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The measurement of relaxation rates by degenerate four-wave mixing with ultrashort light pulses

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Abstract. A method for estimating the relaxation time of nonlinear media, or the ratio of the relaxation time and the laser pulse duration in the presence of moderate or strong phase modulation, is proposed. The validity of our relaxation time measurements is verified using computer simulations of the model and comparing them with the experimental data for CS_2, nitrobenzene and an 8CB liquid crystal.

1. Introduction

Optical phase conjugation (OPC) has been shown to be useful for many applications such as image processing, optical computing, distortion compensation and communications systems [1].

OPC may be achieved by the nonlinear process of degenerate four-wave mixing (DFWM). In this process three input laser-beams mix in a nonlinear medium to yield a fourth, output beam (figure 1). Two intense counterpropagating pump waves interact with a third probe beam which enters the medium at an arbitrary angle θ to the pump waves. All three couple through the third-order susceptibility $\chi^{(3)}$ to produce a fourth wave. This signal beam appears as a phase-conjugate reflection of

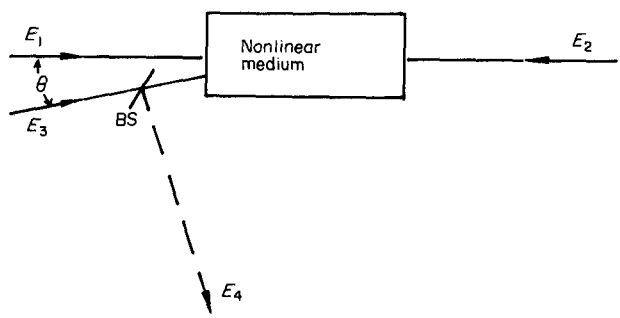

Figure 1. The geometry of four-wave mixing.

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the probe beam, i.e. it is proportional to the spatial complex-conjugate of the probe [2]. By introducing delays between the pump and the probe laser pulses, the generated signal may be related to a pulse autocorrelation function.

In this paper, DFWM produced by picosecond pulses which are characterized by duration t_p, coherence time τ_c and magnitude of phase modulation a is considered.

The energy Q_4 of the phase-conjugate wave E_4 as a function of the delay time τ of the probe beam is determined by the temporal profile of the incident waves E_1, E_2 and E_3. The analysis of this energy distribution starts from the two extreme and simplest cases: the long-pulse ($t_p \gg \tau_r$, where τ_r is the relaxation time of the medium) and the short-pulse ($t_p \ll \tau_r$) interacting in a non-linear medium [3, 4].

For the long-pulse limit, the system's response immediately follows the driving field. The f.w.h.m. of $Q_4(\tau) = t_{\text{f.w.h.m.}}$ is therefore determined by the pulse duration t_p ($t_{\text{f.w.h.m.}} \approx t_p$). For the short-pulse limit, the medium's response cannot follow the electromagnetic field. The f.w.h.m. of $Q_4(\tau) = t_{\text{f.w.h.m.}}$ is approximately equal to the coherence time τ_c ($t_{\text{f.w.h.m.}} \approx \tau_c$).

It is therefore possible to estimate the relaxation time of the medium by considering the form of the DFWM signal as a function of the delay time τ. Alternatively, if the duration of pulse is unknown, the ratio of the relaxation time to the pulse duration can be determined.

2. Theoretical background

A strong electric field $\mathbf{E}(t)$ acting externally on a medium produces a polarization $\mathbf{P}(t)$, whose components P_i can be described by the expression

$$P_i = \sum_j \chi_{ij}^{(1)} E_j + \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l. \tag{1}$$

The first term in the above equation is the linear polarization P_l while the nonlinear part containing second and higher degree terms is denoted by P_{nl}.

If the field $\mathbf{E}(t)$ consists of four waves

$$\mathbf{E}(t) = \sum_{\alpha = 1,2,3,4} \tfrac{1}{2} \epsilon_\alpha(\omega_\alpha, \mathbf{r}) \exp\left[\mathrm{i}(\omega_\alpha t - \mathbf{k}_\alpha \cdot \mathbf{r})\right] + \text{c.c.}, \tag{2}$$

where α is summed over the forward, backward, probe and signal beams, then the third-order polarization term $\chi_{ijkl}^{(3)} E_j E_k E_l$ will give rise to the nonlinear polarization which may radiate with frequencies $\omega_\alpha \pm \omega_\beta \pm \omega_\gamma$ ($\alpha, \beta, \gamma = 1, 2, 3, 4$).

In four-wave mixing only the term that yields the formation of the phase-conjugate wave $\mathbf{E}_4$ with frequency

$$\omega_4 = \omega_1 + \omega_2 - \omega_3, \tag{3}$$

need be taken into account. The spatial and temporal evolution of this wave can be described by the wave equation derived from Maxwell's equation, where the nonlinear polarization serves as a driving term

$$\Delta \mathbf{E} + \frac{1}{c^2} \frac{\delta^2 \mathbf{E}}{\delta t^2} = \mu_0 \frac{\delta^2 \mathbf{P}_{nl}}{\delta t^2}. \tag{4}$$

In general, in the approximation of weak radiation energies [2, 5], the time-dependent nonlinear polarization can be taken to be proportional to the product of the amplitudes of the three input waves. Assuming the adiabatic approximation and

after symmetrization over pairs of interacting fields, the polarization change induced in the medium gives the following relation [6, 7]

$$P^3(\mathbf{r},t)=E_1(\mathbf{r},t-\tau_{\mathrm{del}})\int_{-\infty}^{t}E_3^{*}(\mathbf{r},t'+\tau)E_2(\mathbf{r},t')A_{3,2}(t-t')\,\mathrm{d}t'$$

$$+E_2(\mathbf{r},t)\int_{-\infty}^{t}E_3^{*}(\mathbf{r},t'+\tau)E_1(\mathbf{r},t'-\tau_{\mathrm{del}})A_{3,1}(t-t')\,\mathrm{d}t'$$

$$+E_3^{*}(\mathbf{r},t+\tau)\int_{-\infty}^{t}E_1(\mathbf{r},t'-\tau_{\mathrm{del}})E_2(\mathbf{r},t')A_{1,2}(t-t')\,\mathrm{d}t', \tag{5}$$

where τ is the delay time of the probe beam with respect to the second pump pulse entering the medium, τ_{del} is the delay time between the two pump pulses and the function $A(t)$ is the time-dependent response of the medium.

All three terms contribute to the build-up of the phase conjugate wave. However, physically, the first two terms usually represent an interaction between the probe and one of the pumps producing a spatial modulation of the refractive index of the nonlinear material. This is followed by scattering of the remaining pump in the direction of the probe beam at an angle θ. In other words, these terms are products of one of the pump beam fields with the correlation of the probe beam and the other pump beam. They will have a maximum value at a probe delay $\tau=0$ and $\tau=\tau_{\mathrm{del}}$ respectively. The third term represents a coherent term. It results from a temporal grating created by the pump waves, which then scatters the probe beam. The contribution from this term is usually small, unless strongly enhanced by a two-photon transition.

The shape of the phase conjugate signal in time will therefore be dependent on the intensity and coherence duration of the interacting picosecond laser pulses, as well as on the response relaxation time of the medium. This dependence can be shown by considering the energy distribution of a phase conjugate signal E_4 measured on a slow detector well removed from the interaction volume as being proportional to

$$Q_4\propto\int_{-\infty}^{\infty}|P^3(t)|^2\,\mathrm{d}t. \tag{6}$$

For simplicity only one dominant term of the third-order polarization is considered

$$P^3(t)\propto E_2\int_{-\infty}^{t}E_3^{*}(t'+\tau)E_1(t')A(t-t')\,\mathrm{d}t', \tag{7}$$

assuming that $\tau_{\mathrm{del}}=0$.

The dependence of the conjugate wave energy $Q_4(\tau)$ on the delay time τ between the incident pump and probe pulses therefore has the following form

$$Q_4(\tau)\propto\int_{-\infty}^{\infty}P^3(t)P^3(t)^{*}\,\mathrm{d}t$$

$$\propto\int_{-\infty}^{\infty}E_2(t)E_2^{*}(t)\left|\int_{-\infty}^{t}E_3^{*}(t'+\tau)E_1(t')A(t-t')\,\mathrm{d}t'\right|^2\mathrm{d}t. \tag{8}$$

From the slowly varying envelope approximation (SVEA), the response of the medium, $A(t-t')$, which determines the importance of earlier events by the time t itself, is usually approximated by an exponentially decaying function with a characteristic relaxation time τ_r

$$A(t-t')\approx\frac{1}{\tau_r}\exp\left(-\frac{t-t'}{\tau_r}\right), \tag{9}$$

where $t\geqslant 0$. The dependence $Q_4(\tau)$ has different forms for different ratios of the incident pulse duration to the response relaxation time. It is simplest in the two extreme cases mentioned earlier [4]:

(1) When the pulse duration is much greater than the relaxation time of the medium ($t_p\gg\tau_r$, the long-pulse limit) it can be assumed that the medium reaction is instantaneous and $A(t-t')$ may be expressed in terms of the Dirac δ-function:

$$\int_{-\infty}^{t} E_3^*(t'+\tau)E_2(t')\delta(t-t')\,dt' = E_3^*(t+\tau)E_2(t),$$

and the formula (8) simplifies to

$$Q_4(\tau)\propto\int_{-\infty}^{\infty} E_2(t)E_2^*(t)|E_3(t+\tau)E_1(t)|^2\,dt = \int_{-\infty}^{\infty} I^2(t)I(t+\tau)\,dt, \tag{10}$$

where

$$I(t)=E(t)E(t)^*.$$

In this regime the f.w.h.m.-width of $Q_4(\tau)$ is determined by the pulse duration alone ($t_{f.w.h.m.}\approx t_p$) and is not sensitive to phase modulation. The signal measured by the detector corresponds to the intensity correlation of the pulse.

(2) When the pulse duration is much shorter than the relaxation time of the medium ($t_p\ll\tau_r$, the short-pulse limit), the response relaxation is slow and $A(t-t')$ can be approximated by a constant and $Q_4(\tau)$ is given by

$$Q_4(\tau)\propto\int_{-\infty}^{\infty} E_2(t)E_2^*(t)\int_{-\infty}^{t}|E_3^*(t'-\tau)E_1(t')\,dt'|^2\,dt, \tag{11}$$

which corresponds to an amplitude correlation function of the excitation pulse. Therefore the width of $Q_4(\tau)$ is given by the coherence length ($t_{f.w.h.m.}\approx\tau_c$) [8, 9].

It is not difficult to find an accurate representation of the analytical function of $Q_4(\tau)$ for these two cases, but for intermediate cases it is not so simple. Another important problem in these calculations is connected with the magnitude of the phase modulation which influences the form of picosecond pulses. Therefore phase modulated pulses are described not only by a pulse duration but also by a coherence time τ_c.

We may characterize the degree of phase modulation by a parameter a. The phase modulation is:

(a) insignificant when $a<1$,
(b) moderate when $a=2$–5,
(c) strong when $a>5$.

In the case of moderate modulation (case (*b*)), the coherence time τ_c and pulse duration t_p are related approximately by

$$\tau_c \approx 2t_p/a. \tag{12}$$

The pulse envelope $\epsilon(t)$ may have a Gaussian form [4, 10]

$$\epsilon(t) = \exp[-2\ln(2)(t/t_p)^2], \tag{13}$$

and the analytical function which describes the amplitude of the propagating electric field is defined by

$$E(t) = \epsilon(t)\exp[ia\epsilon^2(t)]. \tag{14}$$

Due to the SVEA the high-frequency factor $\exp(i\omega t)$ is neglected.

3. Computer simulation

The main purpose of the computer simulation was to examine the change in the width of the energy curve $Q_4(\tau)$ between the two extreme cases, i.e. as a function of the change in the ratio of τ_r to t_p. The example of $a=4$ is shown in figure 2 from which it can clearly be seen that $t_{f.w.h.m.}$ decreases with increasing τ_r.

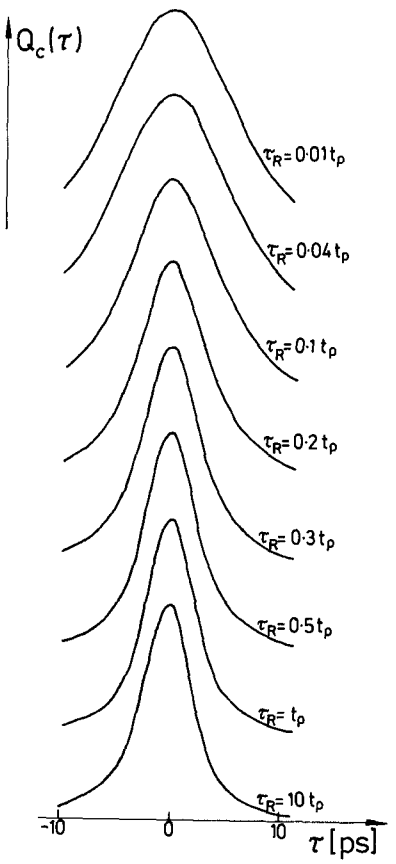

Figure 2. The energy of the phase conjugate wave as a function of the probe time delay τ for $a=4$.

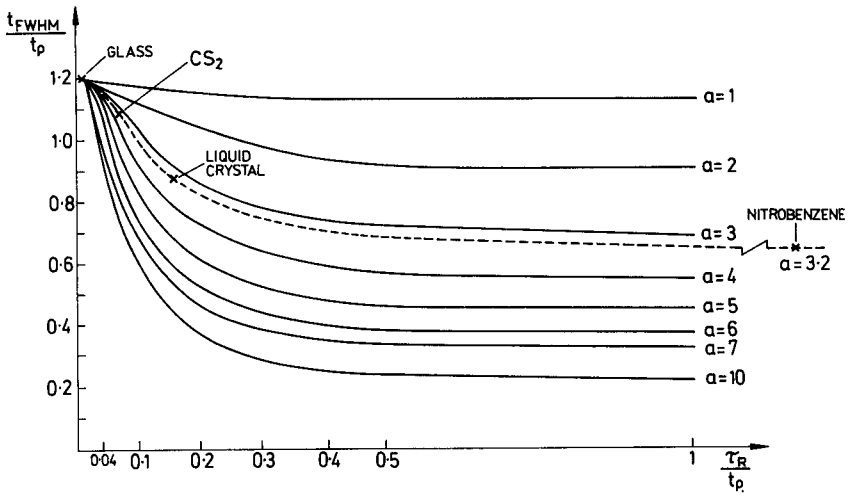

Figure 3. The relationship between the f.w.h.m. of $Q_4(\tau)$ and the relaxation rate τ_r with experimental points for $a=3{\cdot}2$.

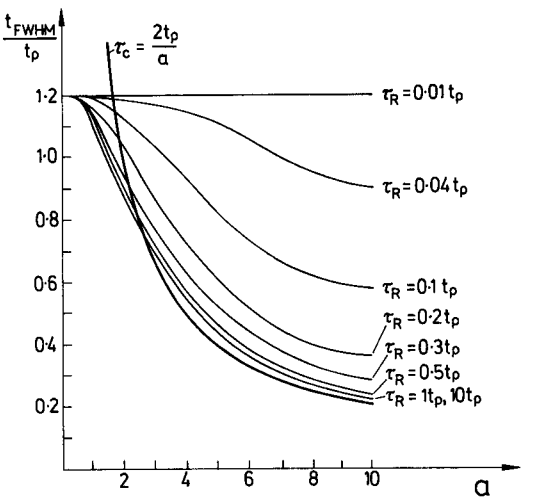

Figure 4. The relationship between f.w.h.m. of $Q_4(\tau)$ and the magnitude of the phase modulation.

The relationship between the f.w.h.m. of $Q_4(\tau)$, $t_{f.w.h.m.}$ and the relaxation rate τ_r is shown in figure 3 for eight different values of the phase modulation parameter a. For $a \leqslant 1$ the modulation is insignificant and so the pulse is approximately transform limited, i.e. $\tau_c \approx 2t_p$ (equation (12)) and we find that $t_{f.w.h.m.}$ is independent of τ_r. Increasing the phase modulation leads to shorter coherence times and so we can observe the transition between the two extreme cases of τ_r. We find that $\tau_r \leqslant 0{\cdot}01\,t_p$ leads to the intensity correlation while $\tau_r > 0{\cdot}5\,t_p$ is sufficient to observe the coherent spike.

Another important relationship occurs between the f.w.h.m. of $Q_4(\tau)$ and the magnitude of the phase modulation (figure 4). It can be seen that for small values of

τ_r, for which the factor a cancels out and so $t_{f.w.h.m.}$ is independent of a, our results confirm the approximation made in equation (10). The signal is simply the intensity autocorrelation function and therefore is not affected by the coherence time. As τ_r is increased we find that $t_{f.w.h.m.}$ tends towards the coherence time $\tau_c = 2t_p/a$.

For the case of strong phase-modulation ($a = 6$–10) and for large relaxation rates ($\tau_r > t_p$) the shape of $Q_4(\tau)$ changes from having just one peak at $\tau = 0$ to having a second maximum at τ approximately equal to $-t_p/2$. The origin of the new peak is caused by a feature of phase-modulated pulses. The power spectrum of such pulses has a semiperiodic structure and so new features may appear in the calculated correlation function. These features occur below the half-width of the energy curve and therefore are not important in a measurement of $t_{f.w.h.m.}$. Furthermore the calculations show that the maximum value of $Q_4(\tau)$ curve does not depend on the magnitude of the phase modulation.

4. Experimental results

Our experimental arrangement for DFWM is very similar to that described in detail in [3] and is shown in figure 5. Using a 90° phase-conjugate geometry, the time distribution of a pulse is transformed into a spatial distribution. The duration of a single laser pulse can therefore be determined by measuring the spatial width of the phase-conjugate beam. This technique is background free and wavelength independent, and there is no need for phase matching as in the SHG method. A mode-

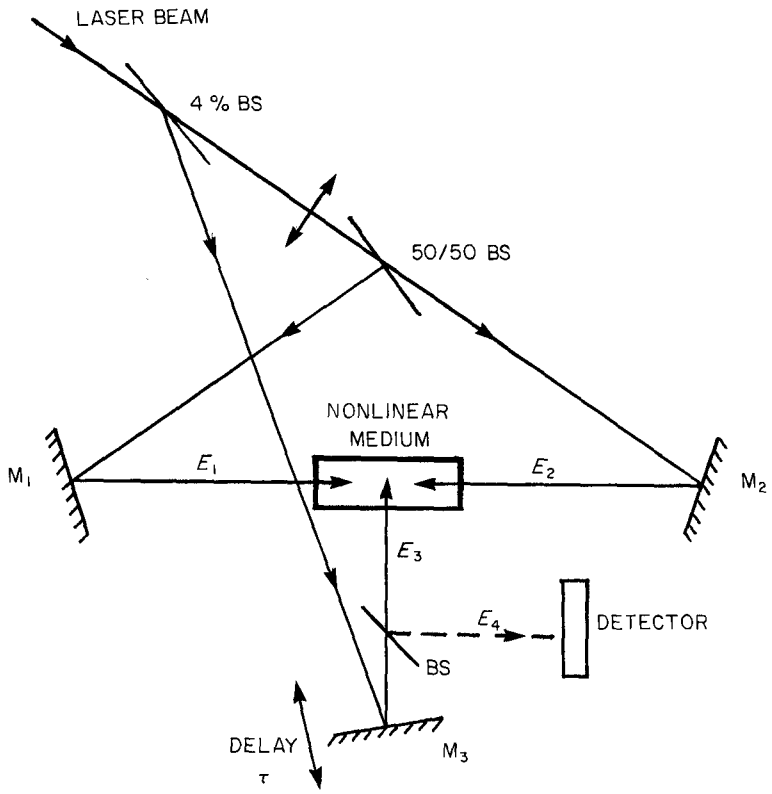

Figure 5. The experimental configuration for relaxation-rate measurements using a 90° phase-conjugate geometry.

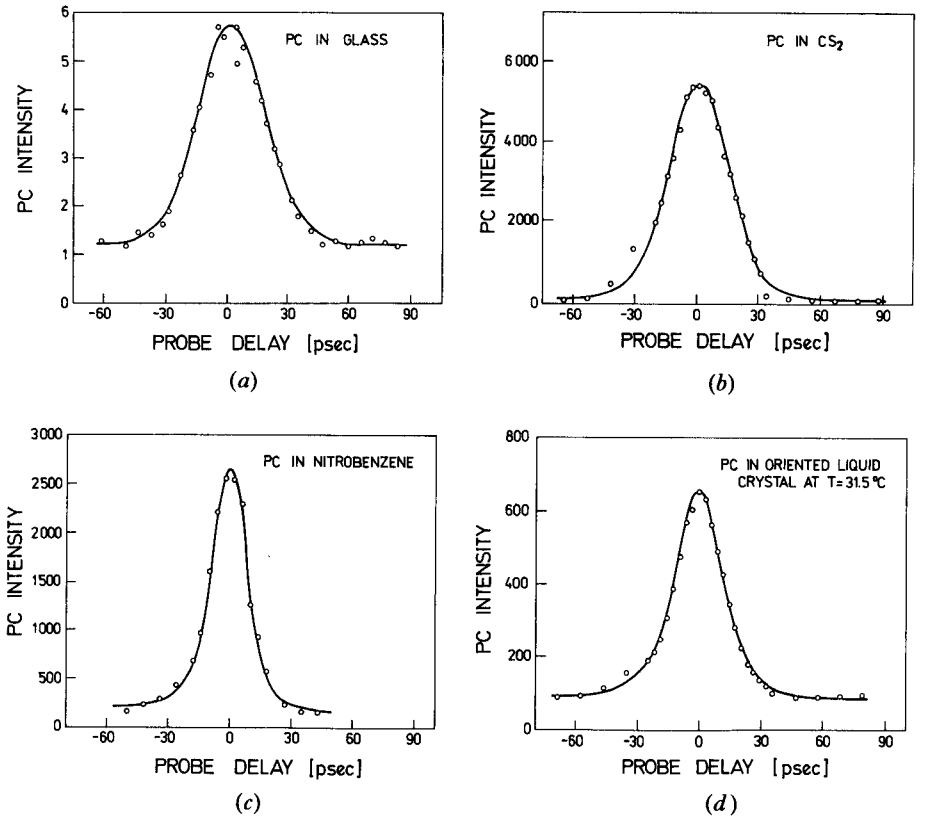

Figure 6. The experimental shape of the phase-conjugate signal as a function of the probe delay for different samples: $t_{\text{f.w.h.m.}} = (38{\cdot}3 \pm 0{\cdot}9)$ ps (*a*), $(34{\cdot}4 \pm 1{\cdot}1)$ ps (*b*), $(21{\cdot}2 \pm 0{\cdot}9)$ ps (*c*) and $(27{\cdot}6 \pm 0{\cdot}6)$ ps (*d*).

locked Nd : YAG laser system produces a single pulse, which is frequency-doubled by KDP crystal to give a 1·0 mJ, 32 ps pulse at 532 nm. The linearly polarized laser beam is split into two (vertically polarized) writing beams and a (horizontally polarized) reading beam. This reading beam, or probe, propagates through an optical delay line. The chosen crossed-polarization of the probe and pump waves avoids diffraction by electrostrictive or thermal gratings. All waves are slightly focused in the 200 μm thick sample cell. The generated DFWM signal is analysed with a 1 cm long reticon diode array with a 25 μm diode-to-diode spacing, allowing a time range of 100 ps with 300 fs resolution.

Measurements were performed (see figure 6) for a silica-glass plate from the cell, carbon disulphide, nitrobenzene and an oriented liquid crystal 8CB at a temperature of $T = 304$ K, interposed between chemically treated fused silica optical windows to achieve homeotropic alignment of the molecules with the director of the nematic films perpendicular to the surface.

The curves displayed in figure 6 (*a*) were obtained with the glassplate of the cell window and have an intensity three orders of magnitude smaller than for CS_2 or nitrobenzene due to the very weak electronic nonlinearity of the material. The expected very fast relaxation time (in the femtosecond range or less) allows

us to calculate from the width $t_{f.w.h.m.} = (38 \pm 0{\cdot}9)$ ps the laser pulse duration $t_p = (31{\cdot}9 \pm 0{\cdot}9)$ ps. The results obtained for carbon disulphide $t_{f.w.h.m.} = 34{\cdot}4 \pm 1{\cdot}1)$ ps and nitrobenzene $t_{f.w.h.m.} = (21{\cdot}2 \pm 0{\cdot}9)$ ps are shown in figures 6 (*b*) and (*c*) respectively. Using the computer simulation, the best fit for these points can be calculated. The curve, plotted as a dashed line in figure 3, has been found to fit the best experimental results and corresponds to the value of $a = 3{\cdot}2$. In this way it is possible to estimate the magnitude of phase modulation for a YAG picosecond laser without any additional measurements. However, from this curve it is not possible to obtain the relaxation time for nitrobenzene because of the flatness of the curve (figure 2) above $\tau_r/t_p > 0{\cdot}5$ and because the relaxation time of nitrobenzene is longer than the pulse duration $t_p = 32$ ps. For CS_2 the estimated relaxation time $\tau_r = (2{\cdot}2 \pm 0{\cdot}7)$ ps is in agreement with the literature [11, 12].

On this basis we were able to estimate the relaxation time for an unknown sample of an oriented 8CB liquid crystal as $\tau_r = (5{\cdot}0 \pm 0{\cdot}8)$ ps. This dynamical information is connected with the rotational reorientation time of the molecule around its axis due to transverse reorientation of the molecules induced by the optical field, whose wave-vector is parallel to the director, interacting with the transverse anisotropy $\gamma_t = \alpha_{22} - \alpha_{11}$, when α_{33} is along the long axis. Motion along the long axis is restricted by the homeotropic alignment of the molecule.

As can be seen, the estimated relaxation times are much shorter than the pulse duration and confirm the present theory as well as other results obtained for our liquid crystal sample at different temperature to be presented elsewhere.

5. Conclusions

We have presented a method which allows us to estimate the relaxation time of nonlinear media, or the ratio of this time to the pulse duration in the presence of moderate or strong phase modulation. The most precise results are obtained in two extreme cases: for $t_p \gg \tau_r$ and $t_p \ll \tau_r$. For intermediate cases the value of τ_r/t_p can only be estimated. The validity of this method is limited by the knowledge of the magnitude of the phase modulation which occurs in the laser. However, provided the phase modulation is well characterized, the technique described in this paper may be used to give clear information about nonlinear media.

Acknowledgments

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References

[1] Pepper, D. M., 1986, *Scient. Am.*, **254**, 56.
[2] Yariv, A., 1978, *IEEE J. quant. Electron.*, **14**, 650.
[3] Buchert, J., Dorsinville, R., Delfyett, P., Krimchansky, S., and Alfano, R. R., 1985, *Optics Commun.*, **52**, 433.
[4] Vasil'ieva, M. A., Vischakas, J., Kabelka, V., and Masalov, A. V., 1985, *Optics Commun.*, **53**, 412.
[5] Eichler, H. J., Klein, U., and Langhans, D., 1980, *Appl. Phys.*, **21**, 215.
[6] Kielich, S., 1977, *Nonlinear Molecular Optics* (Warsaw: PWN).

[7] ALEXIEWICZ, W., BUCHERT, J., and KIELICH, S., 1977, *Acta Phys. Pol.* A, **52,** 445.
[8] EICHLER, H. J., LANGHANS, D., and MASSMANN, F., 1984, *Optics Commun.*, **50,** 117.
[9] VAEDENY, Z., and TAUC, J., 1981, *Optics Commun.*, **39,** 396.
[10] SALA, K. L., KENNEY-WALLACE, G. A., and HALL, G. E., 1980, *IEEE J. quant. Electron.*, **16,** 990.
[11] IPPEN, E. P., and SHANK, C. V., 1975, *Appl. phys. Lett.*, **26,** 92.
[12] KENNEY-WALLACE, G. A., and WALLACE, S. C., 1983, *IEEE J. quant. Electron.*, **19,** 719.