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Measurement of the picosecond population relaxation time of cresyl violet by time-delayed four-wave mixing with incoherent light

Junye Liu, Shihua Huang, Weiping Qin and Jiaqi Yu

Open Laboratory of Excited State Processes of Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China

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Measurements of the picosecond population relaxation time of cresyl violet in methanol were performed by phase-conjugation time-delayed four-wave mixing using incoherent light. This time is about 157 ps. The result was verified with the correlation technique of mode-locked picosecond pulses with different intensities.

1. Introduction

The time resolution of the measurement of transient processes using coherent light is determined by the pulse duration t_p. In order to obtain a higher time resolution, much effort has been made to generate picosecond or femtosecond ultrashort light pulses. Very recently, the shortest pulse of 6 fs was obtained by compressing the output of a group-velocity-dispersion-compensated colliding pulse mode-locked laser [1]. However, such ultrashort pulses can be generated only in a very limited wavelength region and the apparatus is complicated.

Based on transient coherent optical effects, a new spectroscopic technique using incoherent light has recently been developed [2,3]. In the transient coherent spectroscopy used for studies of ultrafast dynamics, the signal light generated or modulated by nonlinear optical effects is detected using the cross-correlation between the excitation and the probe light beams. Therefore, in such cases, one expects the time resolution to be determined by the correlation time τ_c instead of the pulse duration t_p [3]. Based on the uncertainty principle, the correlation time τ_c, is approximately the inverse bandwidth of the incoherent light $\tau_c \sim 1/\Delta\nu$ [2,3]. Obviously, the wider the bandwidth, $\Delta\nu$, of a non-transform-limited pulse, the smaller is the correlation time τ_c and the higher the time resolution which can be obtained.

Since 1984, coherent transient spectroscopy with incoherent light has become a field of particular interest. In this paper we report the population relaxation time, T_1, of cresyl violet in methanol which was measured by phase-conjugation time-delayed four wave mixing with incoherent light (TDFWM-IL). The measured time is about 157 ps. This result is in good agreement with the values of 162 ps, obtained by pump-probe measurements using coherent picosecond pulses [4], and 160 ps with an optical Kerr shutter technique [5].

2. Theory

There are two types of TDFWM-IL, the so-called BOXCARS and phase-conjugation techniques for measurement of the population relaxation time as depicted in fig. 1. In the former

Correspondence to: Dr. J. Liu, Open Laboratory of Excited State Processes of Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China.

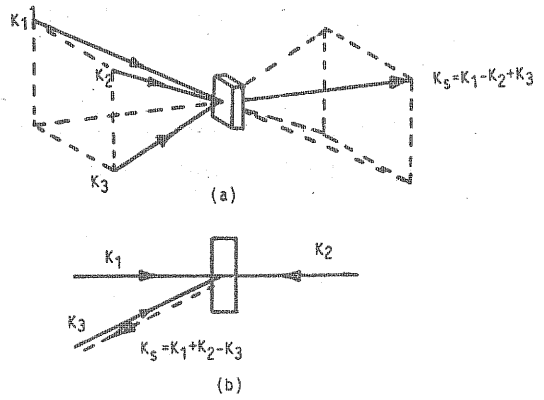

Fig. 1. Schematic of (a) BOXCARS type (b) phase-conjugation type TDFWM-IL experiments for measurement of population relaxation.

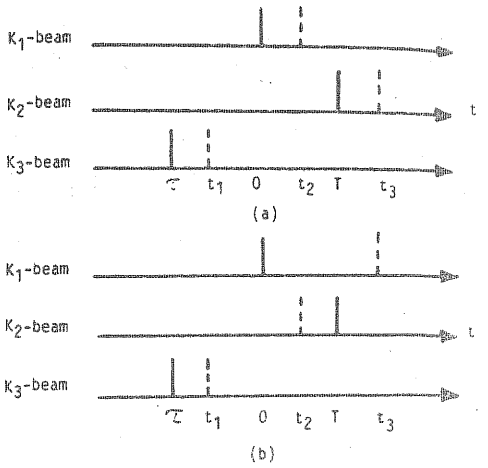

Fig. 2. Time sequence of the pulses, (a) the K_2 beam is scattered by the grating formed by the (K_1, K_3) interference. (b) The K_1 beam is scattered by the grating formed by the (K_2, K_3) interference.

type the pump beams K_1 and K_2 and the probe beam K_3 are noncoplanar [6]. In the latter case the three beams are coplanar. Our experiment was performed in the later configuration. The pump beams K_1 and K_3 intersect at an angle of about 2° and the delay time between them was $-\tau$ i.e. the K_3 beam reached the sample before the K_1 beam. The pump beam K_1 and the probe beam K_2 were counterpropagating and the delay time between them was $T \to 0$. The pump beam K_3 and the signal beam K_s are phase-conjugated with each other [6]. The three beams of this incoherent light field were applied to the resonant nonlinear material in a sequence of time represented in fig. 2. The medium contains a two-level system. The total electric field of the input beams is given by

$$E(t) = E(t)\exp[-\mathrm{i}(\omega t - K_1 r)] + E(t-T)\exp\{-\mathrm{i}[\omega(t-T) - K_2 r]\} + E(t+\tau)\exp\{-\mathrm{i}[\omega(t+\tau) - K_3 r]\}. \quad (1)$$

The notation $E(t)$ represents the envelope function of the electric field slowly varying compared with the optical frequency. The random variations of the amplitude and phase are included in $E(t)$. To derive the dependence of the signal intensity on the delay time $-\tau$ between K_3 and K_1, we consider that the K_2 beam was scattered by the grating formed by K_1 (at t_2) and K_3 (at t_1) shown in fig. 2(a). Similarly, K_1 was scattered by the grating formed by K_2 (at t_2) and K_3 (at t_1) in fig. 2(b). The third-order nonlinear polarization in the direction K_s is obtained as

$$P^{(3)}(t,\tau,\omega) = \chi^{(3)} \int \mathrm{d}\Delta g(\Delta) \int \mathrm{d}t_3 \int \mathrm{d}t_2 \int \mathrm{d}t_1 \times \exp[-(t - t_3 + t_2 - t_1)/T_2 - (t_3 - t_2)/T_1] \times \{[E^*(t_1+\tau)E(t_2)E(t_3 - T) + E^*(t_1+\tau) \times E(t_2 - T)E(t_3)]\exp[-\mathrm{i}\Delta(t - t_3 - t_2 + t_1)] + [E(t_1)E^*(t_2+\tau)E(t_3 - T) + E(t_1 - T) \times E^*(t_2+\tau)E(t_3)]\exp[-\mathrm{i}\Delta(t - t_3 + t_2 - t_1)]\}, \quad (2)$$

where $g(\Delta)$ is the distribution function of the frequency difference $\Delta = \omega - \omega_0$ between the transition frequency of the material ω_0 and the laser frequency ω and T_2 is the dephasing time. The signal intensity as a function of τ is represented by

$$I(\tau) \propto \langle |P^{(3)}(t,\tau,\omega)| \rangle. \quad (3)$$

The scattering efficiency of K_2 by the grating formed by the (K_1, K_3) interference is much higher than that of K_1 by the grating formed by the

(K_2, K_3) interference due to mixing frequency processes. Therefore, the terms containing $E^*(t_1 + \tau)E(t_2 - T)E(t_3)$ and $E(t_1 - T)E^*(t_2 + \tau)E(t_3)$ can be omitted. For the case where the dephasing time T_2 is much shorter than τ_c and T_1, the term $\exp[-(t - t_3 + t_2 - t_1)/T_2]$ is nonzero only for $(t - t_3 + t_2 - t_1) \to 0$; thus

$$\exp[-(t - t_3 + t_2 - t_1)/T_2] \to T_2^2 \delta(t - t_3)\delta(t_2 - t_1). \quad (4)$$

For $\tau > 0$, and eq. (3) is the cases of both homogeneous and inhomogeneous broadening [6],

$$I(\tau) \propto 1 + 1.6(T_1/\Delta\tau)\exp[-2(\tau/\Delta\tau)^2] + 2.9(\Delta\tau/T_1)\exp[-(2/T_1)\tau]. \quad (5)$$

Equation (5) consists of three terms, the first one is a constant background term, the second is a coherence "spike" term, and the last "tail" term contains the information about T_1.

3. Experimental

The experimental setup is shown in fig. 3. As an incoherent light source we used a pulsed dye laser pumped by the second harmonic of a Q-switched

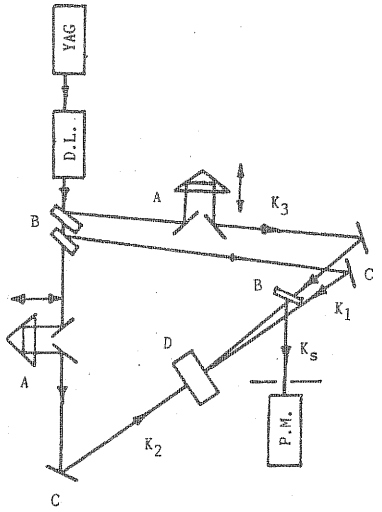

Fig. 3. TDFWM-IL experimental setup. A – variable delay; B – beam splitter; C – mirror; and D – sample.

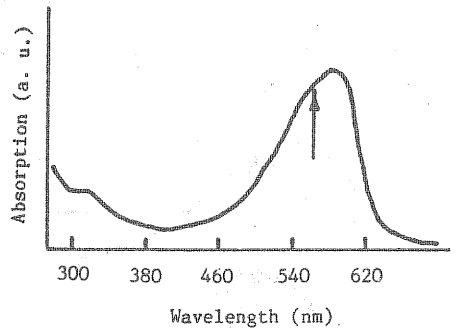

Fig. 4. Absorption spectrum of cresyl violet in methanol. The arrow indicates the excitation wavelength used.

Nd:YAG laser with a repetition rate 20 Hz. The output pulse of the dye laser was 7 ns wide and was tuned to 560 nm. This excitation wavelength is indicated by an arrow in the absorption spectrum of cresyl violet in methanol, (see fig. 4). The bandwidth (FWHM) of the power spectrum was about 0.63 cm^{-1}, corresponding to a correlation time $\tau_c \approx 53$ ps. As a resonant material we chose cresyl violet in methanol because this kind of organic dye solution is known to have an appropriate population relaxation time to demonstrate the applicability of the present method and to satisfy the condition T_2 (for cresyl violet in cellulose $T_2 \approx$ 100 fs [7]) $\ll \tau_c$. The sample was 5×10^{-4} M in concentration and 1.5 mm thick.

4. Results and discussion

The measured traces using phase-conjugation TDFWM-IL of cresyl violet are shown in fig. 5. They represent the signal intensities of the mixing frequency as a function of the delay time $-\tau$ between K_3 and K_1 under various average power densities of the excitation field. Incoherent light can be regarded as a train of incoherently phased ultrashort spike pulses. Although the phase of each spike pulse is random, each correlated spike pulse pair having wave vector K_3 and K_1 has the same relative phase and therefore contributes coherently to forming the population grating. The probe beam K_2 was scattered by the population grating resulting in a signal propagating in the direction $K_s = K_1 + K_2 - K_3$. Because of the phase "memory" of

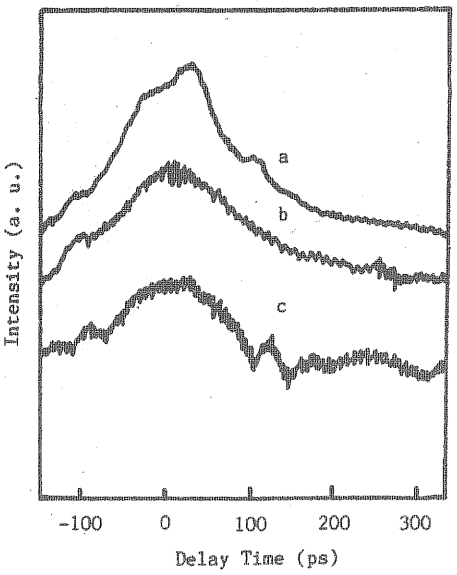

Fig. 5. Experimental traces of the signal intensity of TDFWM-IL vs. delay time $-\tau$ of K_2 to K_1 beam. Various average power densities of the excitation field of (a) 32, (b) 16 and (c) 9 W/cm^2 were used.

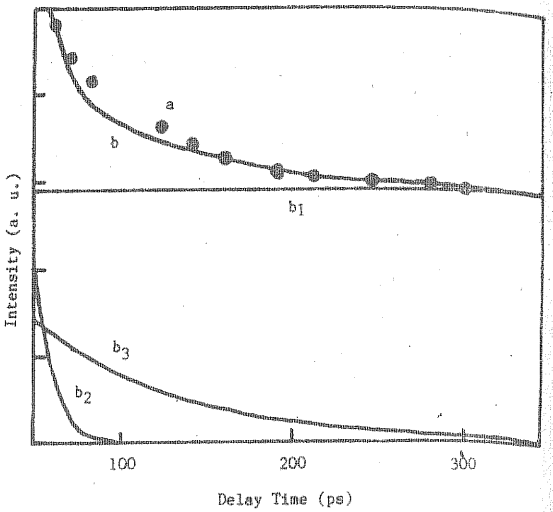

Fig. 6. (a) Experimental data; (b) fit to the curve a calculated with eq. (5); b_1, b_2 and b_3 represent the three terms in eq. (5), with $b = b_1 + b_2 + b_3$.

the medium, and the fact that the three beams reached the sample at different times, the TDFWM-IL signal can be obtained, only for $T \ll \tau_c$ and $T_2 \ll \tau_c \ll T_1$.

The experimental data in figs. 5(a)–(c) were obtained using average power densities of 32, 16 and 9 W/cm^2, respectively. The data were fitted by the curve (b) calculated with eq. (5) (see fig. 6). The population relaxation time obtained was $T_1 =$ 157 ps using $\Delta\tau = 28$ ps in eq. (5). This result is in good agreement with the results reported in refs. [4,5]. The b_1, b_2 and b_3 curves corresponded to the first, second and third terms in eq. (5), respectively, and $b = b_1 + b_2 + b_3$. The b_1 curve gives a constant background, the b_2 curve describes a coherent spike and the b_3 curve contains the information about T_1 and decays with $T_1/2$.

It was shown in fig. 5 that the peaks of the experimental curves split with an increase in the power density. We suggest that these two peaks corresponded to the two cases shown in figs. 2(a) and (b). The nature of the phenomenon will be investigated in detail. Moreover, the signal-to-noise ratios for the "tail" of the experimental curves in fig. 5 are increased with enhancing the power densities of the light field. It is easy to understand that an increase in the power density of the field enhanced the nonlinear effects of the interaction between the medium and the light field. The signal-to-noise ratio of TDFWM-IL, therefore, was enhanced.

In conclusion, it should be said that this configuration avoided the inconvenience in adjusting the optical paths in the BOXCARS type TDFWM-IL in which three beams are noncoplanar. This technique is also better than the pump-probe scheme, because in the latter the probe light is directly incident on the detector and intensity fluctuations of the probe beam often obscures the signal. In the TDFWM-IL scheme, on the other hand, the signal itself is measured easily because the signal can be generated in a different direction from any incident light beam. This is one of the reasons why a better signal-to-noise ratio can be obtained. Due to the advantages stated above, we believe that the TDFWM-IL technique will be widely applied to ultrahigh time resolution spectroscopy.

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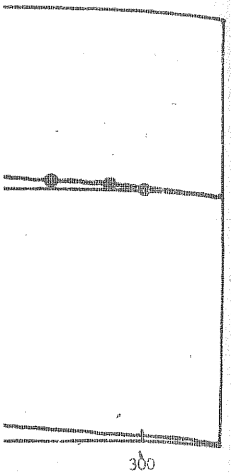

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