SYNCHROSCAN STREAK CAMERA STUDY OF POTENTIAL SATURABLE ABSORBERS IN THE BLUE SPECTRAL REGION

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The viscosity-dependent fluorescence lifetime of some cyanine dyes with peak absorption cross-sections in the 350-500 nm range have been examined using a synchronously operating streak camera in conjunction with the picosecond excitation pulses from a frequency doubled synchronously pumped c.w. dye laser. Through increases in the recovery time of a saturable absorber by employing viscous solutions, the necessary saturation flux is conveniently reduced and passive mode locking of laser systems can occur more easily. This is illustrated by the application of one of the dyes to the mode locking of the coumarin 102 dye laser.

1. Introduction

The generation of tunable picosecond pulses through the passive mode-locking of dye laser systems has traditionally been carried out using polymethine dyes of cyanine family [1] as the saturable absorber. Initially the dicarbocyanine dye 3,3'-diethylxodacarbocyanine iodide (DODCI) was used to modelock the rhodamine 6G dye laser in the orange-red wavelength range [2]. Further application of tricarbocyanines gave rise to modulation in the near infra-red [3] and monocarbocyanines have been used to modelock dye lasers in the blue-green [4] and green-yellow [5] spectral regions. More recently, styryl analogues of these cyanine dyes have been shown to be powerful saturable absorbers over a major part of the visible spectrum [6,7]. However, passive mode locking at wavelengths shorter than 450 nm has yet to be achieved.

Within any vinylogous series of cyanine dyes a distinct shift of the absorption maximum to shorter wavelengths is produced when the length of the linking polymethine chain is reduced [8,9]. Also associated with this decrease in the length of the polymethine bridge is a general lowering in the fluorescence quantum efficiency and fluorescence lifetime [10]. A contributing factor to this is the steric hindrance effects of the terminal groupings which cause deviations
from planarity of the molecules, with a consequential increase in the internal conversion rate \([11]\) and a subsequent decrease in the fluorescence lifetime \([10]\).

At its simplest, a saturable absorber can be considered to be a two level system, the flux necessary to cause complete saturation \(F_{\text{SAT}}\) being given by \((1/\sigma \tau)\), where \(\sigma\) is the absorption cross-section at the wavelength of excitation and \(\tau\) is the recovery time of the absorption. For a typical cyanine dye absorbing in the region of 400 nm this corresponds to a saturation flux of \(-100\ \text{MW cm}^{-2}\) for an absorption cross section of \(2.5 \times 10^{-16}\ \text{cm}^2\) and an aperture time of 25 ps. An intracavity flux of this magnitude is not usually achieved with flashlamp pumped dye lasers. It can be seen, however, that by increasing the recovery time of the saturable absorber the required saturation flux is proportionally reduced. Since the loss of excitation energy within the polymethine chained dyes occurs through the partial rotation of the aromatic terminal groups about the linking aliphatic chain, then any action which restricts this twisting motion, for example an increase in the environmental viscosity, would decrease the rate of internal conversion and consequently lead to longer excited state lifetimes. This technique was initially employed by Mialocq and Goujon \([4]\) to enable passive mode locking of a coumarin dye laser, and verified previous results \([12,13]\) in the passive mode locking of dye lasers, which implied that although important, the relaxation time of the saturable absorber does not greatly affect the ultimate duration of the generated dye laser pulses \([14]\).

In this paper we report of the use of a synchronously operating streak camera in conjunction with a frequency-doubled modelocked c.w. dye laser to measure the relaxation parameters of several dye species which are potential saturable absorbers for the blue spectral region.

2. Experimental

The experimental arrangement used to determine the fluorescence lifetime of the saturable absorbing dyes is shown in fig. 1. A synchronously pumped rhodamine 6G or rhodamine 110 dye laser which was excited using the \(-60\ \text{ps}\) pulses from an actively mode locked Ar\(^+\) laser \([15]\) was frequency-doubled using an intracavity 1.5 mm thick ADP crystal \([16]\). The output in the ultraviolet was tunable from 285–310 nm and consisted of a train of pulses of \(-2\ \text{ps}\) in duration, occurring at a 70 MHz repetition rate. A u.v. filter \(F_1\) was used to remove any visible laser radiation and the u.v. beam was directed via mirror \(M_2\) onto a quartz sample cell containing the dye under investigation. An optical delay line was inserted into the light path which provided a time calibration and a deflection linearity check for the streak camera. (When examining the fluorescence decay profiles only a single beam component from the delay line was used for excitation.) At lens \(L_1\) the peak power per pulse was
Fig. 1. Experiment arrangement.
\( \sim 10 \text{ W (average power } \sim 1.5 \text{ mW)} \) and this was focussed using lens \( L_1 \) to provide a maximum excitation power density of \( \sim 30 \text{ KW cm}^{-2} \). The fluorescence was detected at right angles with respect to the incident beam and was suitably filtered and attenuated before being focussed (lens \( L_2 \)) via the input slit onto the photocathode of the streak camera.

Detection and time resolution of the generated fluorescence was carried out using a Photochron II streak camera [17] in the continuous, synchronous mode of operation which has been described in detail elsewhere [10,18,19] and only a brief outline of the operation is given here. In synchroscan mode, a high voltage sinusoidal deflection voltage is applied to the sweep plates of the streak camera. From fig. 1 it can be seen that this deflection voltage was generated using a fraction of the output of the modelocked dye laser which was incident on a photodiode, the output signal of which was used to drive a tunnel diode oscillator in synchronism with the driving laser pulses. This sinusoidal voltage was amplified before being applied to the streak plates. Since the deflection voltage and the fluorescent signal are both generated from the same source (the modelocked dye laser) synchronism of the sweep deflection with the input light event under investigation is easily achieved, with only minor phase adjustment being necessary. The synchroscan streak camera operates such that the streaked images are accumulated at the repetition rate of the
excitation pulses (70 MHz in this case) and are precisely superimposed with a jitter which can be less than 1 ps [20]. In this way information on weakly emitting light sources can be detected for low levels of excitation power, thus eliminating nonlinear effects in the samples, while ensuring a time resolution of ~1 ps. Using an optical multichannel analyser (OMA) the real-time streak images were recorded and stored for subsequent display on a chart recorder CR or storage scope SS. Because of the nature of the pulse formation mechanism with the synchronously modelocked dye laser, the resolution of the camera when used in conjunction with this laser system is limited to ~7 ps [15] as compared to ~1 ps with the passively modelocked laser as excitation source [20]. The limited resolution was nonetheless adequate for the measurements reported here.

The structure of the four dyes examined are shown in fig. 2. These were 3,3'-diethyloxacyanine iodide (DOl), 3,3'-diethylthiacyanine iodide (DTI), 3,3'-diethylloxathiacanine iodide (DOTI) and 1,3'-diethyl-2,2'-quinolylthiacanine iodide (DQTI). Also shown in fig. 2. is the measured extinction coefficients for the dyes in ethanolic solution. The peak extinction coefficients and wavelength of maximum absorption were 6.6 \times 10^4 \text{ I mol}^{-1} \text{ cm}^{-1} at 363 nm for DOl, 6.6 \times 10^4 \text{ I mol}^{-1} \text{ cm}^{-1} at 403 nm for DOTI, 7.1 \times 10^4 \text{ I mol}^{-1} \text{ cm}^{-1} at 425 nm for DTI and 6.1 \times 10^4 \text{ I mol}^{-1} \text{ cm}^{-1} at 486 nm for DQTI.

3. Result and discussion

All the dyes were made up as 5 \times 10^{-5} M solutions. In order to vary the viscosity of the solution, fixed proportions of spectroscopic grade ethanol and glycerol were mixed together. To ensure homogeneity of the solutions the mixed solvents were placed in a vibration bath for some time before use. As described above the dyes were placed in a 10 mm square quartz sample cell and excitation was generally provided by the picosecond u.v. second harmonic output of the dye laser in the region of 300 nm where the dyes had adequate absorption. All the time resolved spectra, which could be clearly seen in real time, were recorded over a accumulation time of ~1 s which corresponded to the integration of ~7 \times 10^7 fluorescence decay profiles. The effect of the changing viscosity solvent environment on the fluorescence lifetime of the dyes can be clearly seen in the example shown in fig. 3 for DTI. At 60 cp the measured lifetime (time to the 1/e intensity point) was 173 ps while at 6 cp (fig. 3b) and 1.8 cp (fig. 3c) the lifetimes decreased to 52 ps and 19 ps respectively. A similar trend was observed for all the dyes. In fig. 4 the viscosity dependence of the fluorescence lifetime for the dyes DOTI, DTI and DOI is plotted on a logarithmic scale. The fluorescence lifetime of the oxacyanine dye was increased from that of the thia form reflecting earlier trends recorded for quantum yield measurements [8]. Also from fig. 4, it can be
seen that at intermediate viscosities $\eta$ the fluorescence lifetime $\tau_F$ takes the form $\tau_F = C\eta^\alpha$ [21] where $C$ and $\alpha$ are constants. Generally the values of $\alpha$ lie between 0.3 and 1.0 for the polymethine dyes [10,22] and in the case of DOTI, DOI and DTI these were 0.65, 0.63 and 0.62 respectively. This value of $\alpha$ depends on the degree of interaction between the solute molecules and the local solvent environment. The saturation of the linear logarithmic dependence

**Fig. 3.** Measured fluorescence decay profiles of DTI in (a) 60 cp (b) 6 cp and (c) 1.8 cp viscous solution. A calibration of 100 ps is drawn and the $1/e$ intensity decay times indicated.
shown at higher viscosities, and which is related to the decreased intersystem crossing rate is in reasonable agreement with the theoretical considerations [21].

A similar behaviour was also exhibited by DQTI which is not presented in fig. 4. In a 1.1 cp viscous solution the < 10 ps lifetime increased to 63 ps at 22 cp and to 165 ps at 220 cp. This method therefore permits a substantial reduction in the saturation flux of these viscous dye solutions and can therefore be directly applied to their use as saturable absorbers for the passive modelocking of dye lasers. For example with DTI on changing the solvent from ethanol ($\eta = 1.1$ cp at 25°C) to propylene carbonate ($\eta = 56$ cp) the increase in the fluorescence lifetime from 14 ps to 170 ps represents a 12 times decrease in the necessary saturation flux.

In a demonstration of this technique using DQTI in propylene carbonate ($\tau_F = 95$ ps) as saturable absorber, passive modelocking of coumarin 102 in a standard flashlamp pumped dye laser [5] has been achieved. Without the presence of a tuning element, broad band ($\Delta \lambda \sim 4$ nm) lasing took place around 475 nm and the modelocked trains had a temporal form shown in fig. 5(a). This exhibited a build-up time to complete modulation of $\sim 800$ ns followed by a fully 100% modulated period of $\sim 600$ ns. On an expanded time scale, the output clearly consisted of single pulses (fig. 5(b)) and single shot streak camera measurements [23] showed that the individual pulses had durations in the range 5–8 ps with low interpulse noise and peak powers of several megawatts.
Fig. 5. Temporal profile of the modelocked coumarin 102 dye laser output using DQTI as saturable absorber in viscous solution (a) 200 ns/small division and (b) as in (a) only on expanded time scale of 5 ns/small division.

Exploitation of the viscosity dependent recovery time of the cyanine dyes described here conveniently reduces the necessary saturation flux requirements to practical levels for modest flashlamp pumped dye laser systems. It is expected that this tailoring of the saturation parameters to the available flux should provide a simple technique by which passive modelocking and tunable picosecond pulses in the blue spectral region can be produced. The general performance of these dyes is at present under investigation and further details shall be presented at a later date.
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References