A novel observation in the measurement of ultrafast relaxation times using incoherent light

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We present here our experimental results on the measurement of population relaxation times of the excited states of some organic dyes such as erythrosinB, commercial ink and metalloporphyrin using degenerate four wave mixing with incoherent light (DFWM-IL). When the probe beam in the phase conjugate configuration is delayed, we observe a second peak apart from the coherence peak due to forward pump and the probe beams. The second peak, due to backward pump and the probe beams, is observed only for samples having excited state absorption and has different widths for different samples. From the observed line widths, we estimate the relaxation times of the excited states S_n and S_1.

MANY organic materials, with π electron delocalization, are currently being studied for possible device applications in optical communication and optical data processing[1,2]. Most of these materials due to their complex structure, have a large number of vibrational and rotational bands, leading to very fast nonradiative transitions within each electronic band. These relaxations normally occur in ps and fs domain. Different spectroscopic methods have been developed for measuring these ultrafast relaxation times without the use of fs laser[3]. A technique was proposed by Morita and Yajima[4] which uses incoherent light as the source. This technique has been applied to studies of both dephasing times in fs domain and longitudinal relaxation times in the ps domain[5]. Kobayashi *et al.*[6] derived a generalized formula for calculating the relaxation times when one of the beams is delayed with respect to the other beams. Okamoto[7] extended the work of Morita and Yajima for systems with more than two levels, like organic dyes, having different excited and ground state relaxation times and showed that the population relaxation times can be obtained using non-zero delay of beam 2 also. In this communication, we present our new observations in the measurement of population relaxation times of few organic dyes such as erythrosinB, commercial black ink and porphyrins. A counter propagating geometry for the degenerate four wave mixing using incoherent light (DFWM-IL) has been utilized for these studies. For the first time we observe different line widths as compared to Okamoto's results and these are explained in terms of the relaxation times of different excited states.

A schematic of the experimental setup is shown in Figure 1. Home-built dye laser[8] consists of an oscillator and a single stage amplifier. The laser is pumped by second harmonic of Nd:YAG (Continuum, USA, 6 ns, 10 Hz) with an output of ~ 300 mJ in 1064 nm and ~100 mJ in 532 nm. Using a glass plate, 8% of power is reflected and is used for pumping the oscillator. The remaining power is used for amplification of the signal. The oscillator has a plane mirror and a glass plate (~8% R) combination which produces broad band

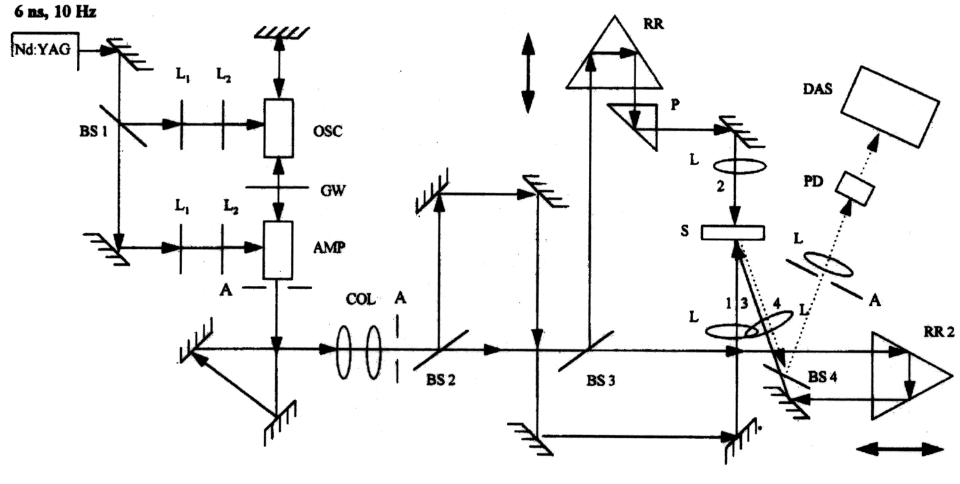

Figure 1. Schematic of the experimental setup. OSC, Oscillator; AMP, Amplifier; RR, Retro reflector; DAS, Data Acquisition System; L_1, Diverging lens; L_2, Cylindrical lens; PD, Photo diode; BS3, BS4, 50-50 Beam splitters; GW, Glass wedge (4% R); Col, Collimater; P, Right angled prism; BS2, 30-70 Beam splitter; L, Converging lens; S, Sample; A, Aperture; BS1, 10-90 Beam splitter.

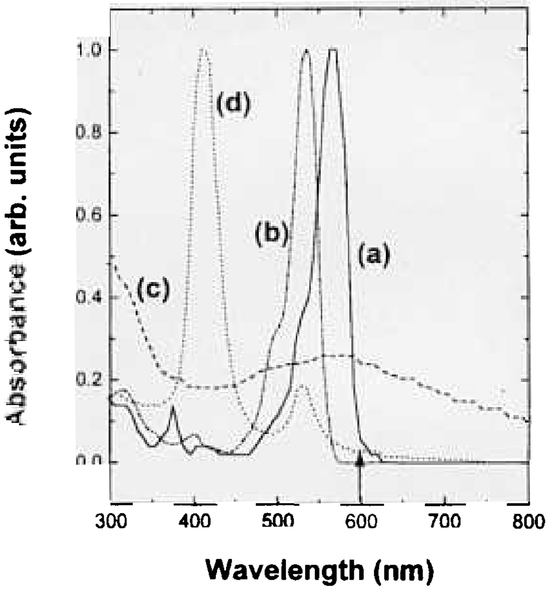

Figure 2. Absorption spectrum of the samples. *a*, RhB; *b*, erythrosinB; *c*, black ink; *d*, CoTTP.

light. FWHM of the output observed is ~ 8 nm (at 595 nm) and the corresponding coherence time (τ_c) calculated is ~ 160 fs. The beam is initially collimated before splitting it into three beams. Two beam splitters (30–70, 50–50) are used to obtain three beams. All the three beams have a diameter of ~ 3 mm. Beam 1 is forward pump ($\mathbf{k}_1$), beam 2 ($\mathbf{k}_2$) is backward pump and beam 3 ($\mathbf{k}_3$) is the probe. Beam 1 is fixed whereas beams 2 and 3 pass through variable delays. Beam 3 makes an angle of ~10° with the forward pump. All the beams are focused into the sample contained in 1 mm/100 μm thick quartz cell using lenses of focal length ~ 20 cm. Beam waist at the focus was found to be ~ 80 μm. The phase conjugate beam (in $-\mathbf{k}_3$ direction) is isolated using a beam splitter and is focused on to a fast photo diode, the output of which is given to the data acquisition system.

The signal is recorded by delaying the beam 3 for different, fixed delays of beam 2 with respect to beam 1. For transient gratings, signal in the direction $\mathbf{k}_s = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ has contribution from two different gratings[9].

1) $\mathbf{k}_2$ at time t_3 gets diffracted by the grating formed with the fields in directions of $\mathbf{k}_3$ and $\mathbf{k}_1$ at t_1 and t_2 respectively.

2) $\mathbf{k}_1$ at time t_3 gets diffracted by the grating formed with the fields in directions $\mathbf{k}_3$ and $\mathbf{k}_2$ at t_1 and t_2 respectively.

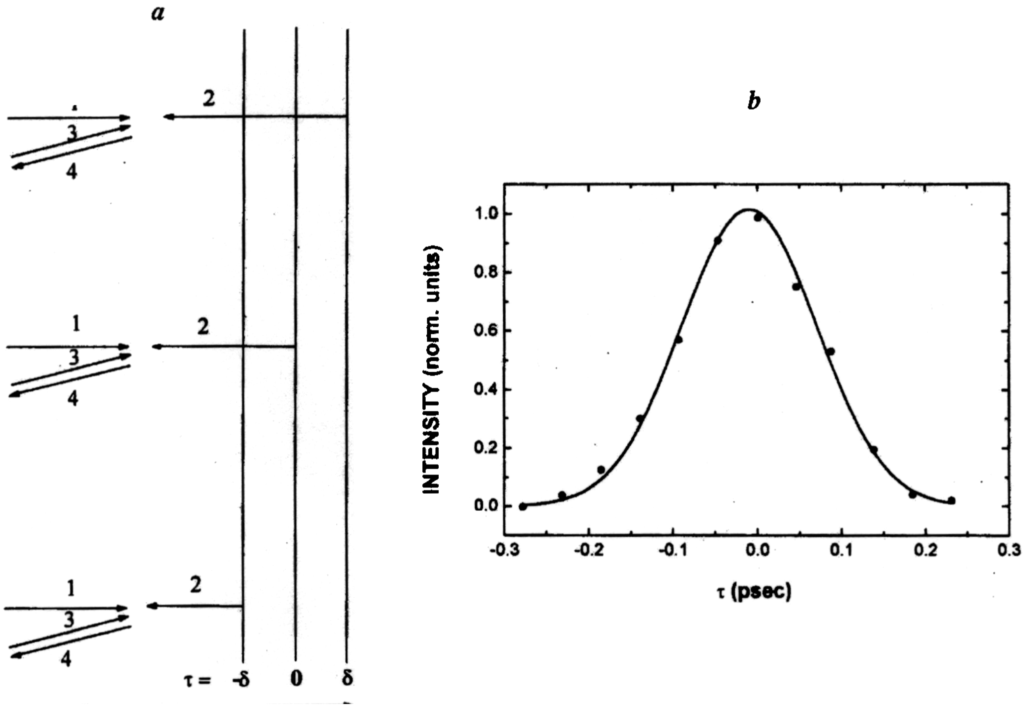

Figure 3. *a*, Pictorial representation of various delays. *b*, Autocorrelation function (RhB in methanol).

The absorption spectra of all the samples are shown in Figure 2. The delay time between $\mathbf{k}_1$ and $\mathbf{k}_2$ is denoted as δ and that of $\mathbf{k}_1$ and $\mathbf{k}_3$ as τ (Figure 3 *a*). Figure 3 *b* depicts the autocorrelation curve of RhB in methanol and the correlation time was found to be ~160 fs. Figure 4 shows time resolved profiles, for different values of δ, in RhB (in methanol), erythrosinB (in menthanol), black ink (in distilled water) and cobalt tetra tolyl porphyrin (CoTTP in chloroform). All the profiles have two peaks except the one in RhB. Peak 1 is due to the coherence of beams 1 & 3 and has a width of ~170–180 fs. The second peak is due to the coherence of beams 2 & 3 and has different widths. The widths (FWHM) of the second peak are ~ 180 fs in erythrosinB, ~ 1.5 ps in black ink, ~ 3 ps in porphyrins. Though earlier reports[7] showed that the second peak has the same width as the first peak, we have observed for the first time in porphyrin dyes and black ink, the second peak as broader than the first one. The second peak moves symmetrically across the main peak with delay of beam 2 and appears exactly at $\tau = |\delta|$. The separation between the two peaks is exactly δ. A constant background appears in all of the profiles.

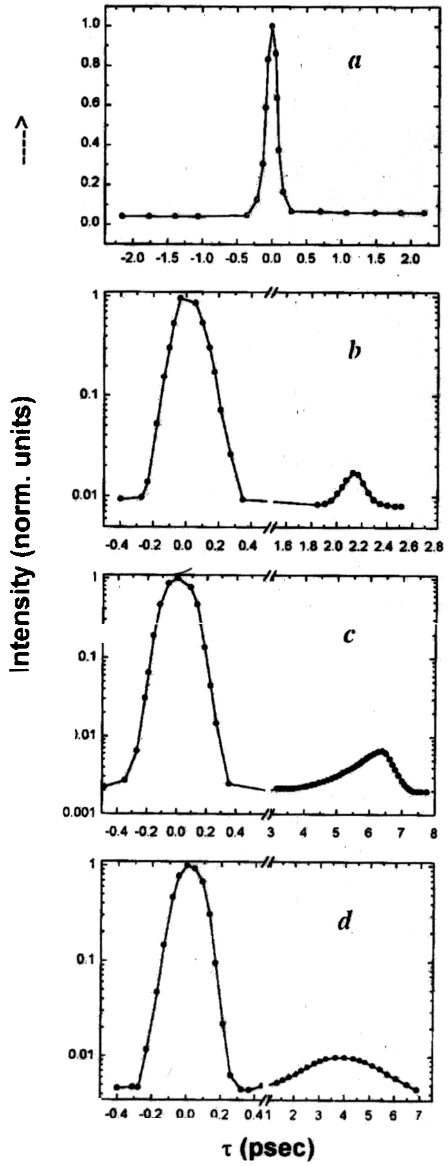

Figure 4. ***a***, Signal profile for $\delta = 1$ ps in sample RhB in methanol; ***b***, Signal profile for $\delta = 2.1$ ps in sample erythrosinB in methanol; ***c***, Signal profile for $\delta = 6.4$ ps in sample black ink in distilled water; ***d***, Signal profile for $\delta = 4$ ps in sample CoTTP.

The population relaxation times have been calculated using the relation[5]

$$I_0 : I_\delta : I_b = (1/\gamma_{gg}\tau_c) : 1:1$$

$$T_1 = 1/\gamma_{gg} = (I_0/I_\delta)^{*}\tau_c.$$

The values of T_1 for various samples are 16 ps in erythrosinB, 26 ps in black ink and 37 ps in CoTTP. There is no decay observed in the coherence peak due to beams 1 and 3 from which one can infer that T_2 of the samples is much less than 160 fs, correlation time of the pulses.

Open aperture Z-scan[10] studies were performed for all the samples to assess their nonlinear absorption. All the samples except RhB show a valley which implies that there is excited state absorption. The samples which showed excited state absorption had two peaks, whereas RhB which shows no excited state absorption, has only one peak. Figure 5 depicts the energy level structure for the organic molecules in general, indicating different transitions. Extensive fs studies on dye molecules revealed the presence of subpicosecond transients which have been attributed to redistribution of excitation energy among the vibrational modes of the molecule[11]. Also reverse saturable absorption in tetra phenyl porphyrins[12], implying that there is excited state absorption, is well established. Our samples also show similar behaviour. The laser pulses excite the molecules from the ground state S_0 into the higher vibrational states of the excited singlet state S_{1v}. The relaxation of the molecules out of this state occurs rapidly into an equilibrium level in the singlet state S_1. This level relaxes either by nonradiative decay into the first triplet state T_1 (K_{ISC}) or by both radiative and nonradiative decay within the singlet system. Depending on the intersystem crossing rates, the excited state absorption may be from singlet S_1 or triplet state T_1 into S_n or T_n respectively. Under steady state conditions, one would expect the population in the S_n as well as T_n levels. Since the pulses have a correlation time of 160 fs, the intersystem crossing rate would not

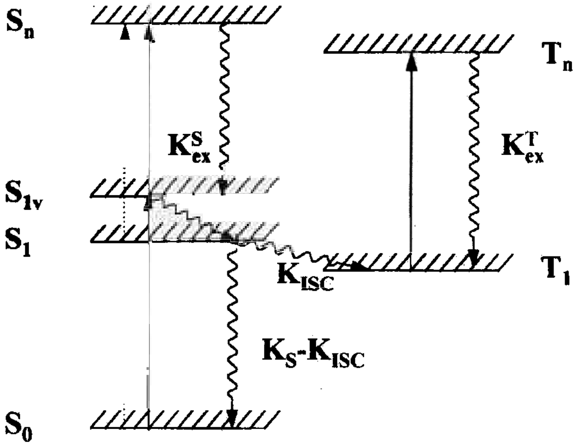

Figure 5. Energy level structure in organic molecules indicating different transitions.

play an important role in these studies. Two photon absorption and the excited state absorption, appearing in the 160 fs time scale, take the molecules from the vibrational manifold to the upper states of S_n. The upper states S_n will relax back to the S_1 state on fs time scale and in the process generate a vibrationally excited state. Peak 1, which has a fast response time in fs, is attributed to the dephasing/relaxations in the excited states S_n. The width of the second peak varies from sample to sample and is attributed to the vibrational relaxation (S_{1v} to S_1) within the molecule. The relaxation time within the vibrational levels, in metalloporphyrins, is reported to be in the order of few ps[13]. The difference in the intensities of the two peaks can be explained as due to the efficiencies of the two gratings. Peak 1 is due to coherence of beams 1 and 3, while beam 2 gets diffracted in $\mathbf{k}_4$ direction and can be imagined as a transmission grating. Whereas the broader peak 2 is due to the coherence of beams 2 and 3 and beam 1 gets diffracted in $\mathbf{k}_4$ direction and can be imagined as a reflection grating. The variation in the widths of the second peak indicates that these systems have different S_1 states dephasing time scales. As the experiments are carried out at room temperature, the 600 nm excitation takes RhB molecules to S_1 (absorbance of 0.01) through vibrational levels of the ground state[14]. Our intensity-dependent studies of the anti-Stokes emission indicate that there is no two-photon absorption for the intensities used in DFWM-IL. As RhB has a dephasing time of the fs order and a longitudinal relaxation of 3 ns, we do not observe the second peak (like in other samples) and the width of the first peak would give us the autocorrelation profile of the pump. The asymmetry in the behaviour of the second peak in Figure 3 *c* could be due to the complex relaxation rate in the ink. A proper analysis of this relaxation phenomenon requires an exact composition of the ink. Further studies are in progress to simulate similar results.

In conclusion, we have estimated the population relaxation times of a few organic dyes using DFWM-IL. When beam 2 delay is non zero, we observe a second peak which is less intense than the coherence peak due to beams 1 & 3. By calculating the intensity ratio of these peaks, we could estimate the population relaxation time. From the width and intensity ratios of the peaks, we could estimate the dephasing times and the longitudinal relaxation rates of the excited states S_n and S_1. We attribute the width of the second peak in erythrosinB, ink and porphyrin to the vibrational relaxation within the singlet state, S_1.

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