

## FEMTOSECOND EXCITED STATE RELAXATION OF DYE MOLECULES IN SOLUTION

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Received 12 December 1984

The bleaching dynamics of organic dye molecules in solution have been investigated using 70 fs pulses from a colliding pulse mode-locked ring dye laser. In addition to ground state relaxation on a nanosecond time scale, a fast partial recovery is observed. For the dyes Nile blue, oxazine 720, cresyl violet and rhodamine 640, this recovery is exponential, with relaxation times in the range 190–480 fs.

### 1. Introduction

The excited state relaxation dynamics of dye molecules in solution has been a subject of experimental interest ever since the development of picosecond lasers [1–13]. Due to the influence of the molecular dynamics on the behavior of mode-locked dye lasers, this subject has relevance to picosecond and femtosecond devices as well as to the understanding of molecular physics. In this Letter we report pump–probe measurements [14] of bleaching in several organic dye solutions, using 70 fs pulses from a colliding pulse mode-locked (CPM) ring dye laser [15]. For each dye examined, we observe a new, transient component of the bleaching in addition to the well known ground state recovery which occurs on nanosecond time scale. The transient bleaching signals exhibit a rapid initial decay followed by a slower exponential decay with a time constant on the order of several hundred femtoseconds. These decay times are relatively insensitive to the choice of solvent and are attributed to intramolecular relaxation.

### 2. Theoretical background

We consider the absorption of a photon by a dye

molecule, accompanied by a transition from a low-lying level within the  $S_0$  electronic ground state to a highly excited level within the  $S_1$  excited state. Following the transition the molecule rapidly relaxes out of the initially photoexcited levels due to vibrational as well as isoenergetic spectral relaxation. An analogous situation is the configurational relaxation of F-centers [16]. Our experiment, using degenerate pump and probe frequencies, measures the total transfer of dye molecules out of the initially photoexcited levels but does not distinguish between vibrational and other spectral relaxation. On a slower time scale, solvent reordering [5] (tens of picoseconds), orientational relaxation [17,18] (tens to hundreds of picoseconds) and radiative relaxation (hundreds of picoseconds to several nanoseconds) may be observed but can be neglected on the femtosecond time scale of our investigation.

Our experiment employs the well known pump–probe technique [14]. A pair of femtosecond pulses is focused non-collinearly through a common spot in the absorbing sample. The change in probe transmission induced by the pump, measured as a function of the relative delay  $\tau$ , indicates the dynamics of the saturation process. Fast molecular dynamics will be observed as a transient feature near zero delay [19]. Immediately after photoexcitation both ground state depletion and stimulated emission from the initial levels in  $S_1$  contribute to the saturation signal. Subsequent to excited state relaxation, the saturation is reduced

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because stimulated emission is no longer possible at the laser frequency. The residual bleaching at large  $\tau$  due to ground state depletion appears as a constant level on our femtosecond time scale. Even for relaxation times shorter than the pulsewidth, the excited state relaxation can still be detected as a peaking in the signal near  $\tau = 0$ . However, because the peaking depends not only on the relaxation time but also on the excited state absorption, the level degeneracies and the dependence of the stimulated emission spectrum on the population distribution within the excited state, it is difficult to unambiguously determine relaxation times shorter than the pulsewidth.

The pump-probe signal is equal to the sum of two distinct contributions: the saturation term  $\gamma(\tau)$  and the coherent coupling artifact  $\beta(\tau)$ . Analytic expressions for  $\gamma(\tau)$  and  $\beta(\tau)$  are given in ref. [14] in the perturbational limit and assuming instantaneous dephasing.  $\gamma(\tau)$  contains the information about molecular dynamics and is simply the convolution of the molecular response function  $A(t)$  with the intensity autocorrelation. For saturation dynamics slow compared to the pulsewidth,  $A(t)$  is the unit step function; and the saturation signal  $\gamma(\tau)$  is just the integral of the intensity autocorrelation. The coherent coupling term  $\beta(\tau)$  depends mainly on the pulse shape and can obscure the bleaching dynamics near zero delay [14,20, 21]. In evaluating our data, we make a careful attempt to account for the coherent coupling contribution. Furthermore, we emphasize the observation of transient signals that are clearly resolved and considerably longer than our pulsewidths.

### 3. Experimental

Our experiments utilized 70 fs pulses from a CPM ring dye laser [15] with a center wavelength at 625 nm, a bandwidth of 10 nm and a repetition rate of 125 MHz. Pump and probe beams of comparable intensity ( $\approx 5$  mW each) were focused non-collinearly by a 10 cm lens to a common 30  $\mu\text{m}$  spot in the dye sample. The induced saturation was limited to a few tenths of a percent. Orthogonal polarizations were used to eliminate the thermally enhanced coherent coupling [22] which can occur in a high-repetition-rate system like the CPM dye laser. Dye samples were held in thin (50 or 100  $\mu\text{m}$ ) cells and has small signal

absorptions in the range 10–30%.

To minimize timing jitter, a single pulse train from the laser was used to derive pump and probe pulses. The probe delay was controlled using a stepper-motor driven translation stage with a 0.1  $\mu\text{m}$  resolution. The delay origin was determined via autocorrelation by substitution of a second harmonic crystal for the dye sample; the autocorrelation trace was stored for later use in the data evaluation. The laser power spectrum was also recorded for use in calculating the electric field autocorrelation [23,24]. In order to increase our sensitivity, we detected the difference between transmitted and incident probe power. This was accomplished using two photodiodes, one to measure the transmitted probe and the other to measure a reference beam. The photodiode voltages are adjusted for equal amplitude and subtracted at the input of a lock-in amplifier. A signal averager indexed to the stepper motor was used to accumulate data from the lock-in.

### 4. Results and discussion

In order to clarify our procedure for data reduction, we first discuss in detail data for a single dye. Fig. 1a shows pump-probe data (solid line) for a thin, 50  $\mu\text{m}$  cell of Nile blue in methanol. The large peaking of the signal near zero delay and the clearly resolved tail on the peak demonstrate that, on this time scale, excited state relaxation is indeed evident.

In order to process these data, we must first account accurately for the coherent coupling artifact. This is accomplished by subtracting from the data the squared electric field autocorrelation envelope, normalized for an amplitude equal to one half the total signal at  $\tau = 0$ . This particular amplitude is selected because for dye solutions the saturation and coherent coupling terms are equal at zero delay [14,20]. In the case of orthogonal polarizations, this presumes that orientational relaxation is slow on a femtosecond timescale, an assertion corroborated by the literature [17,18]. The use of the squared electric field autocorrelation as an approximation to the coherent coupling becomes exact in the limit of long relaxation times. In the opposite limit of fast relaxation, the coherent coupling term is proportional to the intensity autocorrelation. Because the long-lived saturation makes the larger contribution to the pump-probe signal, the

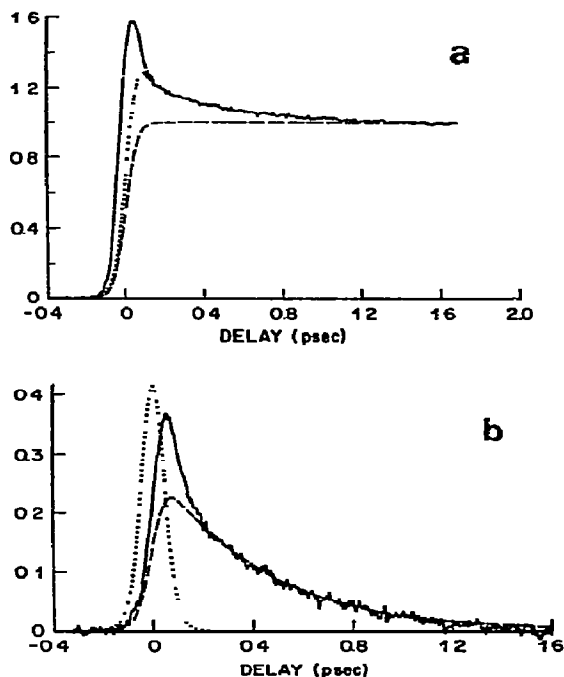


Fig. 1. Pump-probe data for Nile blue in methanol. (a) The original data (solid), the data after removal of the coherent artifact (dotted), and the integral of the intensity autocorrelation (dashed). (b) That portion of the pump-probe signal due to fast molecular dynamics (solid), the fit assuming a single exponential response with a 410 fs time constant (dashed), and the intensity autocorrelation (dotted).

squared electric field autocorrelation is the preferable estimate. In any case the error in our approximation cannot be very large since the measured intensity autocorrelation width (at the half-power points) is only 10% greater than the width of the squared field autocorrelation. Note that the electric field autocorrelation can be determined very accurately by calculating the Fourier transform of the measured laser power spectrum [23,24].

The signal which remains after removal of the coherent coupling is plotted with a dotted line in fig. 1a, together with the original data (solid) and the integral of the intensity autocorrelation (dashed). Since the latter curve represents that portion of the saturation signal due to a long-lived population change, the difference between the dotted and dashed curves yields the contribution associated with fast molecular dynamics. This difference is shown as the solid line in

fig. 1b, along with the intensity autocorrelation (dotted) for comparison. Although the transient bleaching exhibits a rapid initial decay, a subsequent exponential tail is clearly resolved. We have attempted to fit the data by convolving the intensity autocorrelation with assumed response functions  $A(t)$ . The tail of the experimental curve is well matched assuming simple exponential decay:  $A(t) = 0.29 \exp(-t/410 \text{ fs}) \times u(t)$ , where  $u(t)$  is the unit step function. The amplitude of  $A(t)$  is normalized such that the long-lived component of the response has unit amplitude, and the exponential time constant is determined to within  $\pm 5$  fs. The calculated response, shown as the dashed line in fig. 1b, provides a good fit in the region  $\tau \geq 200$  fs, but severely underestimates the peak near zero delay. By including a second, faster exponential response, an acceptable fit over the entire range of delay can be obtained. Note that double or multiple exponential recovery curves have been observed, on a slower time scale, in several other organic systems [25-27]. For Nile blue the best choice for a response function appears to be

$$A(t) = u(t)[0.29 \exp(-t/410 \text{ fs}) + 0.3 \exp(-t/70 \text{ fs})]$$

Due to uncertainty about the coherent coupling as well as the inherent difficulty in determining a response time below the pulsewidth, the fast, 70 fs time constant and its amplitude must be regarded as approximate. The possibility that the initial fast response is non-exponential also cannot be excluded. Nevertheless, it does appear that the extra peaking in the transient bleaching signal is a true manifestation of fast molecular dynamics.

As a second example, data for oxazine 720 dye in methanol are shown in fig. 2a. Also shown are the data with coherent coupling removed and the integrated intensity autocorrelation. The transient bleaching signal, obtained in the same fashion as for Nile blue, is depicted in fig. 2b together with the fit obtained assuming a single exponential response with a 480 fs time constant. There is again an extra peaking at small positive delays. A double exponential response, given by

$$A(t) = a(t)[0.21 \exp(-t/480 \text{ fs}) + 0.13 \exp(-t/80 \text{ fs})]$$

is sufficient to fit the data over the entire range of delay. As previously, the values quoted for the fast component of the response must be regarded as approximate.

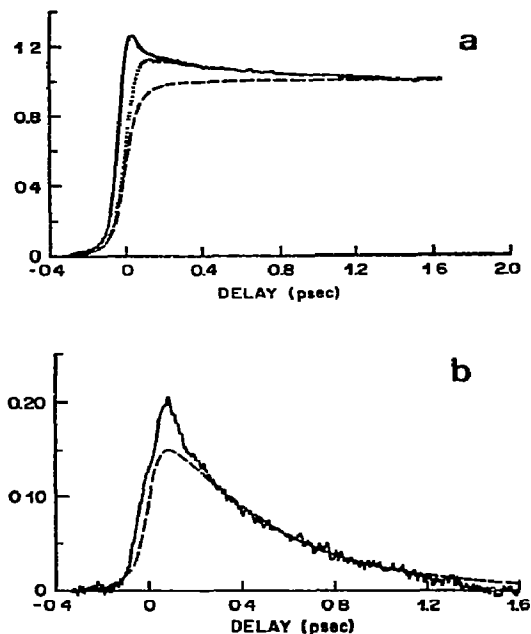


Fig. 2. Pump-probe data for oxazine 720 in methanol. (a) The original data (solid), the data after removal of the coherent artifact (dotted), and the integral of the intensity autocorrelation (dashed). (b) That portion of the pump-probe signal due to fast molecular dynamics (solid) and the fit assuming a single exponential response with a 480 fs time constant (dashed).

Similar results are obtained in other dyes. For cresyl violet in methanol, the excitation wavelength is at the long-wavelength edge of the absorption band, not at the absorption peak as for Nile blue and oxazine 720. Nevertheless, a rapid initial decay followed by slower exponential decay is still observed. We fit the slower decay component to a response function  $A(t) = 0.23 \exp(-t/330 \text{ fs})u(t)$ . For rhodamine 640 in methanol, in which we excite and probe the long-wavelength thermal tail of the absorption spectrum, the absorption arises primarily from vibrationally excited molecules. In this case not only excited state relaxation but also thermalization within the ground state influence the transient bleaching signal. The resolved portion of the transient signal is fit using a response function  $A(t) = 0.3 \exp(-t/190 \text{ fs})u(t)$ . As usual there is an additional pulsewidth-limited saturation for small positive delays. We note that the magnitude of the induced transmission signal was comparable to

the other dyes tested even though rhodamine 640 is far off resonance. This observation supports the notion that, in the long-wavelength tail, only a fraction of the molecules interact with the laser light but with a large cross section [28].

In order to confirm our results, we also did measurements using a jet stream of Nile blue in ethylene glycol. The data were similar to those observed using cells. Rapid initial decay, followed by exponential decay with a 450 fs time constant, was observed. Furthermore, pump-probe and three-pulse transient-grating measurements performed using a low-repetition-rate (10 Hz) amplified CPM laser system [29] also gave consistent results.

Note that the decay times of 410 and 450 fs measured for Nile blue in methanol and ethylene glycol, respectively, are quite close, considering the large difference in solvent viscosities. Excited state relaxation on a time scale of several hundred femtoseconds is also observed when dye molecules are embedded in PMMA polymer hosts [30,31]. The fact that the observed time constants are relatively insensitive to the choice of solvent or host suggests that, on a femtosecond time scale, solvent reordering is unimportant and intramolecular relaxation processes dominate.

We further note that for each dye examined, the transient response is weaker than the long-lived molecular response. Even for well resolved relaxation, the strength of the transient response relative to the long-lived saturation should depend on the relative densities of states in  $S_0$  and  $S_1$ , the excited state absorption, and the stimulated emission cross section (at the laser frequency) of the relaxed excited state. In the absence of the latter two factors, the contrast ratio is given by  $1 + g_0/g_1$ , where  $g_0$  and  $g_1$  are the densities of states of  $S_0$  and  $S_1$ , respectively. When excitation occurs from low-lying levels in  $S_0$  to highly excited levels in  $S_1$ ,  $g_1$  is expected to be larger than  $g_0$ , and the contrast ratio is decreased. The reduced contrast ratios, on the order of 0.3, can reconcile our present results with those of previous investigations [8,10,19] using the somewhat longer pulses from a linear passively mode-locked laser. These previous studies reported relaxation times to be less than their experimental resolution, estimated assuming transient and long-lived saturation of equal strength.

In summary, we have demonstrated that the rapid excited state relaxation which occurs following pho-

toexcitation of dye molecules can be resolved using femtosecond laser pulses. The transient bleaching consists of a rapid initial decay followed by an exponential tail with a time constant ranging from 190 fs for rhodamine 640 to 480 fs for oxazine 720. The time scale for the transient decay is relatively insensitive to the choice of solvent or host and is attributed to intramolecular relaxation. Our finding that the excited state relaxation requires at least several hundred femtoseconds may also have important implications for the operation of femtosecond dye lasers.

### Acknowledgement

The authors gratefully acknowledge S. De Silvestri for his help in performing measurements with the amplified laser pulses. This work was supported in part by the Joint Services Electronics Program under Grant No. DAAG-29-83-K-003. AMW was a Fannie and John Hertz Foundation Graduate Fellow.

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