Saturable absorption dynamics of a cyanovinyl-diethylaniline dye

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The saturable absorption dynamics of 4-tricyanovinyl-N,N-diethylaniline (TCVA) in methanol is investigated with intense picosecond light pulses at 527 nm. An excited-state absorption cross-section of $\sigma_{ex} = (2.5 \pm 0.3) \times 10^{-17}$ cm^2 and an absorption recovery time of $\tau_A = 3 \pm 1$ ps are determined. The fast deactivation of the S_1 state is due to internal conversion.

1. Introduction

Dicyanovinyl-dialkylaniline dyes [1–3] (=dialkylamino-dicyanostyrenes=dialkylamino-benzylidene malonitriles) and tricyanovinyl-dialkylaniline dyes [1] (=dialkylamino-tricyanostyrenes) are applied for coloring synthetic polymer fibers [1]. They are used as sublimable dyes in heat-transfer recording materials [4,5] and photoconductive recording materials [6]. They act as cytotoxic agents against tumors [7], as X-ray protective agents [8], and as photostabilizers in plastics against ultraviolet radiation [2].

The absorption and emission spectroscopic properties of 4-dicyanovinyl-N,N-diethylaniline (DCVA) [9–16] and 4-tricyanovinyl-N,N-diethylaniline (TCVA) [15,16] have been investigated recently. The fluorescence quantum efficiencies q in the vapor phase [15] and in liquid solutions [9–12,16] were found to be very small ($q < 10^{-3}$). Temperature-dependent fluorescence-quantum-efficiency measurements indicated an intrinsic barrierless deactivation [16]. Since the viscous drag of the dye surroundings determines the fluorescence lifetime of these dyes [9–13,17–21], they are applied as micro-viscosity probes and free-volume probes in micellar emulsions [9] and polymers [10–13,17–21]. The analysis of the solvent-dependent spectral absorption and emission shifts revealed a partial intramolecular charge transfer in the excited S_1 state [9,10,13,16,18,22,23].

The low fluorescence quantum efficiencies may be due to fast internal conversion caused by the rotational movement of flexible molecular groups [10,11,13,16,17,24]. In this case, the fluorescence signal is emitted from the vibrationally relaxed excited S_1 state which has a radiative lifetime $\tau_{rad}^{S_1}$, and the fluorescence lifetime, $\tau_F^{S_1} = q\tau_{rad}^{S_1}$, is equal to the absorption recovery time τ_A.

Low fluorescence quantum efficiencies could also be the result of fast intersystem crossing to triplet states. In this case, the absorption recovery time τ_A would become equal to the phosphorescence time $\tau_p^{T_1} = q\tau_{rad}^{T_1}$. But the investigated dyes exhibit very little triplet yield [13], so fast intersystem crossing may be excluded.

In electron-donor–acceptor systems like the disubstituted benzenes DCVA and TCVA [10,13,24], an excited orthogonal zwitterionic singlet state might be formed [25–29] (twisted intramolecular charge-transfer state, TICT state [30–34]). The TICT state would have a long radiative lifetime τ_{rad}^{TICT} because its radiative transition to the electronic ground state is electric-dipole forbidden [30]. Therefore the fluorescence emission from TICT states would result in

low fluorescence quantum efficiencies even at slow nonradiative decay rates. The ground-state absorption recovery time τ_A would become equal to the TICT fluorescence lifetime $\tau_F^{TICT} = q\tau_{rad}^{TICT}$.

Saturable absorption studies, which measure the absorption recovery time, allow one to distinguish between internal conversion (short absorption recovery time) and TICT state formation (slow absorption recovery time).

In this paper the saturable absorption of TCVA dissolved in methanol is investigated at room temperature. The dye solutions are excited with second-harmonic picosecond light pulses of a mode-locked Nd:glass laser. The excited-state absorption cross-section σ_{ex} at the second-harmonic laser frequency ($\lambda_P = 527$ nm) and the absorption recovery time τ_A are determined by measuring the intensity dependence of transmission.

2. Experimental

The experimental arrangement for pump-pulse bleaching and time-delayed probe-pulse transmission measurements is displayed in fig. 1. A passively mode-locked Nd:phosphate glass laser [35] generates trains of picosecond light pulses (wavelength $\lambda_L = 1054$ nm, duration $\Delta t_L \approx 5$ ps). Single pulses are selected with an electro-optic shutter and are amplified in a Nd:phosphate glass amplifier (single-pulse energy up to 5 mJ). The second-harmonic light
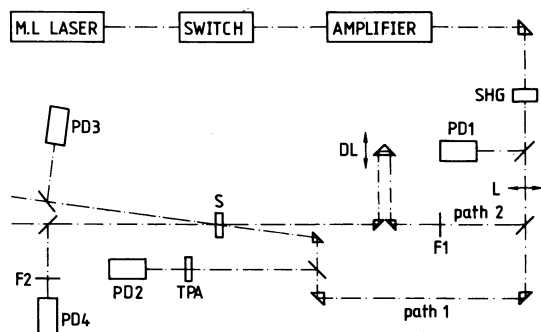

Fig. 1. Experimental setup. PD1–PD4, photodetectors, L, lens. F1, F2, filters. DL, optical delay line. SHG, KDP crystal for second-harmonic generation. TPA, rutile crystal for peak-intensity detection. S, sample.

pulses (wavelength $\lambda_P = 527$ nm, duration $\Delta t_P \approx 4$ ps) used for the saturable absorption studies are generated in a KDP crystal. For the determination of the intensity-dependent pump-pulse transmission through the saturable absorber, only the pump pulse along path 1 is passed through the sample S and the probe pulse (path 2) is covered. The input pump-pulse peak intensity is determined by transmission measurements through a two-photon absorbing rutile crystal (photodetectors PD2 and PD1) [36]. The relative error of the peak-intensity detection is estimated to be $\pm 20\%$. The pump-pulse transmission through the TCVA sample is measured with the photodetectors PD3 and PD1. The temporal behaviour of the saturable absorber at a fixed pump-pulse peak intensity is studied by measuring the transmission of a weak probe pulse (path 2) of variable delay (photodetectors PD4 and PD1). The experiments are carried out at room temperature.

3. Results

Intensity-dependent transmission measurements allow the determination of excited-state absorption cross-sections σ_{ex} at high pump-pulse intensities, and the determination of absorption recovery times τ_A if they are shorter than the pump-pulse duration ($\tau_A \lesssim \Delta t_P$) by comparing experimental data with numerical simulations [37,38]. Time-delayed probe-pulse transmission measurements allow the measurement of absorption recovery times if they are longer than the pump-pulse duration ($\tau_A > \Delta t_P$) [39].

3.1. Pump-pulse transmission

The pump-pulse energy transmission T_E through TCVA in methanol versus input peak intensity I_{0P} is shown by the circles in fig. 2 (small signal transmission $T_0 = 0.021$, sample length $l = 1$ mm).

The saturable absorption dynamics is simulated by transitions in a four-level energy diagram. The level system is displayed by the inset in fig. 2. The system of differential equations describing the level populations N_i ($i = 1$ to 4) and the laser propagation is given by [38]
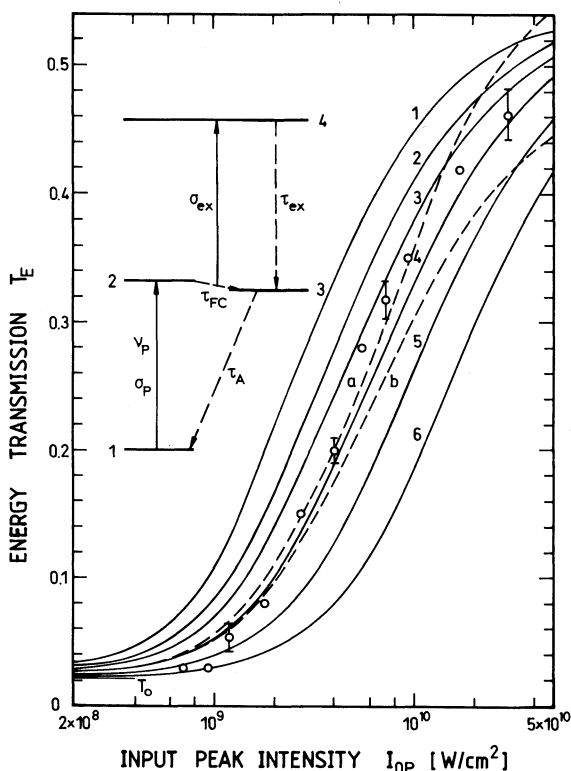
Fig. 2. Pump-pulse energy transmission versus input-peak intensity. Circles represent measured data. The solid curves are calculated for $\sigma_P = 1.6 \times 10^{-16}$ cm^2 [16], $\sigma_{ex} = 2.5 \times 10^{-17}$ cm^2, $\tau_{FC} = 0.5$ ps (assumed), $\tau_{ex} = 10^{-13}$ s (assumed), $\tau_{or} = 150$ ps (assumed, no relevance here), $\Delta t_P = 4$ ps, and $T_0 = 0.021$. The absorption recovery times are (1) $\tau_A = \infty$, (2) $\tau_A = 8$ ps, (3) $\tau_A = 4$ ps, (4) $\tau_A = 2$ ps, (5) $\tau_A = 1$ ps, and (6) $\tau_A = 0.5$ ps. The dashed curve belong to $\tau_A = 2$ ps and $\sigma_{ex} = 2 \times 10^{-17}$ cm^2 (a) and $\sigma_{ex} = 3 \times 10^{-17}$ cm^2 (b). The other parameters are the same as for the solid curves. The energy-level diagram applied to the calculations is inserted in the figure.

$$\frac{\partial N_1(\theta)}{\partial t'} = -\frac{I_P}{h\nu_P} 3\sigma_P \cos^2\theta \, [N_1(\theta) - N_2(\theta)]$$

$$+ \frac{N_2(\theta) + N_3(\theta)}{\tau_A} - \frac{N_1(\theta) - \bar{N}_1}{\tau_{or}}, \qquad (1)$$

$$\frac{\partial N_2(\theta)}{\partial t'} = \frac{I_P}{h\nu_P} \left[3\sigma_P \cos^2\theta \, [N_1(\theta) - N_2(\theta)] \right.$$

$$\left. - \sigma_{ex}\left(N_2(\theta) - \frac{N_2(\theta)}{N_2(\theta) + N_3(\theta)} N_4(\theta)\right) \right]$$

$$- \left(\frac{1}{\tau_A} + \frac{1}{\tau_{FC}}\right) N_2(\theta) - \frac{N_2(\theta) - \bar{N}_2}{\tau_{or}}, \qquad (2)$$

$$\frac{\partial N_3(\theta)}{\partial t'}$$

$$= -\frac{I_P}{h\nu_P}\sigma_{ex}\left(N_3(\theta) - \frac{N_3(\theta)}{N_2(\theta) + N_3(\theta)} N_4(\theta)\right)$$

$$+ \frac{N_2(\theta)}{\tau_{FC}} - \frac{N_3(\theta)}{\tau_A} + \frac{N_4(\theta)}{\tau_{ex}} - \frac{N_3(\theta) - \bar{N}_3}{\tau_{or}}, \qquad (3)$$

$$\frac{\partial N_4(\theta)}{\partial t'}$$

$$= \frac{I_P}{h\nu_P}\sigma_{ex}[N_2(\theta) + N_3(\theta) - N_4(\theta)] - \frac{N_4(\theta)}{\tau_{ex}}, \qquad (4)$$

$$\frac{\partial I_P}{\partial z'} = -I_P \int_0^{\pi/2} \{3\sigma_P \cos^2\theta \, [N_1(\theta) - N_2(\theta)]$$

$$+ \sigma_{ex}[N_2(\theta) + N_3(\theta)]\} \sin\theta \, d\theta. \qquad (5)$$

The transformation $t' = t - c_0 z/n$ and $z' = z$ is used (c_0 is the vacuum light velocity, n is the refractive index). The initial conditions are

$$N_1(\theta, t' = -\infty, z', r) = N_0,$$

$$N_2(\theta, t' = -\infty, z', r) = N_3(\theta, t' = -\infty, z', r)$$

$$= N_4(\theta, t' = -\infty, z', r) = 0$$

and

$$I_P(t', z' = 0, r) = I_{0P} \exp[-(t'/t_P)^2 - (r/r_P)^2].$$

$t_P = \Delta t_P/2(\ln 2)^{1/2}$ is half the $1/e$ width of the pump-pulse duration and r_P is the $1/e$ width of the laser-beam radius. N_0 is the total number density of dye molecules. The orientation-averaged number densities of the level populations are

$$\bar{N}_i = \int_0^{\pi/2} N_i(\theta) \sin\theta \, d\theta \quad (i = 1, 2, 3).$$

The absorption anisotropy of the electric-dipole in-

teraction is taken into account for the ground-state absorption $(\sigma_P(\theta) = 3\sigma_P \cos^2\theta)$. θ is the angle between the transition dipole moment for ground-state absorption of the molecules and the direction of the electric field of the pump laser (linearly polarized). τ_{or} describes the molecular reorientation of the transition dipole moments. The energy transmission of the pump laser is given by

$$T_E = \frac{\int_0^\infty r \, dr \int_{-\infty}^\infty I_P(t', z'=l, r) \, dt'}{\int_0^\infty r \, dr \int_{-\infty}^\infty I_P(t', z'=0, r) \, dt'}, \qquad (6)$$

where l is the sample length.

The curves in fig. 2 are calculated by solving numerically eqs. (1)–(6). The dye parameters used are listed in the figure caption. The best numerical fit to the experimental points corresponds to an excited-state absorption cross-section of $\sigma_{ex} = (2.5 \pm 0.3) \times 10^{-17}$ cm^2 $(\sigma_{ex}/\sigma_P = 0.16 \pm 0.02)$ and a ground-state absorption recovery time of $\tau_A = 3 \pm 1$ ps.

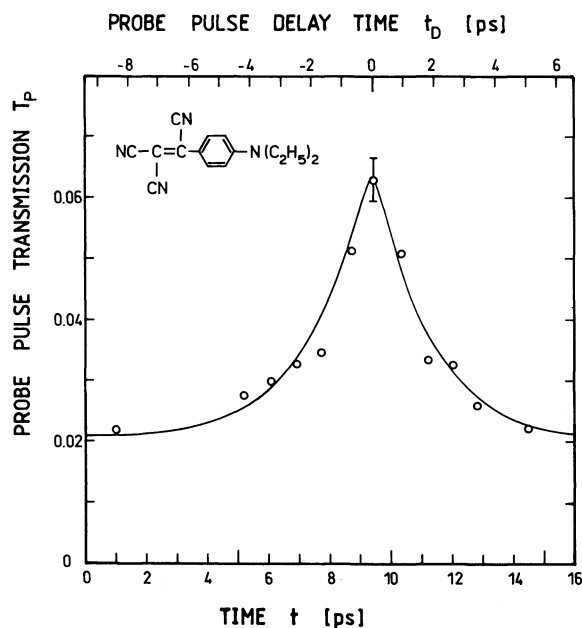
Fig. 3. Probe-pulse energy transmission versus time. Pump-pulse input peak intensity is $I_{0P} \pm 2 \times 10^9$ W/cm^2. The small signal transmission is $T_0 = 0.021$. The structural formula of TCVA is inserted in the figure.

3.2. Probe-pulse transmission

The temporal position of the probe pulse relative to the pump pulse is varied. The probe-pulse transmission versus time is displayed in fig. 3. Only laser shots with measured pump-pulse peak intensities between 1.5×10^9 and 2.5×10^9 W/cm^2 were remained for the plot. The probe pulses were attenuated by a factor of 50 compared to the pump pulse.

The probe-pulse transmission curve versus delay time is symmetric relative to the transmission maximum where pump pulse and probe pulse pass simultaneously through the sample (delay time $t_D = 0$). This symmetric shape indicates that the absorption recovery time τ_A is shorter than the laser-pulse duration Δt_P in agreement with the computer simulations of the pump-pulse transmission (section 3.1).

4. Discussion

In ref. [16], the fluorescence quantum efficiency of TCVA in methanol at room temperature was found to be $q \approx 7 \times 10^{-4}$ and a radiative lifetime of the vibrationally relaxed S_1 state was estimated to be $\tau_{rad}^{S_1} \approx 6$ ns. The assumption of S_1–S_0 internal conversion gives a fluorescence lifetime of $\tau_F^{S_1} = q \tau_{rad}^{S_1} \approx 4$ ps. This value is in good agreement with the ground-state absorption recovery time of $\tau_A = 3 \pm 1$ ps determined in this paper. The excited TCVA molecules in methanol relax to the ground state by fast internal conversion at room temperature. Rotational motions of the cyanovinyl group and the diethylamino group seem to be responsible for the fast excited-state deactivation [10,11,13,16]. The fast relaxation seems to hinder an efficient TICT state formation.

5. Conclusions

The combined measurements of fluorescence quantum efficiencies and absorption recovery times allow the distinction between different relaxation channels of excited molecules. The same information could be obtained by the combined measurements of fluorescence quantum efficiencies and time-resolved fluorescence decays (e.g. streak-camera measurements) [40]. The bleaching behaviour of

TCVA in methanol at 527 nm allows the application of the dye as a fast saturable absorber for lasers in this wavelength region (e.g. second-harmonic pulses of Nd lasers).

Acknowledgement

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