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Theoretical study of ultra-fast dephasing by four-wave mixing

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ABSTRACT

Microscopic dynamics of materials can be studied by time delayed four-wave mixing spectroscopy. Dephasing constants can be measured by such experiments. Experimental results are easily analysed when the correlation time τ_c of the exciting electric field is much shorter than the dephasing time T_2 . However, when these quantities are on the same time scale, numerical fits are necessary. In the present work, we analysed theoretically a time delayed four-wave mixing experiment. The material is described by an ensemble of two-level systems and a large inhomogeneous broadening is assumed. Using the third order term of the density matrix we establish a relation between T_2 , τ_c and τ_m the time delay for which the maximum of the diffracted light intensity is observed. The conditions to obtain an estimate of T_2 from the measurement of τ_m , are discussed.

1. INTRODUCTION

The study of relaxation processes after light excitation are essential to understand the microscopic dynamics of materials. In organic materials, relaxation times are generally very short, and often fall far below 1 psec¹. To study such ultrafast relaxation processes, a variety of nonlinear optical techniques have been developed. Because the frequency-domain methods^{2,3} were usually indirect and require careful interpretation, time delayed four-wave mixing (TDFWM) techniques have been elaborated^{1,4-19}. The basic analysis of TDFWM has been carried out by Yajima and co-workers^{4,5}. These experiments involve self diffraction of two or three noncollinear delayed pulses by an optically induced grating. It was shown that the time resolution is not determined by the pulse width, instead it corresponds to the correlation time τ_c of the exciting electric-field^{5,6}. Accordingly a time resolution much shorter than the pulse width can be achieved using temporally incoherent light^{1,5-14}. Some of the previous works^{4,5,8,16} analysed TDFWM using a third order density matrix expansion, in the rotating wave and electric dipole approximations, applied to two-level systems. An estimation of the dephasing time T_2 can readily be obtained only for T_2 much longer than τ_c but much shorter than the relaxation time T_1 , from the single exponential decay with the rate $2/T_2$ and $4/T_2$ in the homogeneous and large inhomogeneous broadening cases respectively⁵. However, up to now, for T_2 of the order of τ_c , one has to numerically fit experimental data to theoretical curves to estimate T_2 . To simplify this evaluation, several authors^{1,8,16} have suggested that an estimate of T_2 may be deduced from a measurement of τ_m , the time delay between the pulses corresponding to the maximum of the diffracted light intensity.

Our purpose, in this work, is to establish a relation between T_2 , τ_c and τ_m . We consider three-pulse scattering experiments described by Weiner et al.¹⁵ and illustrated in figure 1. We just recall here the main advantages of this interaction scheme, instead of the two pulses used elsewhere. The three-pulse method plainly distinguishes between homogeneous and inhomogeneous broadening. In the case of homogeneous broadening the scattering curves are always symmetric with respect to the time delay τ between pulses 1 and 2. On the other hand, in the inhomogeneous broadening case the scattering curves are asymmetric and exhibit a shift toward positive or negative delay. For τ_c much longer than T_2 , the TDFWM signal is given by the square of the electric-field autocorrelation function for both homogeneous and inhomogeneous

broadening. Because the electric-field autocorrelation function can be measured, fast dephasing times can be resolved by looking at small differences between the scattering curves and the autocorrelation function. In addition, the three-pulse scattering technique is only sensitive to the transverse relaxation time T_2 , and not to T_1 . Finally, analytic calculation with this model are easier than with the two-pulse one, and because the shift vanishes when homogeneous broadening is present we consider the case of large inhomogeneous broadening.

2. THEORY

We consider the situation illustrated in figure 1. The active medium is constituted by an ensemble of N two-level systems. They are characterized by a transition moment μ_{12} , longitudinal and transverse relaxation times T_1 and T_2 respectively, and a transition energy $\hbar\omega_{21}$. The electric-fields are expressed in the form :

$$E_j(\vec{r}, t) = \mathcal{E}_j(\vec{r}, t) \exp[i(\omega t - \vec{k}_j \cdot \vec{r})] + \text{c.c.}, \quad j = 1, 2, 3. \quad (1)$$

All fields are assumed to have parallel polarizations, so that vector notation can be omitted.

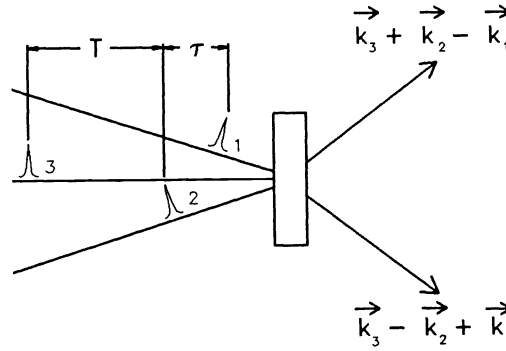


fig.1 Geometry for three pulse time-delayed four-wave mixing experiment.

The macroscopic polarization is given by :

$$P(\vec{r}, t, \tau) = \mathcal{P}(\vec{r}, t, \tau) + \mathcal{P}^*(\vec{r}, t, \tau), \quad (2)$$

with

$$\mathcal{P}(\vec{r}, t, \tau) = N \int_{-\infty}^{+\infty} d\omega_{21} \mu_{21} \rho_{12}(\vec{r}, t, \tau, \omega_{21}) g(\omega_{21}), \quad (3)$$

where $g(\omega_{21})$ is the distribution function of ω_{21} characterizing the inhomogeneous broadening, and $\rho_{12}(\vec{r}, t, \tau, \omega_{21})$ is a nondiagonal element of the density matrix ρ , which satisfies the relations²⁰ :

$$\frac{\partial w}{\partial t} + \frac{1}{T_1}(w - w_0) = \frac{2i}{\hbar}[H_{12}\rho_{21} - H_{21}\rho_{12}], \quad (4)$$

$$\frac{\partial \rho_{12}}{\partial t} + \left(\frac{1}{T_2} - i\omega_{21}\right)\rho_{12} = -\frac{i}{\hbar}H_{12}w. \quad (5)$$

Here, $w = \rho_{22} - \rho_{11}$ stands for population difference and is equal to w_0 at $t = -\infty$. The matrix elements of the interaction Hamiltonian take the form :

$$H_{12} = -\mu_{12} \sum_{j=1}^3 E_j(\vec{r}, t) \quad (6)$$

Using a perturbative technique, the third order term of the density matrix in the rotating wave approximation corresponds to¹⁶

$$\rho_{12}^{(3)}(\vec{r}, t) \sim \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' \hat{E}(\vec{r}, t') \exp[(-1/T_2 + i\Delta)(t - t')] \exp[-(t' - t'')/T_1] \\ \times \left\{ \hat{E}^*(\vec{r}, t'') \hat{E}(\vec{r}, t''') \exp[(-1/T_2 + i\Delta)(t'' - t''')] + \text{c.c.} \right\}, \quad (7)$$

where $\rho_{12}^{(3)}$ and $\hat{E}(\vec{r}, t)$ are defined by :

$$\rho_{12}^{(3)} = \rho_{12}^{(3)} \exp[i\omega t] \\ \hat{E}(\vec{r}, t) = \sum_{j=1}^3 \mathcal{E}_j(\vec{r}, t) \exp[-i\vec{k}_j \cdot \vec{r}],$$

if

$$\Delta = \omega_{21} - \omega.$$

Using Weiner's notation¹⁶, we write $\hat{E}(\vec{r}, t)$ as :

$$\hat{E}(\vec{r}, t) = a_1 e(t + \tau) \exp[-i\vec{k}_1 \cdot \vec{r}] + a_2 e(t) \exp[-i\vec{k}_2 \cdot \vec{r}] + a_3 e(t + T) \exp[-i\vec{k}_3 \cdot \vec{r}]. \quad (8)$$

With the restriction that pulse 3 arrives at least several pulse widths after pulses 1 and 2, and if the population does not change appreciably within the duration of pulse 3, then, the polarization in direction $\vec{k}_4 = \vec{k}_3 - \vec{k}_2 + \vec{k}_1$ is written as follows :

$$\mathcal{P}_{k_4}(\vec{r}, t) \sim \exp[-i\vec{k}_4 \cdot \vec{r}] \exp(-T/T_1) \int_{-\infty}^{+\infty} d\Delta g(\Delta) \int_{-\infty}^t dt_1 \int_{-\infty}^{+\infty} dt_2 \int_{-\infty}^{t_2} dt_3 \\ \times \exp[(-1/T_2 + i\Delta)(t - t_1)] e(t_1 - T) \\ \times \left\{ e^*(t_2) e(t_3 + \tau) \exp[-(1/T_2 - i\Delta)(t_2 - t_3)] \right. \\ \left. + e^*(t_3) e(t_2 + \tau) \exp[-(1/T_2 + i\Delta)(t_2 - t_3)] \right\}. \quad (9)$$

The output light intensity detected in direction \vec{k}_4 is proportional to the time integral of the square of \mathcal{P}_{k_4} ⁴:

$$I_{k_4}(\tau) \sim \int_{-\infty}^{+\infty} dt \left| \mathcal{P}_{k_4}(\vec{r}, t, \tau) \right|^2. \quad (10)$$

Performing the average over a Gaussian inhomogeneous line shape :

$$g(\Delta) = \frac{1}{\sqrt{\pi}\sigma} \exp[-(\Delta/\sigma)^2], \quad (11)$$

and considering the case of large inhomogeneous broadening, we get :

$$I_{k_4}(\tau) \sim \int_0^{+\infty} dt_1 \int_0^{+\infty} dt_2 \exp[-2(t_1 + t_2)/T_2] G(t_1 + \tau) G^*(t_2 + \tau) G(t_2 - t_1). \quad (12)$$

$G(u)$ represents the electric-field autocorrelation function :

$$G(u) = \int_{-\infty}^{+\infty} dt e^*(t)e(t+u). \quad (13)$$

Note that the output signal in direction $\vec{k}_5 = \vec{k}_3 + \vec{k}_2 - \vec{k}_1$ can be obtained by substituting $-\tau$ for τ in relation (12). This relation has been given in a different form by Weiner et al.¹⁶, and also by Nakatsuka and co-workers¹⁷ in the case of two-pulse TDFWM, when the conditions for T are replaced by $T_1 \gg T_2, \tau_c$. Consequently, the following discussion will be valid also for two-pulse TDFWM in those limits.

In order to obtain a relationship between τ_m , the value of τ for which $I_{k_4}(\tau)$ is maximum, T_2 and τ_c , we assume that the electric-field autocorrelation function is of the form¹⁸ :

$$G(\tau) = \exp[-2|\tau|/\tau_c], \quad (14)$$

where τ_c is the correlation time. τ_m satisfies the relation: $\frac{d}{d\tau} I_{k_4}(\tau_m) = 0$ that can be expressed in the form :

$$\int_0^{+\infty} \int_0^{+\infty} dt_1 dt_2 \exp[-2(t_1 + t_2)/T_2] G(t_1 + \tau_m) \frac{dG}{du}(t_2 + \tau_m) G(t_2 - t_1) = 0. \quad (15)$$

After integration, we obtain the following implicit relation :

$$\begin{aligned} 6 \frac{T_2}{\tau_c} \exp[4\tau_m/T_2] - 2 \left(1 + \frac{2T_2}{\tau_c}\right) \left(1 - \frac{T_2^2}{\tau_c^2}\right) \exp[(2 + 4T_2/\tau_c)\tau_m/T_2] \\ + \left(1 - 4 \frac{T_2^2}{\tau_c^2}\right) \left(1 + \frac{T_2}{\tau_c}\right) \exp[4\tau_m/\tau_c] = 0. \end{aligned} \quad (16)$$

The scattering curves into direction \vec{k}_4 exhibits a shift towards negative delay. Therefore, when establishing expression (16), we just keep the negative values of τ_m ; hence, positive solutions of this expression have no physical meaning. In addition, we can note that our approach excludes the values $T_2 = \tau_c$ and $T_2 = \tau_c/2$. Expression (16) gives us a simple relationship between τ_m , T_2 and τ_c , and does not assume any other particular condition between τ_c and T_2 . Two limits can be deduced from this expression. First, when $\tau_c \gg T_2$, we obtain:

$$\frac{\tau_s}{\tau_c} = \frac{T_2}{\tau_c} \times \ln 2, \quad (17)$$

where τ_s is defined as the separation between the peaks of the \vec{k}_4 and \vec{k}_5 scattering curves and is equal to $2|\tau_m|$. On the other hand, for large values of T_2/τ_c , the normalised peak shift τ_s/τ_c increases with T_2 as $\ln(T_2/\tau_c)$.

3. DISCUSSION

The scattering curves into direction \vec{k}_4 and \vec{k}_5 exhibit a shift, increasing with T_2 , towards negative or positive delay, respectively. To illustrate this behaviour, we have plotted the normalised peak shift τ_s/τ_c as a function of T_2/τ_c in figure 2, and τ_s/T_2 as a function of τ_c/T_2 in figure 3. For $\tau_c \gg T_2$, figure 2 and especially figure 3 exhibit the linear behaviour of τ_s with T_2 . The proportionality factor is $\ln 2$ as can be deduced from equation (17). We have to mention that this factor is depending on the analytical form of the electric-field autocorrelation function. Hence, for small values of T_2 , the peak shift gives us a direct estimation of the dephasing time. We can note here that relation (16) was obtained by studying

the scattered energy in direction \vec{k}_4 ; in this case, the maximum of I_{k_4} is achieved for negative values of τ . Therefore, in order to evaluate T_2 in the general case, we have to introduce the values of τ_c and $\tau_m = -\tau_s/2$ in expression (16).

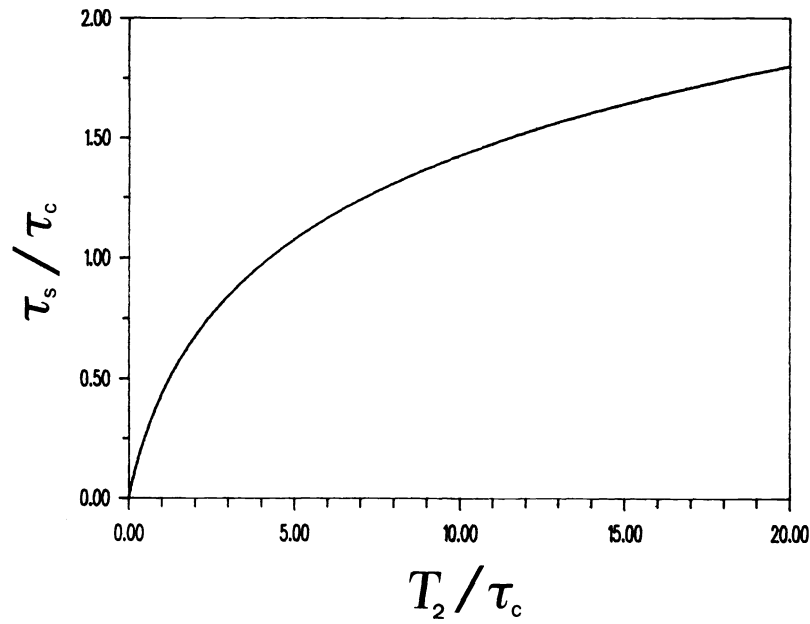


fig.2 Calculated normalised peak shift τ_s/τ_c as a function of normalised dephasing time T_2/τ_c as obtained from Eq. (16).

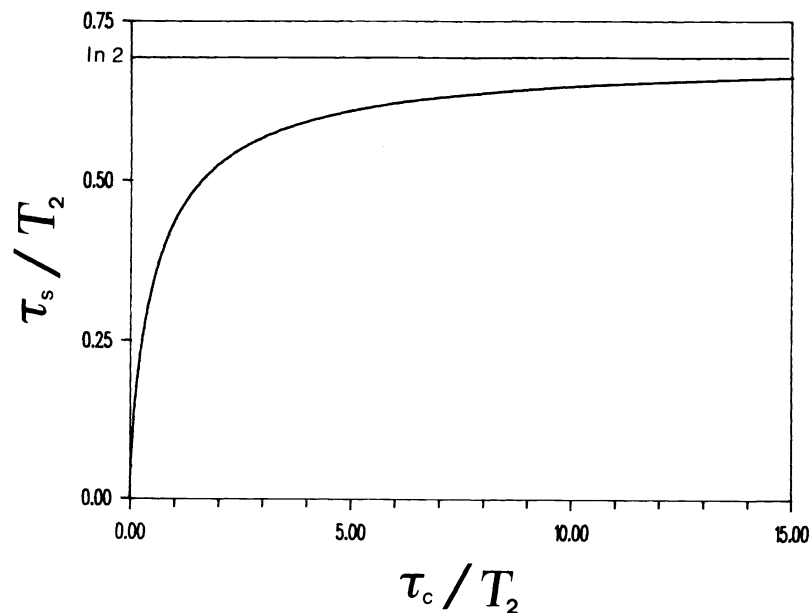


fig.3 Calculated normalised peak shift τ_s/T_2 as a function of normalised correlation time τ_c/T_2 as obtained from Eq. (16).

This method enables us to estimate all possible values of the dephasing time by measuring the peak shift and the correlation time. However, as T_2/τ_c increases, the curve slope decreases and so does the accuracy of the T_2 estimate. Consequently, the evaluation of the dephasing time becomes rather doubtful when $T_2 \gg \tau_c$. Moreover, for such large values of T_2 , the width of the scattered energy $I(\tau)$ is no longer governed by τ_c but increases with T_2 . This broadening of the curves also diminishes the time resolution. Nevertheless, this case has been solved already, and the dephasing time can be estimated from the single exponential decay of the scattering curves⁵.

Now, we try to apply our result to measurements achieved in some previously mentioned experiments. First we consider the Weiner et al. results¹⁶. Thin samples of cresyl violet dissolved in a polymer host have been studied with 75 fsec transform-limited pulses. At the temperature of 15 K a shift of 60 fsec has been obtained. With these values we get an estimation of about 200 fsec. However, nonphotochemical hole-burning measurements on cresyl violet in polyvinyl alcohol polymer indicate that T_2 must be in the psec range²¹. From these observations Weiner et al. deduce that a two-level energy structure is too drastic to study this sample.

Kobayashi et al. have published results obtained with a film of poly-3BCMU on a glass plate¹. They do not give the correlation time of their incoherent excitation light. Now, if we assume that they can be deduced from the widths of the signal, we get a correlation time of 100 fsec for 648 nm and 130 fsec for 582 nm. The peak separations are 30 and 90 fsec at these two wavelengths, respectively. Using equation (16) and the observed peak shift, dephasing times are calculated to be 60 fsec at 648 nm and 270 fsec at 582 nm.

Fujiwara and co-workers consider a sample of cresyl fast violet in a cellulose film⁷. Their 10 nsec pulses have a correlation time of about 300 fsec. At a sample temperature of 10 K they obtain a shift of the order of 250 fsec. By fitting the experimental results with the curves deduced from expression (12), they get a dephasing time of 0.7 psec. Our method gives an evaluation of about 0.8 psec. We cannot compare these two values because such a precision for the measurements is not available. We can just note that we have assumed a double exponential form for the autocorrelation function while Fujiwara and co-workers have assumed a Gaussian form.

Asaka and co-workers have performed experiments on Nd^{3+} -doped silicate glass⁶. Their T_2 estimation was achieved owing to the exponential decay of the experimental curves, the dephasing time deduced was of 60 psec. In this case, T_2 was large with respect to τ_c and, if we try to estimate it from the peak shift, we just get an approximate value of a few tens of psec. As already mentioned, in this case, the peak shift measurement is not a suitable method to evaluate T_2 .

4. CONCLUSION

In summary, we have established a simple relation between peak shift, dephasing time and correlation time for large inhomogeneous broadening. From measurement of the peak shift and correlation time, this expression enables us to give an easy estimation of T_2 when the use of the exponential decrease of $I(\tau)$ fails. This method is valid for three-pulse scattering when the third pulse arrives at least several pulse widths after pulses 1 and 2, and when the population does not change appreciably within the duration of pulse 3. It is also valid for two-pulse TDFWM with the condition $T_1 \gg T_2, \tau_c$. Nevertheless, the restriction that inhomogeneous broadening must be large is not suitable in all the samples previously studied. The case of a finite inhomogeneous broadening will be discussed in a forthcoming publication.

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