

ABSORPTION RECOVERY OF THE PYRIMIDOCARBOCYANINE DYE PYC

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The ground-state absorption recovery time of the dye 1,3,1',3'-tetramethyl-2,2'-dioxypyrimido-6,6'-carbocyanine hydrogen sulfate (PYC) dissolved in hexafluoroisopropanol, determined by picosecond pump and time-delayed probe pulse transmission measurements, is found to be 14 ± 2 ps. The S_1-S_0 excited-state absorption cross-section at 527 nm is determined by pump pulse bleaching experiments and found to be $\sigma_{ex} = (3 \pm 0.7) \times 10^{-17}$ cm².

1. Introduction

The dye 1,3,1',3'-tetramethyl-2,2'-dioxypyrimido-6,6'-carbocyanine hydrogen sulfate (PYC) dissolved in hexafluoroisopropanol (HFIP) [1,2] was applied recently to efficient phase-matched third-harmonic generation [3,4] and to two-photon pumped travelling-wave laser action [5]. Picosecond pump pulses of a passively mode-locked Nd:glass laser were used in these experiments. Fluorescence quantum yield measurements indicate a fluorescence lifetime of $\tau_F \approx 13 \pm 2$ ps [1].

In this paper the saturable absorption behaviour of PYC dissolved in HFIP is studied. The ground-state absorption recovery time τ_R and the excited-state absorption cross-section σ_{ex} at the pump laser frequency ($\lambda_p = 527$ nm) are determined. The absorption recovery time is found to be equal to the fluorescence lifetime. The weak excited-state absorption makes the dye suitable for fast mode-locking applications.

2. Experimental

The experimental apparatus for the excited-state absorption cross-section determination is shown in fig. 1a. A passively mode-locked Nd:phosphate glass laser is used. A single pulse is selected and amplified. The second harmonic is generated in a KDP crystal (pulse duration $\Delta t_p \approx 4$ ps). The peak intensity of the

pump pulses at the dye sample is determined by two-photon transmission measurements through a rutile crystal [6] (photodetectors PD1 and PD2). The en-

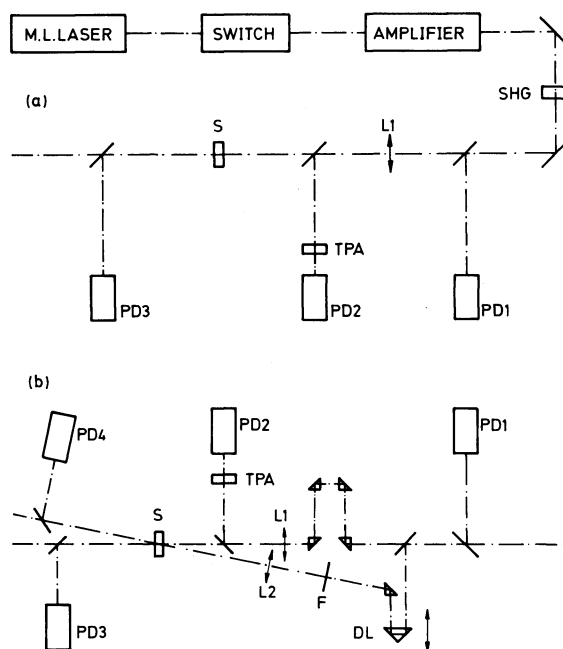


Fig. 1. Experimental apparatus. (a) Arrangement for bleaching measurements (determination of excited-state absorption cross-section). (b) Pump and probe arrangement for absorption recovery time measurement. SHG, KDP crystal for second-harmonic generation. L1, L2, lenses. S, dye sample. PD1-PD4, photodetectors. TPA, rutile crystal for peak intensity detection [6]. DL, optical delay line. F, filter.

ergy transmission through the dye sample is recorded with the detectors PD1 and PD3.

The ground-state absorption recovery time is measured using the experimental arrangement shown in fig. 1b. A probe pulse is split off from the pump pulse, sent through a variable optical delay line, and passed through the dye sample region excited by the pump pulse. The input pump pulse peak intensity is measured as above. The pump pulse transmission (detectors PD1 and PD3) and the probe pulse transmission (detectors PD1 and PD4) through the sample are detected.

3. Results

The absorption and emission cross-section spectrum of PYC dissolved in HFIP is shown in fig. 2 [1]. The pump laser wavelength λ_p and excited-state

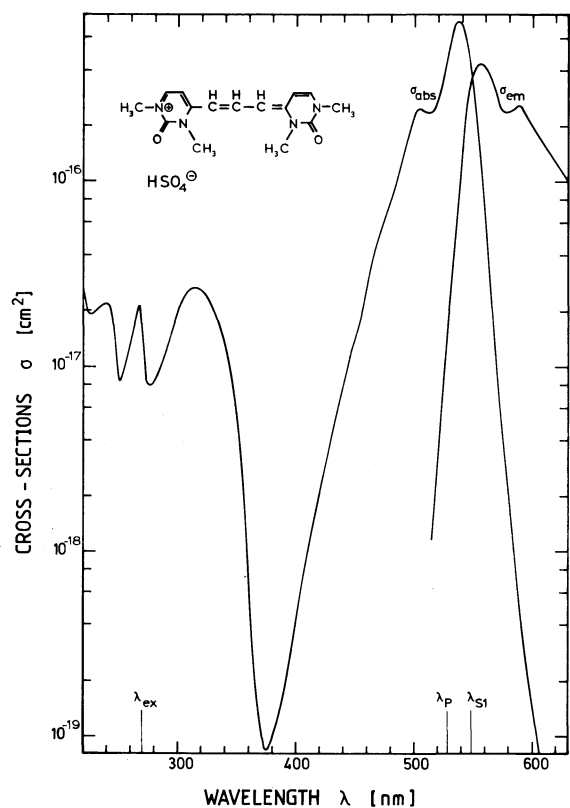


Fig. 2. Absorption and emission cross-section spectrum of PYC in hexafluoroisopropanol (from ref. [1]).

absorption wavelength λ_{ex} are indicated ($\lambda_{ex}^{-1} = \lambda_p^{-1} + \lambda_{S1}^{-1}$; λ_{S1} is the electronic S_0 - S_1 transition wavelength). The structural formula of PYC is included in fig. 2.

The determination of the ground-state absorption recovery time [7-9] and of the excited-state absorption cross-section [10] are discussed separately in the following.

3.1. Ground-state absorption recovery time

After pump pulse excitation the S_1 -level population N_{S1}^{pu} relaxes according to

$$N_{S1}^{pu}(t) = N_{S1,0}^{pu} f(t), \quad (1)$$

where $f(t)$ is the S_1 -state relaxation function. $N_{S1}^{pu}(t)$ is determined by the probe pulse transmission measurement. The probe pulse transmission T_{pr} is

$$T_{pr}(t) = \exp\{-\sigma_p l [N_0 - N_{S1}^{pu}(t) - N_{S1}^{pr}] - \sigma_{ex} l [N_{S1}^{pu}(t) + N_{S1}^{pr}]\}. \quad (2)$$

N_{S1}^{pr} is the S_1 -state population caused by the probe pulse. N_0 is the total number density of dye molecules. l is the sample length and σ_p is the ground-state absorption cross-section at the pump pulse laser frequency. $T_0 = \exp(-\sigma_L N_0 l)$ is the small-signal transmission at λ_p .

Solving eq. (2) for $N_{S1}^{pu}(t)$ gives

$$N_{S1}^{pu}(t) = \frac{1}{(\sigma_p - \sigma_{ex})l} \ln\left(\frac{T_{pr}(t)}{T_0}\right) - N_{S1}^{pr}. \quad (3)$$

N_{S1}^{pr} is given by

$$N_{S1}^{pr} = \frac{1}{(\sigma_p - \sigma_{ex})l} \ln\left(\frac{T_{pr}(\infty)}{T_0}\right). \quad (4)$$

Insertion of eq. (4) into eq. (3) gives

$$N_{S1}^{pu}(t) = \frac{1}{(\sigma_p - \sigma_{ex})l} \ln\left(\frac{T_{pr}(t)}{T_{pr}(\infty)}\right). \quad (5)$$

The temporal dependence of $\ln[T_{pr}(t)/T_{pr}(\infty)]$ at a fixed pump pulse peak intensity determines the S_1 -state relaxation function $f(t)$ (eq. (1)).

If the pump pulse intensity varies from shot to shot the relaxation function $f(t)$ may be approximately recorded by normalizing the transmission measurements according to

$$f(t) \approx \frac{\ln[T_{pr}(t)/T_{pr}(\infty)]}{\ln(T_{pu}/T_0)} = f_m(t). \quad (6)$$

T_{pu} is the pump pulse transmission (measured with photodetectors PD1 and PD3 in fig. 1b).

The $f_m(t)$ function determined experimentally is plotted in fig. 3. It shows single-exponential decay with an absorption recovery time constant of $\tau_R = 14 \pm 2$ ps.

The measured absorption recovery time is – within the error bars – equal to the fluorescence lifetime [1]. This equality indicates that the S_1 -state relaxes to the S_0 ground state without a long-lived intermediate state (no remarkable intersystem crossing; fast relaxation due to internal conversion or twisted internal charge transfer [11]).

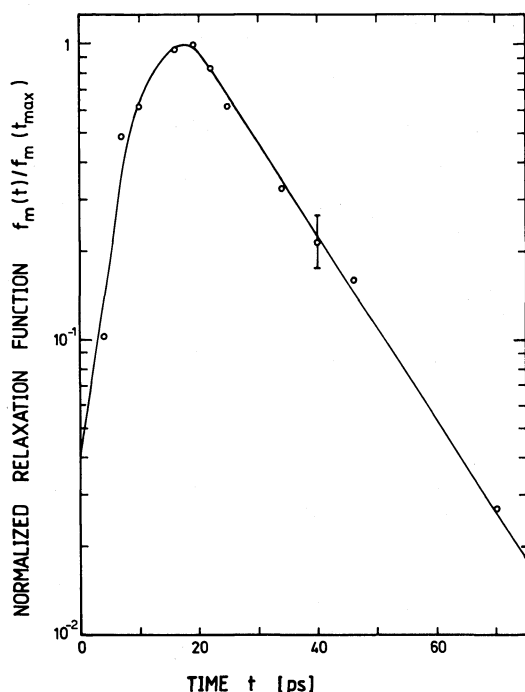


Fig. 3. Normalized time-delayed probe pulse transmission for absorption recovery time determination (eq. (6)). Single exponential decay with $\tau_R = 14$ ps is observed.

3.2. Excited-state absorption cross-section

The excited-state absorption cross-section of PYC in HFIP at the pump laser frequency is determined by measuring the energy transmission versus pump pulse peak intensity and comparing with calculations. The measured energy transmission points are plotted in fig. 4 (dye concentration 10^{-4} mol/dm³, sample length $l=0.1$ cm). An estimate of the excited-state absorption cross-section is obtained by assuming complete ground-state depletion at the highest pump pulse intensity applied and setting the highest transmission, T_{max} , equal to the S_1 - S_n excited-state transmission, i.e.

$$T_{max} \approx \exp(-\sigma_{ex} N_0 l). \quad (7)$$

Application of eq. (7) gives $\sigma_{ex} \approx 3.2 \times 10^{-17}$ cm².

A more rigorous determination of σ_{ex} using a four-level energy diagram (inset of fig. 4) is described in ref. [14]. The solid curve in fig. 4 is calculated with

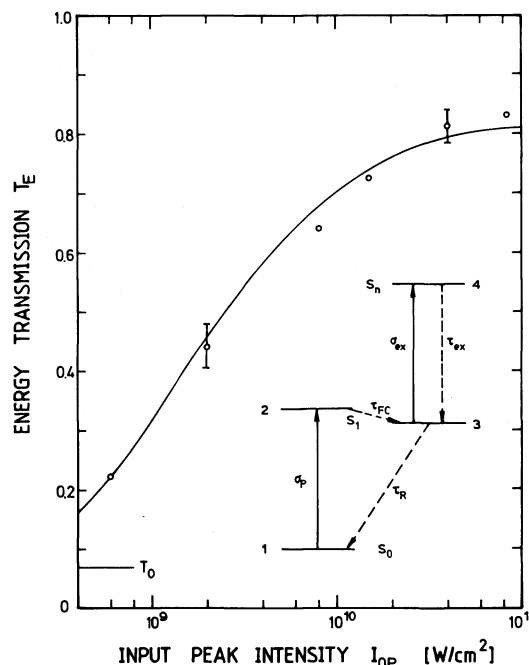


Fig. 4. Energy transmission, T_E , versus input pump pulse peak intensity, I_{op} . 10^{-4} molar PYC in HFIP. Sample length $l=1$ mm. Curve is calculated for $\sigma_{ex} = 3 \times 10^{-17}$ cm² and $\sigma_p = 4.4 \times 10^{-16}$ cm², $\tau_R = 14$ ps, $\tau_{FC} = 0.7$ ps, $\tau_{ex} = 0.1$ ps [12], $\tau_{or} = 150$ ps (re-orientation time [13]). Inset: Energy level diagram for saturable absorption calculations [14].

the rate equation system of ref. [14] for $\sigma_{\text{ex}} = 3 \times 10^{-17} \text{ cm}^2$. The ratio of excited-state absorption cross-section, σ_{ex} , to the ground-state absorption cross-section, σ_{P} , is $\sigma_{\text{ex}}/\sigma_{\text{P}} \approx 0.07$ indicating a high bleaching capability. The dye PYC dissolved in HFIP is thought to be a good fast saturable absorber [15] in the spectral region between 480 and 580 nm [16].

4. Conclusions

The described analyses indicate that PYC dissolved in HFIP is a fast saturable absorber ($\tau_{\text{R}} \approx 14$ ps) with low excited state absorption ($\sigma_{\text{ex}} = (3 \pm 0.7) \times 10^{-17} \text{ cm}^2$ at $\lambda_{\text{P}} = 527 \text{ nm}$; $\sigma_{\text{ex}}/\sigma_{\text{P}} \approx 0.07$). The dye should be applicable as a saturable absorber for second harmonic light pulses of mode-locked Nd lasers and as a fast mode-locking dye for passive or hybrid mode-locking of both pulsed and cw mode-locked dye lasers in the spectral region between 480 and 580 nm.

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