

S_1-S_0 RELAXATION TIME OF SATURABLE ABSORBER DDI

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The saturable dye DDI is excited with picosecond ruby laser pulses to the S_1 singlet state and the relaxation to the ground state S_0 is determined by measuring the transmission of the exciting pulses through the sample. The relaxation time is found to be $\tau = 17 \pm 3$ ps for DDI dissolved in methanol. Admixtures of rhodamine 6G, potassium iodide, or tetrabutylammonium iodide do not change the decay time.

1. Introduction

The dye DDI (1,1'-diethyl-2,2'-dicarbocyanine iodide) is a frequently used saturable absorber for passive mode-locking of ruby lasers [1]. Its relaxation time τ from the first excited singlet state S_1 to the ground state S_0 has been determined by fluorescence decay [2-5] and absorption recovery measurements [6-9]. The reported results are listed in table 1. They vary between 7 ps and 25 ps for the solvent methanol.

Time resolved fluorescence measurements which may be carried out with fast shutters [2] or streak cameras [6] require excitation pulse durations and response times shorter than the relaxation time τ . The calculation of τ from measured fluorescence quantum yields [5,5] or fluorescence depolarization ratios [3] is independent of the duration of the excitation source, i.e. short relaxation times may be determined with long pump pulses.

The absorption recovery techniques with intense pump pulses and time delayed weak probe pulses [6-9] require pump and probe pulse durations which are short compared to the relaxation time. Otherwise, only the convolution of the pulses is measured.

In this letter we measure the nonlinear transmission of pump pulses of various peak intensities through the dye sample. The relaxation time is determined by comparing the measured energy transmission

with model calculation [10-12]. This technique is applicable for relaxation times τ comparable to or shorter than the pump pulse durations ($\tau \lesssim 2\Delta t_L$). The bleaching effect at a fixed pump pulse intensity is reduced if the excited molecule return to the ground state within the pump pulse duration.

The S_1-S_0 relaxation time of 3.8×10^{-6} molar DDI in methanol is measured at room temperature (295 K). The influence of admixtures of rhodamine 6G [13], KI and tetrabutylammonium iodide [14,15] on the relaxation time is investigated and found to be negligible.

The excited state absorption of pump laser light from the S_1 -state to higher lying singlet states S_n is included in the analysis. The excited state absorption limits the energy transmission at high pump intensities. Excited state absorption cross-sections at the pump laser frequency are obtained in addition to the relaxation times.

2. Theory

The DDI molecules are described by the level system of fig. 1. A pump laser of frequency ν_L (mode-locked ruby laser) excites molecules from the ground state S_0 to the Franck-Condon state 2 within the first excited singlet band S_1 . This transition is caused by electric dipole interaction and generates an aniso-

Table 1
 S_1-S_0 relaxation time τ of DDI at room temperature

Method	Solvent	Viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)	τ (ps)	Ref.
<i>Fluorescence techniques</i>				
Time resolved decay with Kerr shutter	methanol	6×10^{-4}	14 ± 3	[2]
	acetone	3.2×10^{-4}	14 ± 3	[2]
Calculation of fluorescence depolarization	methanol	6×10^{-4}	10 ± 10	[3]
Quantum yield	methanol	6×10^{-4}	7 ± 2	[4]
	ethanol	1.2×10^{-3}	11.5 ± 2.5	[5]
<i>Absorption recovery techniques</i>				
Pump and probe pulses within laser external	methanol	6×10^{-4}	25	[6]
	methanol	6×10^{-4}	10×5	[7]
	ethanol	1.2×10^{-3}	27 ± 2	[8]
	glycerol	1.49	110	[9]
Bleaching of pump pulse	methanol	6×10^{-4}	17 ± 3	this work

tropic population distribution in the ground state ($N_1(\theta)$) and the excited state ($N_2(\theta)$) since the absorption cross-section depends on the angle θ between the electrical field strength E of the light pulse and the transition dipole moment μ of the molecules ($\sigma_{12}(\theta) = 3\sigma_{12} \cos^2(\theta)$). The molecules reorient with a time constant τ_{or} . The molecules in the state 2 relax to the lower lying ground level 3 of the S_1 -state with-

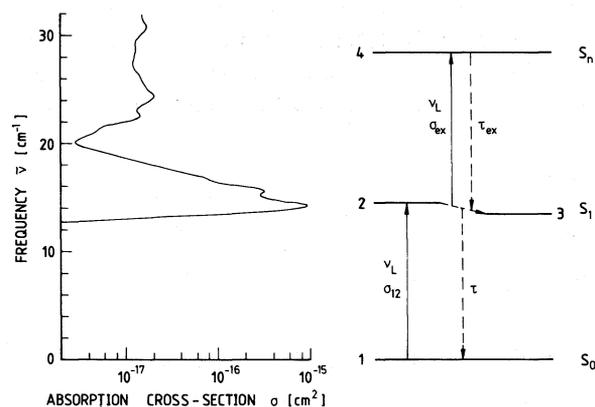


Fig. 1. Absorption spectrum of DDI dissolved in methanol and level system of DDI. Relevant interactions with ps ruby laser pulses and transitions are indicated.

typically 1 ps. Molecules in the S_1 -state may be transferred to a higher singlet state S_n by excited state absorption. This transition is taken into account by an effective absorption cross-section σ_{ex} . The orientational dependence of σ_{ex} is not considered since the angle between the transition dipole moments of S_1 and S_n is unknown. Molecules excited to S_n relax predominantly to the S_1 -level (in the calculations only this decay route is included).

The molecules in the S_1 -state return to the ground state with a time constant τ . In the case of DDI this relaxation time is mainly determined by radiationless transitions (internal conversion), since $\tau \approx 17$ ps (table 1) while the radiative lifetime is $\tau_{rad} \approx 4.1$ ns [5]. A shortening of τ by amplified spontaneous emission is negligible under our experimental conditions and is not included in the calculations (eq. (26)) of [16] gives $1 \geq \tau/\tau_F \{1 + g_F \Delta\Omega/4\pi [T_0^{-\sigma_{em}/\sigma_{12}} - 1] [\sigma_{em}/(\sigma_{em} - \sigma_{ex})]\}^{-1} \approx \{1 + q_F \Delta\Omega [T_0^{-1} - 1]\}/4\pi\}^{-1} = 0.9998$; fluorescence quantum efficiency $q_F \approx 4 \times 10^{-3}$, solid angle of amplified spontaneous emission $\Delta\Omega \approx \pi r_0^2/l^2 \approx 4 \times 10^{-2}$ sr, beam radius $r_0 \approx 0.2$ cm, sample length $l = 2$ cm, small signal transmission $T_0 = 0.03$, stimulated emission cross-section $\sigma_{em} \approx \sigma_{12}$; τ_F is fluorescence lifetime without

amplified spontaneous emission). A leakage of molecules out of the singlet system by intersystem crossing is extremely small in DDI and is not included in the model calculations (intersystem crossing rate $k_{\text{ISC}} \ll 2 \times 10^7 \text{ s}^{-1}$ [4,5]).

The propagation of a pump pulse of intensity $I_{\text{L}}(r, t', z)$ through the sample and the dynamics of the level populations $N_i(\theta, r, t', z)$ ($i = 1$ to 4) are described by the following rate equations ($t' = t - nz/c$; z distance; n refractive index; c vacuum light velocity):

$$\frac{\partial N_1}{\partial t'} = -\frac{I_{\text{L}}}{h\nu_{\text{L}}} 3\sigma_{12} \cos^2(\theta)(N_1 - N_2) + \frac{N_2 + N_3}{\tau} - \frac{N_1 - \bar{N}_1}{\tau_{\text{or}}}, \quad (1)$$

$$\frac{\partial N_2}{\partial t'} = \frac{I_{\text{L}}}{h\nu_{\text{L}}} [3\sigma_{12} \cos^2(\theta)(N_1 - N_2) - \sigma_{\text{ex}}(N_2 - N_4)] - \left(\frac{1}{\tau_{23}} + \frac{1}{\tau}\right)N_2 - \frac{N_2 - \bar{N}_2}{\tau_{\text{or}}}, \quad (2)$$

$$\frac{\partial N_3}{\partial t'} = -\frac{I_{\text{L}}}{h\nu_{\text{L}}} \sigma_{\text{ex}}(N_3 - N_4) + \frac{N_2}{\tau_{23}} + \frac{N_4}{\tau_{\text{ex}}} - \frac{N_3}{\tau} - \frac{N_3 - \bar{N}_3}{\tau_{\text{or}}}, \quad (3)$$

$$\frac{\partial N_4}{\partial t'} = \frac{I_{\text{L}}}{h\nu_{\text{L}}} \sigma_{\text{ex}}(N_2 + N_3 - N_4) - \frac{N_4}{\tau_{\text{ex}}} - \frac{N_4 - \bar{N}_4}{\tau_{\text{or}}}, \quad (4)$$

$$\frac{\partial I_{\text{L}}}{\partial z} = -I_{\text{L}} \int_0^{\pi/2} [3\sigma_{12} \cos^2(\theta)(N_1 - N_2) + \sigma_{\text{ex}}(N_2 + N_3)] \sin(\theta) d\theta. \quad (5)$$

The initial conditions are $N_1(\theta, r, t' = -\infty, z) = N$, $N_2(t' = -\infty) = N_3(t' = -\infty) = N_4(t' = -\infty) = 0$, $I_{\text{L}}(r, t', z = 0) = I_0 g(r) f(t')$. N is the total number density of dye molecules. \bar{N}_i denote the orientational averages $\bar{N}_i = \int_0^{\pi/2} N_i(\theta) \sin(\theta) d\theta$, ($i = 1, 2, 3, 4$). $g(r)$ and $f(t')$ are the spatial and temporal input pulse profiles, respectively. The energy transmission T_{E} of a laser pulse through the sample is obtained by

$$T_{\text{E}} = \frac{W_{\text{I}}}{W_0} = \frac{\int_0^{\infty} \int_{-\infty}^{\infty} I_{\text{L}}(r, t', l) dt' r dr}{I_0 \int_0^{\infty} g(r) r dr \int_{-\infty}^{\infty} f(t') dt'}. \quad (6)$$

W_{I} is the transmitted and W_0 the incident pulse energy. In the calculations the following reasonable values are assumed for unmeasured dye parameters: $\tau_{23} = 1$ ps [17], $\tau_{\text{ex}} = 10^{-13}$ s [16], $\tau_{\text{or}} = 100$ ps [18]. The exact values of these parameters are uncritical in the calculation of τ and σ_{ex} as long as $\tau_{23} < \tau/10$, $\tau_{\text{ex}} < \tau/5$, and $\tau_{\text{or}} > 3\tau$ [19]. The ground state S_0 is represented by single level 1. This simplification is correct if the relaxation times within the S_0 sublevels are fast compared to the S_1-S_0 relaxation time τ [19].

The absorption cross-sections σ_{12} are measured with a spectrophotometer (table 2). The relaxation time τ and the excited state absorption cross-section σ_{ex} are obtained by fitting the calculated T_{E} -values to the measured energy transmissions.

3. Experiments

The experimental set-up is depicted in fig. 2. The laser system consists of a passive mode-locked ruby laser (absorber DDI, single pass small signal transmission 78%), a krytron triggered Kerr shutter for single pulse selection [20], a ruby laser amplifier (amplifica-

Table 2
Absorption cross-sections and S_1-S_0 relaxation times of DDI-methanol solutions

Admixtures	σ_{12} (cm ²)	σ_{ex} (cm ²)	τ (ps)
-	7.6×10^{-16}	$(5 \pm 1) \times 10^{-17}$	17 ± 3
2×10^{-4} mol/l rhodamine 6G	7.8×10^{-16}	$(5 \pm 1) \times 10^{-17}$	17 ± 3
0.4 mol/l KI	8.0×10^{-16}	$(5 \pm 1) \times 10^{-17}$	17 ± 3
1 mol/l tetrabutyl-ammonium iodide	5.8×10^{-16}	$(5 \pm 1) \times 10^{-17}$	17 ± 3

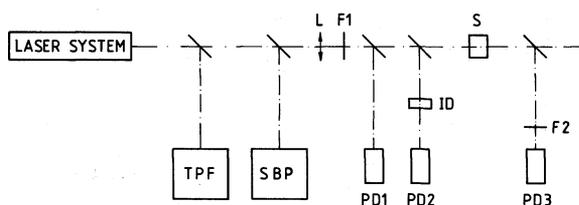


Fig. 2. Experimental setup. TPF: two-photon fluorescence arrangement for pulse duration measurement, SBP: measurement of spatial beam profile with optical multichannel analyzer. PD1–PD3, photodetectors; L, lens ($f = 1$ m); F1, F2, filters; ID, intensity detection by two-photon absorption in CdS; S, sample.

tion in double passage ≈ 80), and a lens-saturable dye soft aperture [21] (focal length of lens combination 4 m, dye DDI in methanol, small signal transmission 10^{-4} , position in focal plane).

The pulse duration is measured by the two-photon fluorescence technique [22] (two-photon absorber 2×10^{-3} molar rhodamine 6G in ethanol). The pulse shape has been measured previously and found to be slightly asymmetric [23]. ($f(t') = \exp(-t'^2/t_0^2) [1 - \theta(t')] + \cosh^{-2}[t'/(kt_0)]\theta(t')$; $\kappa \approx 1.8$; $\theta(t') = 1$ for $t' \geq 0$, 0 otherwise). The spatial pulse profile is monitored with an optical multichannel analyzer. It is approximately gaussian ($g(r) = \exp(-r^2/r_0^2)$). The intensity of the light pulses incident to the sample S is varied by lens L and filters F1. The peak intensity is determined by measuring the transmission through a two-photon absorbing CdS crystal (length 1 cm, photodetectors PD1 and PD2) [23]. The intensity dependent energy transmission through the sample is measured with photodetectors PD1 and PD3.

4. Results

The energy transmission versus input peak intensity is measured for DDI and mixtures of DDI with rhodamine 6G, KI and tetrabutylammonium iodide. The solvent methanol is used. The small signal transmission is adjusted to $T_0 = 0.03$ (sample length $l = 2$ cm). The results for DDI dissolved in neat methanol are shown in fig. 3. Each data point represents an average over about 25 shots. Only shots with pulse durations in the range of $\Delta t_L = (25 \pm 5)$ ps are included. The curves are calculated using the experimen-

tal parameters of pulse shape and duration ($\Delta t_L = 25$ ps) together with the dye parameters listed above. Data points with other pulse durations were analyzed similarly.

Comparison of the data points with the calculated curves gives $\tau = (17 \pm 3)$ ps and $\sigma_{ex} = (5 \pm 1) \times 10^{-17}$ cm². Mixtures of DDI with rhodamine 6G, KI and tetrabutylammonium iodide lead to the same values (table 2).

The influence of rhodamine 6G on τ was tested since shorter pulse durations of mode-locked ruby lasers are generated when DDI-rhodamine 6G mixtures were used as saturable dyes [13]. Explanations of this behaviour by two-photon absorption are reported in [13,24].

The I⁻ ions of KI or tetrabutylammonium iodide are known to enhance intersystem crossing and to

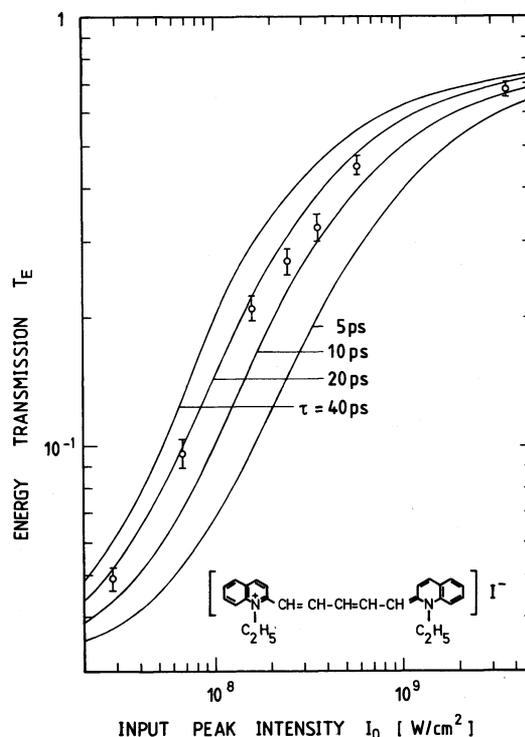


Fig. 3. Energy transmission of ruby laser pulses through DDI dissolved in methanol versus input peak intensity. Dye parameters: $T_0 = 0.03$; sample length 2 cm. Pulse parameters: duration $\Delta t_L = 25 \pm 5$ ps, spatial shape gaussian, temporal shape gaussian rise and hyperbolic secant decay. Curves are calculated for $\Delta t_L = 25$ ps and $\sigma_{ex} = 5 \times 10^{-17}$ cm² (other parameters see text).

cause charge transfer interactions [14,15]. Our results indicate that these enhanced transition rates remain small compared to the fast nonradiative (internal conversion) relaxations of DDI in neat methanol even at the high Γ^- -concentrations which were used.

Our results on the relaxation time τ of DDI dissolved in methanol is in good agreement with the time resolved fluorescence measurements of ref. [2] (see table 2). The fluorescence quantum yield measurements give somewhat too short relaxation times. This fact is probably due to the difficulties in measuring exactly quantum yields and calculating precisely radiative lifetimes.

5. Conclusions

The S_1-S_0 decay time of DDI-methanol solutions has been determined by measuring the nonlinear transmission of picosecond pump pulses and comparing with realistic calculations. The potential importance of this technique lies in the fact that relaxation times shorter than the pump pulse durations are measurable ($\tau \lesssim 2\Delta t_L$).

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