser (curve C_1). The ratio of the pumping powers required to obtain equal output powers from R6G-CV and R6G is 2. These results suggest the possibility of obtaining cw emission in the far red region from CV-R6G solutions by argon ion laser excitation – provided that the triplet accumulation in the CV can be overcome by suitable triplet quenching agents.

Acknowledgements

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