

## EXCITED STATE ABSORPTION DYNAMICS OF FAST RELAXING DYE NO. 5

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The excited state absorption dynamics of the fast mode-locking dye No. 5 for Nd-glass lasers is investigated. The excited state absorption cross-section  $\sigma_{\text{ex}}$  for 1.053  $\mu\text{m}$  picosecond pulse excitation is determined from energy transmission measurements. The excited state absorption populates a higher lying singlet state  $S_4$ . The population lifetime  $\tau_4$  of this state is determined from two-step excited fluorescence quantum yield measurements. The obtained values are  $\sigma_{\text{ex}} = (5.5 \pm 1) \times 10^{-17} \text{ cm}^2$  and  $\tau_4 = 60 \pm 20 \text{ fs}$ .

### 1. Introduction

The polymethine pyrylium dye No. 5 [1] from Kodak or Lambda Physik has a favourably short absorption recovery time of only 2.7 ps [2] when dissolved in 1,2-dichloroethane. It was successfully used as mode-locking dye for Nd-glass lasers and shorter pulse durations were achieved than with the generally used dye Kodak No. 9860 [3,4]. The short recovery time increases the laser intensity necessary for bleaching. Therefore, the conventional linear resonator geometry had to be changed to a folded z geometry with four mirrors to obtain a focal region of high intensity where the dye had to be placed [3]. The excited state absorption of the dye increases the saturation intensity and reduces the efficiency of mode-locking (bleaching is reduced). The dye No. 5 was also applied as an infrared laser dye. Laser action was obtained in a thin cavity with picosecond pulse excitation [5] and in a traveling-wave dye laser [6].

Here we study the excited state absorption dynamics of the dye. The nonlinear transmission of picosecond light pulses ( $\lambda = 1.053 \mu\text{m}$ ) through the dye No. 5 is measured. The energy transmission at high input light intensities allows to determine the excited state absorption cross-section from level  $S_1$  to  $S_4$ . The population lifetime of the  $S_4$ -state (around 530 nm) is determined from  $S_4$ - $S_0$  fluorescence quantum yield measurements after two-step

excitation [7]. The direct single step  $S_0$ - $S_4$  excitation by second harmonic picosecond pulses of the Nd-glass laser is not applied to avoid complications by single step excited  $S_0$ - $S_1$  fluorescence of impurities.

### 2. Theory

The ground state absorption spectrum of dye No. 5 is depicted in fig. 1. The absorption peaks are labeled  $S_1$  to  $S_6$ . From the absorption spectrum the

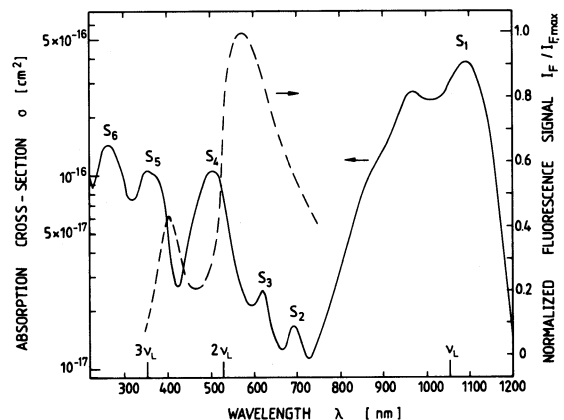


Fig. 1. Absorption and fluorescence spectrum of dye No. 5 in 1,2-dichloroethane. Fluorescence spectrum was excited with pump pulses of  $\lambda_L = 1.053 \mu\text{m}$ ,  $I_{0L} \approx 10^{10} \text{ W/cm}^2$  and  $\Delta t_L \approx 5 \text{ ps}$ .

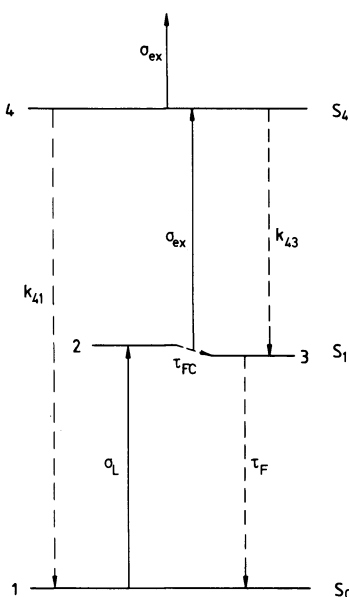


Fig. 2. Energy level diagram used in calculations.

level system of fig. 2 is derived. The light propagation through the dye is described by the following equation system [8]

$$\begin{aligned} \partial N_1(\theta)/\partial t' = & -(3\sigma_L I_L/h\nu_L)[N_1(\theta) - N_2(\theta)] \cos^2\theta \\ & + \tau_F^{-1}[N_2(\theta) + N_3(\theta)] + k_{41}N_4(\theta) \\ & - \tau_{or}^{-1}[N_1(\theta) - \bar{N}_1], \end{aligned} \quad (1)$$

$$\begin{aligned} \partial N_2(\theta)/\partial t' = & (I_L/h\nu_L)3\sigma_L \cos^2\theta \{ \sigma_L [N_1(\theta) - N_2(\theta)] \\ & - \sigma_{ex} [N_2(\theta) - N_4(\theta)N_2(\theta)/[N_2(\theta) + N_3(\theta)]] \} \\ & - (\tau_{FC}^{-1} + \tau_F^{-1})N_2(\theta) - \tau_{or}^{-1}[N_2(\theta) - \bar{N}_2], \end{aligned} \quad (2)$$

$$\begin{aligned} \partial N_3(\theta)/\partial t' = & -(I_L/h\nu_L)3\sigma_{ex} \cos^2\theta [N_3(\theta) \\ & - N_4(\theta)N_3(\theta)/[N_2(\theta) + N_3(\theta)]] + (\tau_{FC}^{-1} - \tau_F^{-1})N_2(\theta) \\ & + k_{43}N_4(\theta) - \tau_{or}^{-1}[N_3(\theta) - \bar{N}_3]. \end{aligned} \quad (3)$$

$$\begin{aligned} \partial N_4(\theta)/\partial t' = & (I_L/h\nu_L)3\sigma_{ex} \cos^2\theta [N_2(\theta) \\ & + N_3(\theta) - N_4(\theta)] - k_4 N_4(\theta) - \tau_{or}^{-1}[N_4(\theta) - \bar{N}_4], \end{aligned} \quad (4)$$

$$\bar{N}_i = \int_0^{\pi/2} N_i(\theta) \sin \theta \, d\theta, \quad (i = 1 \text{ to } 4), \quad (5)$$

$$\begin{aligned} \partial I_L/\partial z = & -3I_L \int_0^{\pi/2} \{ \sigma_L [N_1(\theta) - N_2(\theta)] \\ & + \sigma_{ex} [N_2(\theta) + N_3(\theta)] \} \cos^2\theta \sin \theta \, d\theta. \end{aligned} \quad (6)$$

The transformation  $t' = t - nz/c$  has been used with  $n$  the refractive index and  $c$  the vacuum light velocity.  $\tau_F$  is the  $S_1$ -state lifetime.  $\tau_{FC}$  is the relaxation time of the populated Franck-Condon state 2 within the  $S_1$  band. The relaxation rates of level 4 are  $k_{43}$  and  $k_{41}$  ( $k_4 = \tau_4^{-1} = k_{41} + k_{43}$ ).  $\tau_{or}$  is the molecular re-orientation time. The ground and excited state absorption cross sections are  $\sigma_L$  and  $\sigma_{ex}$ , respectively. The initial number densities of the level populations are  $N_1(\theta, r, t' = -\infty, z) = N_0 = -\ln(T_0)/(\sigma_L l)$ ,  $N_2(t' = -\infty) = N_3(t' = -\infty) = N_4(t' = -\infty) = 0$ . The initial laser intensity is  $I_L(t', r, z = 0) = I_{0L} \exp(-t'^2/t_0^2) \exp(-r^2/r_0^2)$ .  $N_0$  is the total number density of dissolved dye molecules.  $T_0$  is the small signal dye transmission and  $l$  the sample length. The angular anisotropy of ground state and excited state absorption is taken into account by  $\sigma_L(\theta) = 3\sigma_L \cos^2\theta$  and  $\sigma_{ex}(\theta) = 3\sigma_{ex} \cos^2\theta$  [8].  $\theta$  is the direction between electric dipole transition moment and electrical field strength. The  $S_0$ - $S_1$  and  $S_1$ - $S_4$  transition dipole moments are assumed to be parallel to one another. The last term in eq. (6) includes excited state absorption from level 4 to higher lying states (open system with fixed cross-section  $\sigma_{ex}$ :  $\sigma_{ex}[(N_2(\theta) + N_3(\theta))] = \sigma_{ex}[N_2(\theta) + N_3(\theta) - N_4(\theta)] + \sigma_{ex}[N_4(\theta) - N_5(\theta)] + \dots$ ). The experimentally measured energy transmission  $T_E$  is given by

$$T_E = \frac{W_{L,O}}{W_L} = \frac{\int_0^\infty \int_{-\infty}^\infty I_L(r, t', l) dt' 2\pi r dr}{\pi^{3/2} r_0^2 t_0 J_{0L}} \quad (7)$$

$W_{L,O}$  and  $W_L$  are the output and input pulse energies, respectively. A spatial and temporal gaussian input pulse shape is assumed. The comparison of measured  $T_E(I_{0L})$  values with calculated curves allows to determine the  $S_1$ - $S_0$  absorption recovery time  $\tau_F$  and the excited state absorption cross-section  $\sigma_{ex}$ .

The lifetime  $\tau_4 = k_4^{-1}$  of level 4 slightly influences the energy transmission at high input peak intensities. This lifetime will be determined by  $S_4$ - $S_0$  fluorescence signal and radiative lifetime ( $\tau_{rad, S_4-S_0}$ ) measurements. The  $S_4$ -state (level 4) is populated by excited state absorption (two-step excitation) of plane polarized picosecond light pulses. The  $S_4$ - $S_0$  fluorescence is observed under  $90^\circ$  to the pump pulse propagation without polarizers. The pump pulse is polarized perpendicular to the observation direction. The influence of the anisotropy of the  $S_1$ -state population and of the angle between the direction of the  $S_1$ - $S_4$  and

the  $S_4-S_0$  transition dipole moments on the influence signal is neglected. An anisotropy analysis [9,10] will be given elsewhere [11]. The derived formulas agree within  $\pm 20$  percent with a more rigorous discussion [11].

The detected  $S_4-S_0$  fluorescence energy  $W_{F,S_4-S_0}$  normalized to the input pulse energy  $W_L$  is given by

$$\eta_{S_4-S_0} = W_{F,S_4-S_0}/W_L$$

$$= (\Delta\Omega h\nu_F/n_F^2 \tau_{\text{rad},S_4-S_0}) M_4/W_L \quad (8)$$

with

$$M_4 = \int_{-\infty}^{\infty} dt' \int_0^l dz \int_0^{\infty} 2\pi r dr$$

$$\times \int_0^{\pi/2} N_4(r, z, t', \theta) \sin \theta d\theta. \quad (9)$$

$M_4$  is the time integrated total population of level 4.  $\Delta\Omega$  is the solid angle accepted by the detection system.  $\Delta\Omega/n_F^2$  is the internal acceptance angle in the sample.  $n_F$  is the mean refractive index of the solution in the fluorescence wavelength region.  $\nu_F$  is the mean fluorescence frequency.  $N_4(r, z, t', \theta)$  is obtained by solving the equation system (1-6).  $M_4/W_L$  depends on the input pulse parameters  $I_{0L}$  and  $\Delta t_L = 2[\ln(2)]^{1/2} t_0$  as well as on the dye parameters  $\sigma_{\text{ex}}$  and  $\tau_4$ . The radiative lifetime  $\tau_{\text{rad},S_4-S_0}$  is obtained from the  $S_0-S_4$  absorption spectrum and the  $S_4-S_0$  fluorescence spectral distribution according to the Strickler-Berg formula [12,13]:

$$\frac{1}{\tau_{\text{rad},S_4-S_0}} = 8\pi c \frac{n_F^3}{n_A} \frac{\int E(\lambda)\lambda d\lambda}{\int E(\lambda)\lambda^4 d\lambda} \int \frac{\sigma(\lambda)}{\lambda} d\lambda. \quad (10)$$

$E(\lambda)$  represents the spectral shape of the  $S_4-S_0$  fluorescence spectrum (quantum distribution  $\int E(\lambda)d\lambda = 1$ ).  $\sigma(\lambda)$  is the absorption cross-section of the  $S_0-S_4$  transition.  $n_A$  is the mean refractive index of the solution in the absorption band.

To avoid a determination of  $\eta_{S_4-S_0}$  in absolute units and to avoid the determination of  $\Delta\Omega$ , the  $S_4-S_0$  fluorescence signal is compared to the  $S_1-S_0$  fluorescence signal of a dye of known quantum efficiency close to one. The fluorescence of the reference is excited by single step excitation. Neglecting anisotropy effects the fluorescence energy  $W_{F,S_1-S_0,R}$  of the reference normalized to the input pulse energy

$W_{L,R}$  is

$$\eta_{S_1-S_0,R} = W_{F,S_1-S_0,R}/W_{L,R}$$

$$= (\Delta\Omega h\nu_{F,R}/n_{F,R}^2 \tau_{\text{rad},S_1-S_0,R}) M_R/W_{L,R}. \quad (11)$$

The picosecond pulse excitation of the reference dye may be approximated by  $\delta$ -pulse excitation ( $\Delta t_L \ll \tau_{F,R}$ ) leading to a  $S_1$  state population density of  $\bar{N}_{S_1}(r, z, t') = \bar{N}_{S_1}(r, z) \exp(-t'/\tau_{F,R})$  for  $t' > 0$  and  $\bar{N}_{S_1}(r, z, t') = 0$  for  $t' < 0$ .  $M_R/W_{L,R}$  is given by (see eq. (9))

$$\frac{M_R}{W_{L,R}} = \frac{\int_{-\infty}^{\infty} dt' \int_0^l dz \int_0^{\infty} 2\pi r \bar{N}_{S_1}(r, z, t') dr}{W_{L,R}}$$

$$= \frac{\tau_{F,R} \int_0^l dz \int_0^{\infty} 2\pi r dr \bar{N}_{S_1}(r, z)}{W_{L,R}}$$

$$= (\tau_{F,R}/W_{L,R}) W_{\text{abs}}/h\nu_{L,R}$$

$$= \tau_{F,R} (1 - T_{0,R})/h\nu_{L,R}. \quad (12)$$

In eq. (12) the relations  $\int \bar{N}_{S_1} dV = W_{\text{abs}}/h\nu_{L,R}$  and  $W_{\text{abs}} = W_{L,R}(1 - T_{0,R})$  have been used. Insertion of eq. (12) into eq. (11) gives

$$\eta_{S_1-S_0,R} = \nu_{F,R} \Delta\Omega q_{F,R} (1 - T_{0,R})/\nu_{L,R} n_{F,R}^2, \quad (13)$$

where  $q_{F,R} = \tau_{F,R}/\tau_{\text{rad},S_0-S_1,R}$  is the fluorescence quantum efficiency of the reference dye.

The ratio of  $S_4-S_0$  fluorescence yield of the investigated saturable dye to the  $S_1-S_0$  fluorescence yield of the reference dye is found from eqs. (8) and (13)

$$\eta_{S_4-S_0}/\eta_{S_1-S_0,R}$$

$$= \frac{n_{F,R}^2 h\nu_{L,R} \nu_F}{n_{F,R}^2 \tau_{\text{rad},S_4-S_0} \nu_{F,R} q_{F,R} (1 - T_{0,R})} \frac{M_4}{W_L} \quad (14)$$

$M_4/W_L$  is obtained from eq. (14) by measuring all other quantities. The dependence of  $M_4/W_L$  on  $\tau_4$  is used to determine the  $S_4$ -state lifetime.

### 3. Experiments

The experimental set-up is shown in fig. 3. Single picosecond light pulses from a mode-locked Nd-phosphate glass laser are used. The energy transmission

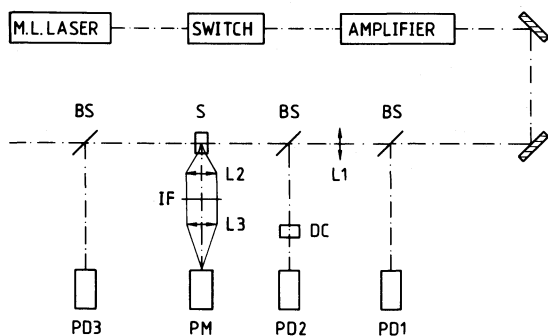


Fig. 3. Experimental setup for energy transmission and  $S_4-S_0$  fluorescence measurement. BS, beam splitters; L1-L3, lenses (L1:  $f = 70$  cm, L2:  $f = 5$  cm, L3:  $f = 10$  cm). DC, dye cell for intensity detection. S, sample; IF, interference filter; PD1-PD3, vacuum photodiodes; PM, photomultiplier.

through the dye sample S is measured with photodetectors PD1 and PD3. The input peak intensity is obtained by energy transmission measurement through the saturable absorber cell DC (dye No. 9860,  $T_0 = 0.173$ ) [14]. The fluorescence signal is gathered under  $90^\circ$  with lenses L2 and L3 and directed to a photomultiplier. A broad band interference filter or spectrometer are used for spectral selection. The laser pump pulses were polarized perpendicular to the observation direction. For the  $S_1-S_0$  fluorescence measurements of the reference the second harmonic was generated with a KDP crystal behind the amplifier (polarization rotated by  $90^\circ$  with half wave plate) and the sample cell S was filled with rhodamine 6G dissolved in ethanol ( $T_{0,R} = 0.9$ ). The second harmonic pulse was attenuated in order not to bleach the reference dye.

#### 4. Results

Fig. 4 depicts the measured energy transmission data of dye No. 5 together with calculated energy transmission curves. The laser parameters used in the calculations are  $\Delta t_L = 5$  ps and  $\lambda_L = 1.053$   $\mu\text{m}$ . The dye parameters are listed in the figure captions. The depopulation of level 4 is assumed to proceed via level 3, i.e.  $\tau_4 = k_4^{-1} = k_{43}^{-1}$ ,  $k_{41} = 0$ . The solid curves exhibit the influence of excited state absorption cross-section  $\sigma_{\text{ex}}(\tau_4 = 10^{-13}$  s). The dashed curves show the influences of  $\tau_4$  ( $\sigma_{\text{ex}} = 6 \times 10^{-17}$   $\text{cm}^2$ ). For

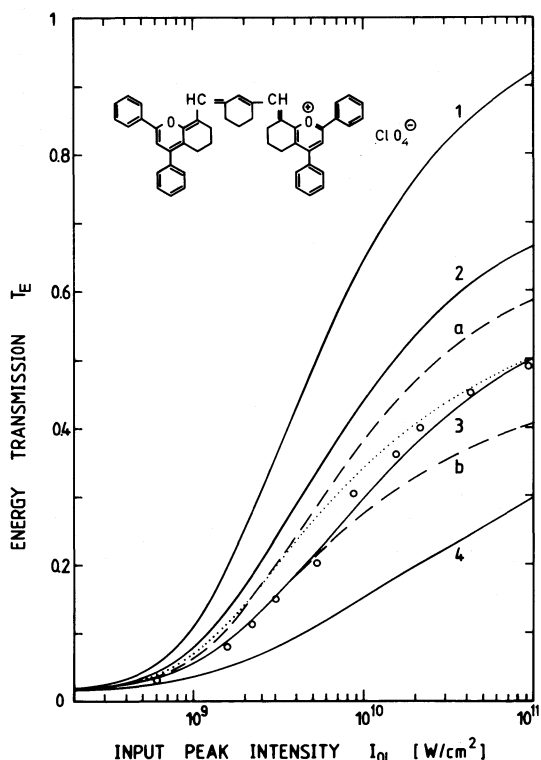


Fig. 4. Energy transmission through dye No. 5. Laser parameters  $\Delta t_L = 5$  ps, frequency  $\nu_L = 9497$   $\text{cm}^{-1}$ . Dye parameters  $T_0 = 0.01$ ,  $\tau_F = 2.7$  ps,  $\sigma_L = 3 \times 10^{-16}$   $\text{cm}^2$ ,  $\tau_{\text{OR}} = 150$  ps. Solid curves:  $\tau_4 = k_4^{-1} = k_{43}^{-1} = 10^{-13}$  s and  $S_0-S_1$  transition dipole moment parallel  $S_1-S_4$  transition dipole moment, (1)  $\sigma_{\text{ex}} = 0$ , (2)  $\sigma_{\text{ex}} = 3 \times 10^{-17}$   $\text{cm}^2$ , (3)  $\sigma_{\text{ex}} = 6 \times 10^{-17}$   $\text{cm}^2$ , (4)  $\sigma_{\text{ex}} = 1.2 \times 10^{-16}$   $\text{cm}^2$ . Dotted curve:  $\tau_4 = k_4^{-1} = 10^{-13}$  s,  $\sigma_{\text{ex}} = 6 \times 10^{-17}$   $\text{cm}^2$  isotropic value. Dashed curves:  $\sigma_{\text{ex}} = 6 \times 10^{-17}$   $\text{cm}^2$  ( $\sigma_{\text{ex}} \parallel \sigma_L$ ), (a)  $\tau_4 = k_{43}^{-1} = 10^{-12}$  s, (b)  $\tau_4 = k_{43}^{-1} = 10^{-14}$  s. Structural formula of dye No. 5 is inserted.

$\tau_4 \lesssim 3 \times 10^{-14}$  s the energy transmission becomes practically independent of  $\tau_4$ . The dotted curve is calculated for isotropic excited state absorption  $\sigma_{\text{ex}}(\theta) = \sigma_{\text{ex}} = 6 \times 10^{-17}$   $\text{cm}^2$  [8]. The experimental points fit better to solid curve 3 than to the dotted curve indicating a nearly parallel orientation of  $S_0-S_1$  and  $S_1-S_4$  transition dipole moments.

The normalized fluorescence spectrum resulting from  $S_n-S_0$  transitions is included in fig. 1. It was detected with a spectrometer in front of the photomultiplier of fig. 1 (without a polarizer in fluorescence path). The  $S_4-S_0$  and  $S_5-S_0$  fluorescence are clearly indicated. The  $S_5-S_0$  fluorescence indicates  $S_4-S_5$  excited state absorption which is included in our calculations by the open level system of fig. 2. Calcula-

tions with an open 5-level system ( $S_5$  state explicitly included) and equal  $S_1$ – $S_4$  and  $S_4$ – $S_5$  excited state absorption led to the same  $T_E$  and  $M_4/W_L$  values as shown in figs. 4 and 5. The  $S_5$  level population was found to be about 10 percent of the  $S_4$  level population at  $I_{0L} = 10^{10}$  W/cm<sup>2</sup> and  $\tau_4 = \tau_5 = 10^{-13}$  s. Variation of the  $S_4$ – $S_5$  absorption cross-section by a factor of two has negligible influence on the  $\sigma_{ex}$  and  $\tau_4$  determination.

Fig. 5 depicts experimental ratio points  $M_4/W_L$  obtained from fluorescence yield measurements (eq. (14)). The used reference data are  $n_{F,R} = 1.37$ ,  $q_{F,R} = 0.88$  [15],  $\nu_{F,R} \approx 17600$  cm<sup>-1</sup> and  $T_{0,R} = 0.9$ . The  $S_4$ – $S_0$  radiative lifetime of dye No. 5 is calculated from the absorption and fluorescence spectrum of fig. 1 ( $\nu_F \approx 17500$  cm<sup>-1</sup>). A value of  $\tau_{rad,S_4-S_0} = (9.2 \pm 0.5)$  ns is found. The refractive index of the dye solution in 1,2 dichloroethane is  $n_F = 1.45$ .  $\eta_{S_4-S_0}$  and  $\eta_{S_1-S_0,R}$  were measured with an interference filter in front of the photomultiplier. The curves in

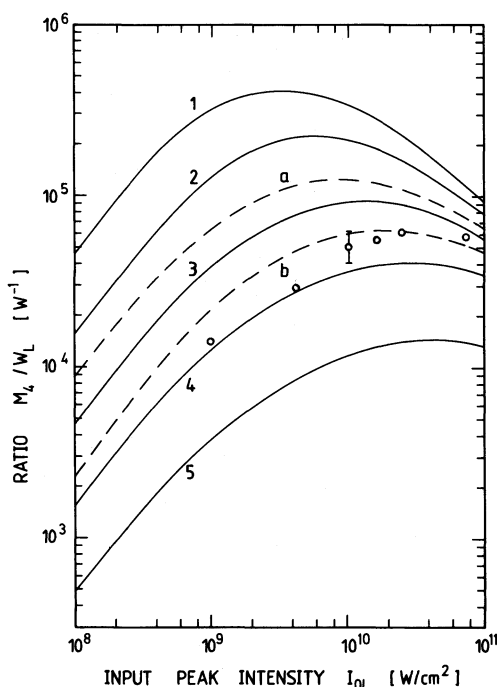


Fig. 5.  $S_4$ -state lifetime determination from plot of  $M_4/W_L$  versus  $I_{0L}$ . Experimental points derived from eq. (14). Solid curves:  $\sigma_{ex} = 6 \times 10^{-17}$  cm<sup>2</sup>,  $k_4$  values are (1)  $10^{12}$  s<sup>-1</sup>, (2)  $3 \times 10^{12}$  s<sup>-1</sup>, (3)  $10^{13}$  s<sup>-1</sup>, (4)  $3 \times 10^{13}$  s<sup>-1</sup>, (5)  $10^{14}$  s<sup>-1</sup>. Dashed curves:  $k_4 = 10^{13}$  s<sup>-1</sup> and (a)  $\sigma_{ex} = 1.2 \times 10^{-16}$  cm<sup>2</sup>, (b)  $\sigma_{ex} = 3 \times 10^{-17}$  cm<sup>2</sup>.

fig. 5 are calculated by use of eq. (9) where  $N_4$  is determined from the differential equation system 1–6. The solid curves belong to various  $\tau_4$  values ( $\sigma_{ex} = 6 \times 10^{-17}$  cm<sup>2</sup>). The dashed curves indicate the influence of  $\sigma_{ex}$  ( $\tau_4 = 10^{-13}$  s). From figs. 4 and 5 we deduce  $\sigma_{ex} = (5.5 \pm 1) \times 10^{-17}$  cm<sup>2</sup> and  $\tau_4 = (6 \pm 2) \times 10^{-14}$  s.

The polarization degree  $P = (I_{F\parallel} - I_{F\perp}) / (I_{F\parallel} + I_{F\perp})$  was detected with a dichroitic polarizer in the fluorescence path.  $P_{S_4-S_0} = 0.17 \pm 0.04$  was found indicating a preferable parallel orientation of  $S_1$ – $S_4$  absorption and  $S_4$ – $S_0$  emission dipole moments [9]. In case of rhodamine 6G,  $P_{S_1-S_0} = 0$  was measured indicating isotropic fluorescence emission (reorientation time short compared to fluorescence lifetime).

## 5. Conclusions

The excited absorption dynamics of the dye No. 5 by 1.053  $\mu$ m picosecond pulse excitation was studied. An  $S_1$ – $S_4$  excited state absorption cross-section  $\sigma_{ex} \approx 5.5 \times 10^{-16}$  cm<sup>2</sup> and an  $S_4$  state lifetime  $\tau_4 \approx 60$  fs were found. The dyes No. 5 from Kodak and Lambda Physik give the same results. Care must be taken if  $S_n$ -state lifetimes are tried to be measured by single step excitation. In our case we obtained  $\tau_4 \approx 14$  ps for the Kodak dye and  $\tau_4 \approx 0.2$  ps for the Lambda Physik dye. The long apparent lifetime of the dye from Kodak is due to impurity fluorescence. Dye degradation with time rises the single-step excited fluorescence signal (fluorescence from photo-products).

The transmission behaviour of dye No. 5 complicates its use as mode-locking dye. The peak spike intensity slightly above laser threshold hardly reaches the mode-locking threshold in conventional oscillators. To use the advantage of short  $S_0$  absorption recovery time for shortening the duration of picosecond light pulses we applied dye No. 5 and 9860 together (single path transmission of each dye about 88%) either in separate cells or mixed together. The pulse duration could be shortened from about 5 ps in case of Kodak 9860 to about 2.5 ps.

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