Three-pulse scattering for femtosecond dephasing studies: theory and experiment

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A novel transient three-pulse scattering technique for measuring ultrafast dephasing times in condensed matter is analyzed using a perturbative solution of the density matrix equation. The advantages of this technique include subpulsewidth resolution, a clear distinction between homogeneous and inhomogeneous broadening, and sensitivity to spectral cross-relaxation. Its application to the case of a multilevel resonance is also considered. We report results of femtosecond dephasing experiments with dye molecules in liquids and in a polymer host. The dephasing time is determined to be less than 20 fsec for dyes in solution at room temperature. At low temperatures in polymers, a transition from homogeneous to inhomogeneous broadening has been observed and studied as a function of temperature.

1. INTRODUCTION

Optical dephasing experiments can be used to investigate fundamental static and dynamic properties of condensed matter and to elucidate the nature of photophysical and photochemical interactions. Recent applications have included studies of guest–guest and guest–lattice interactions in mixed molecular crystals,[1] tunneling mechanisms in low-temperature amorphous solids,[2] dynamics of dye molecules in solution,[3,4] and exciton localization in multiple-quantum-well structures.[5] In many cases of interest, dephasing may occur on a rapid, subpicosecond time scale, and inhomogeneous broadening may obscure the true phase relaxation dynamics. A variety of nonlinear optical techniques, such as hole burning,[6–9] fluorescence line narrowing,[10] resonant Rayleigh scattering,[3] and polarization spectroscopy,[11] has been developed for frequency-domain measurement of the homogeneous linewidth within an inhomogeneous broadened line. For time-domain measurements, techniques such as the photon echo[12–14] and two-pulse self-diffraction[15] have also been valuable. We have recently developed a transient three-pulse scattering scheme that seems particularly advantageous for femtosecond dephasing studies.[4,16–18] Our method provides subpulsewidth resolution, clear distinction between homogeneous and inhomogeneous broadening, and sensitivity to spectral cross-relaxation effects.

In this paper we present a comprehensive theory of our three-pulse scattering technique, considering both homogeneous and inhomogeneous broadening. The possibilities of spectral cross-relaxation and of a multilevel system are also incorporated. Further, we report the application of three-pulse scattering to a study of dephasing of dye molecules, in solution and in a low-temperature polymer host, on a femtosecond time scale. The results in solution indicate the validity of the homogeneous-broadening model and substantiate the predictions of our theory in this case. Inhomogeneous-broadening effects are clearly evident in the low-temperature polymer and demonstrate the ability of our technique to discriminate between the two broadening mechanisms.

2. THEORY

A. General Formalism

The interaction geometry for three-pulse scattering is illustrated in Fig. 1. The method relies on an optically induced grating formed by the interference of pulses #1 and #2. When the two pulses are separated temporally, a grating can still be formed provided that the dephasing time T_2 is sufficiently long. By measuring the grating amplitude as a function of the delay between pulses #1 and #2, one can measure the dephasing time. This is accomplished using pulse #3 as a delayed probe to scatter off the grating into background-free directions $\bar{k}_4 = \bar{k}_3 + (\bar{k}_1 - \bar{k}_2)$ and $\bar{k}_5 = \bar{k}_3 - (\bar{k}_1 - \bar{k}_2)$.

We have analyzed three-pulse scattering in an optically thin medium, using a third-order density-matrix expansion in the rotating-wave and electric-dipole approximations.[19,20] For a three-level system (an excited state coupled to a reservoir and a ground state), which is appropriate for materials such as dye molecules or semiconductors, this third-order term may be written as follows:

$$\begin{aligned}\hat{\rho}_{ge}^{(3)}(\bar{r},t) \sim & \int^{t} \mathrm{d}t'\hat{E}(\bar{r},t')\exp\left[\left(-\frac{1}{T_2}+i\Delta\omega\right)(t-t')\right] \\ & \times \int^{t'} \mathrm{d}t'' \int^{t''} \mathrm{d}t'''\{\exp[-(t'-t'')/T_g] \\ & + \exp[-(t'-t'')/T_e]\}\Big\{\hat{E}^{*}(\bar{r},t'')\hat{E}(\bar{r},t''') \\ & \times \exp\left[\left(-\frac{1}{T_2}+i\Delta\omega\right)(t''-t''')\right] + \mathrm{c.c}\Big\} \qquad (1)\end{aligned}$$

where $\hat{E}$ and $\hat{\rho}_{ge}^{(3)}$ refer to positive frequency amplitudes, i.e., $E(\bar{r},t) = \hat{E}(\bar{r},t)\exp(i\omega_L t) + \text{c.c.}$, $\rho_{ge}^{(3)}(\bar{r},t) = \hat{\rho}_{ge}^{(3)}(\bar{r},t)\exp(i\omega_L t)$, and $\Delta\omega$ is the frequency detuning defined as the material resonance frequency ω_0 minus the laser frequency ω_L. T_g is the ground-state recovery time; T_e is the excited-state relaxation time. We have assumed $T_g \gg T_e, T_2$. For the more general case in which vibrational relaxation, ground-state recovery, and dephasing occur on a comparable time scale, the

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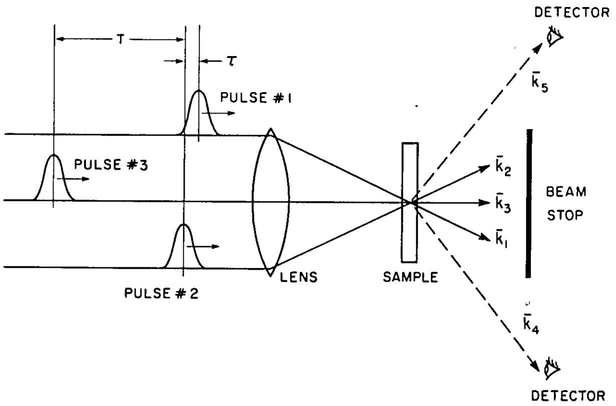

Fig. 1. Interaction scheme for dephasing measurements by the three-pulse scattering technique.

analysis becomes more complicated; but three-pulse scattering can still be used to extract information about these processes. Although simple exponential dephasing (with time constant T_2) has been assumed here, an arbitrary transverse relaxation function $h_T(t)$ is easily incorporated and will be used interchangeably throughout.[21] For homogeneous broadening the polarization positive frequency amplitude $\hat{P}$ is simply the product of $\hat{\rho}_{ge}^{(3)}$ and the electric-dipole matrix element; when inhomogeneous broadening is present, one must integrate the expression for $\hat{\rho}_{ge}^{(3)}$ over the distribution of resonant frequencies $g(\omega_0)$.

If we now write the electric field as a superposition of the three plane-wave input pulses of the same shape, we can identify the source term for the scattering. Specifically, we write

$$\hat{E}(\bar{r}, t) = a_1 e(t + \tau)\exp(-i\bar{k}_1 \cdot \bar{r}) + a_2 e(t)\exp(-i\bar{k}_2 \cdot \bar{r}) + a_3 e(t - T)\exp(-i\bar{k}_3 \cdot \bar{r}), \tag{2}$$

where $e(t)$ is the (complex) electric-field envelope function and the a_i allow for different pulse intensities. The delay τ is positive when pulse #1 precedes pulse #2. With the restrictions that pulse #3 arrives at least several pulse widths after pulses #1 and #2 and that the population does not change appreciably within the duration of pulse #3 (generally valid if pulse #3 arrives after any rapid excited-state relaxation is complete), the polarization source term for scattering into direction $\bar{k}_4$ is written as follows:

$$\begin{aligned}\hat{P}_{k4}^{(3)}(\bar{r}, t) \sim \exp(-i\bar{k}_4 \cdot \bar{r}) \int \mathrm{d}\omega_0 g(\omega_0) \int^{t} \mathrm{d}t' e(t' - T) \\ \times \exp\left[\left(-\frac{1}{T_2} + i\Delta\omega\right)(t - t')\right] \\ \times \exp(-T/T_g)\hat{\gamma}(\tau, \Delta\omega),\end{aligned} \tag{3a}$$

where

$$\begin{aligned}\hat{\gamma}(\tau, \Delta\omega) \sim \int^{\infty} \mathrm{d}t'' \int^{t''} \mathrm{d}t''' \Big\{ e^*(t'')e(t''' + \tau) \\ \times \exp\left[\left(-\frac{1}{T_2} + i\Delta\omega\right)(t'' - t''')\right] + e(t'' + \tau)e^*(t''') \\ \times \exp\left[\left(-\frac{1}{T_2} - i\Delta\omega\right)(t'' - t''')\right]\Big\}.\end{aligned} \tag{3b}$$

$\hat{\gamma}(\tau, \Delta\omega)$ represents the complex grating amplitude generated by the interference of the second pulse with the coherent polarization left behind by the first. The source for scattering into direction $\bar{k}_5$ can be obtained by substituting $-\tau$ in place of τ in relations (3). This is equivalent to replacing $\hat{\gamma}$ with $\hat{\gamma}^*$. The actual population grating is written

$$\begin{aligned}\gamma(\bar{r}, \tau, \Delta\omega) = \exp(-T/T_g) \times \{\hat{\gamma}(\tau, \Delta\omega) \\ \times \exp[-i(\bar{k}_1 - \bar{k}_2) \cdot \bar{r}] + \text{c.c.}\},\end{aligned} \tag{4}$$

where the maximum positive value of γ corresponds to the maximum ground-state depletion.

The quantity actually measured is the total scattered energy U as a function of the delay τ between pulses #1 and #2 and is proportional to the time integral of the squared polarization:

$$U_{k_4}(\tau) \sim \int \mathrm{d}t |\hat{P}_{k4}^{(3)}(\bar{r}, t)|^2 \tag{5}$$

and similarly for direction $\bar{k}_5$.

B. Homogeneous Broadening

In the case of homogeneous broadening, the scattered energy as a function of τ is proportional to the squared complex grating amplitude, i.e.,

$$U_{k_4} = U_{k_5} \sim |\hat{\gamma}(\tau, \Delta\omega)|^2. \tag{6}$$

The scattering curves are always symmetric with respect to the delay τ between pulses #1 and #2, independent of pulse #3. The scattered energy depends on the delay T of pulse #3 relative to the ground-state recovery time T_g [see relation (3a)]. However, because the dephasing is revealed through the shape of the scattering curve as a function of τ, we omit the $\exp(-2T/T_g)$ factor in Eq. (6) and the following expressions.

For pulses much shorter than the dephasing time T_2, the scattered energy has the following simple form:

$$U_{k_4} = U_{k_5} \sim \exp(-2|\tau|/T_2). \tag{7}$$

On the other hand, for pulses much longer than T_2, the expression for the scattered energy reduces to the squared envelope of the electric-field autocorrelation, for both homogeneous and inhomogeneous broadening:

$$U_{k_4} = U_{k_5} \sim |\int \mathrm{d}t e(t)e^*(t + \tau)|^2. \tag{8}$$

This property was used previously to measure the coherence properties of mode-locked pulses.[22] Even when arbitrary pulse shapes are considered, the electric-field autocorrelation function is still sufficient to characterize the scattering. This feature is particularly advantageous in the picosecond and femtosecond time domains, in which pulse shapes themselves cannot yet be directly measured. By rewriting the complex grating amplitude $\hat{\gamma}$ from relation (3b) as a symmetrized convolution of the transverse relaxation function $h_T(\tau)$ with the electric-field autocorrelation $G(\tau)$, we obtain the following expression:

$$\begin{aligned}\hat{\gamma}(\tau, \Delta\omega) \sim \int \mathrm{d}\tau' h_T(\tau' + \tau)\exp[i\Delta\omega(\tau' + \tau)]G(\tau') \\ + \int \mathrm{d}\tau' h_T^*(\tau' - \tau)\exp[-i\Delta\omega(\tau' - \tau)]G^*(\tau')\end{aligned} \tag{9}$$

where $G(\tau') = \int \mathrm{d}t e(t)e^*(t + \tau')$ and $h_T(\tau)$ is zero for negative values of τ. Because the electric-field autocorrelation function is readily measured,[4] fast dephasing times can be resolved by looking for small differences between the scattering data and $|G(\tau)|^2$, which represents the response for $T_2 = 0$. Furthermore, because $|G(\tau)|^2$ depends not on the pulse width but

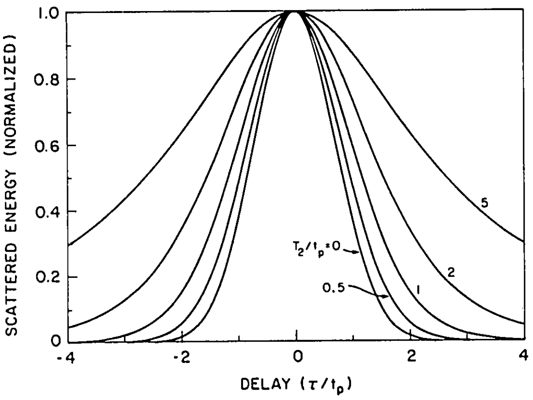

Fig. 2. Calculated scattered energy for Gaussian pulses as a function of the normalized delay τ/t_p between pulses #1 and #2, in a homogeneously broadened medium for several values of T_2/t_p. The laser frequency is on resonance.

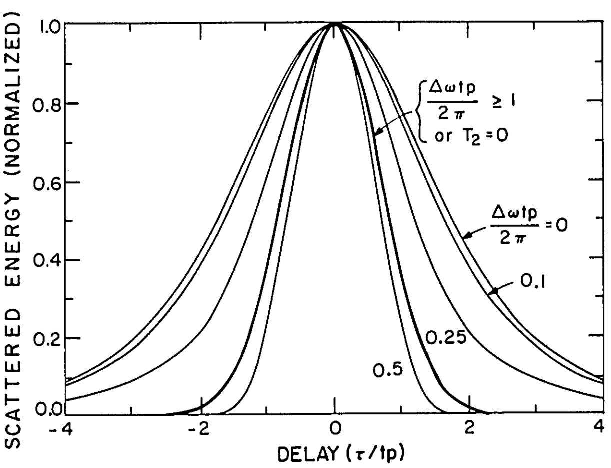

Fig. 3. Off-resonance scattering curves for Gaussian pulses as a function of τ/t_p for various frequency offsets $\Delta\omega t_p/2\pi$. The dephasing time T_2 was set to $2.5t_p$.

on the pulse coherence, resolution well below the pulse width can be achieved using spectrally broadened pulses.

Relation (9) can be restated more elegantly in the frequency domain; the Fourier transform of the complex grating amplitude $\hat{\gamma}$ is the product of the absorption spectrum $\alpha(\omega)$ and the laser power spectrum $\phi(\omega)$:

$$\hat{\gamma}(\tau, \Delta\omega) \sim \int d\Omega \exp(i\Omega\tau)\alpha(\omega_L + \Omega)\phi(\omega_L + \Omega), \quad (10)$$

where ω_L is the laser carrier frequency and $\Omega = \omega - \omega_L$. The derivation of relation (10) is based on the Fourier-transform relationships between the laser power spectrum and the electric-field autocorrelation and between the absorption spectrum and the phase-relaxation function, respectively.

Figure 2 shows calculated curves for the scattering produced by Gaussian pulses $e(t) = \exp(-t^2/t_p{}^2)$ in a homogeneously broadened medium with simple exponential dephasing. The laser frequency is exactly coincident with the material resonance. Dephasing times as short as $0.3t_p$ should be observable, provided that a 10% broadening of the squared electric-field autocorrelation can be measured. Assuming a pulse duration of 70 fsec full width at half-maximum (FWHM), this corresponds to a resolution of 20 fsec. In practice the resolution will depend on the experimental signal-to-noise ratio and on the accuracy of the instantaneous response measurement. Based on our previous experimental results, resolution down to 20 fsec is indeed feasible.[4,16–18]

Figure 3 shows off-resonance scattering curves for Gaussian pulses for a fixed $T_2 = 2.5t_p$ but for various frequency offsets $\Delta\omega t_p/2\pi$. As the detuning is increased, the scattering curve deviates from the $\Delta\omega = 0$ curve and eventually approaches the instantaneous response. For intermediate-frequency offsets (i.e., $\Delta\omega t_p/2\pi \sim 0.5$) the scattering curve can actually be narrower than the $T_2 = 0$ response. This behavior can be explained on the basis of relation (10). For large detunings only the wings of the Lorentzian, which are flat far from line center, are of importance. In this case the product in relation (10) is dominated by the power spectrum, and the scattering reflects the pulse characteristics only. The narrower scattering curves calculated for intermediate detunings arise because of the positive curvature of the absorption at these frequencies. Note that the off-resonant behavior discussed above may not be of general validity but depends on the assumed Lorentzian line shape.

C. Inhomogeneous Broadening

In the case of inhomogeneous broadening, the scattering curves are asymmetric in τ, in contrast to those for homogeneous broadening. This asymmetry provides a simple criterion for differentiating between the two types of line broadening. For an inhomogeneously broadened system, pulses #1 and #2 create a series of population gratings $\gamma(\Delta\omega)$, spatially shifted with respect to each other because of the different subgroup frequencies. This is particularly evident from Eq. (4), evaluated for the case of delta-function pulses:

$$\gamma(\bar{r}, \tau, \Delta\omega) \sim \exp(-|\tau|/T_2)\cos[(\bar{k}_1 - \bar{k}_2)\cdot\bar{r} - \Delta\omega\tau]. \quad (11)$$

If the inhomogeneous broadening is large, the total population may become almost uniform spatially. Nevertheless, scattering may still occur, as follows. The arrival of pulse #3 at time T generates for each grating a third-order polarization, whose initial phase is determined by the spatial shift of the grating and which oscillates at the appropriate resonant frequency. The total polarization, again for delta-function pulses, is obtained for each scattering direction from relations (3) using relation (11):

$$\begin{aligned}(\hat{P}_{k4}^{(3)} + \hat{P}_{k5}^{(3)}) \sim \exp[-(t - T + |\tau|)/T_2] &\int d\omega_0 g(\omega_0) \\ \times (\exp\{-i[\bar{k}_4\cdot\bar{r} - \Delta\omega(t - T + \tau)]\} \\ + \exp\{-i[\bar{k}_5\cdot\bar{r} - \Delta\omega(t - T - \tau)]\}). \quad (12)\end{aligned}$$

At time $T = |\tau|$, all the polarization components interfere constructively to form a phased array for radiation in direction $\bar{k}_4$ for $\tau < 0$ or in direction $\bar{k}_5$ for $\tau > 0$. Thus, for a fixed value of τ, scattering occurs preferentially in a single direction. In the limit of T_2 much longer than the inverse inhomogeneous width (wide inhomogeneous broadening), we obtain the following expressions for the scattered energy:

$$\tau \geq 0: \quad U_{k_4} = 0; \quad U_{k_5} \sim \exp(-4\tau/T_2), \quad (13a)$$

$$\tau \leq 0: \quad U_{k_4} \sim \exp(4\tau/T_2); \quad U_{k_5} = 0. \quad (13b)$$

Note that the inhomogeneous limit of our three-pulse scattering technique gives the same result as the weak-field limit of the stimulated photon echo.[13] We wish though to emphasize the generality of three-pulse scattering, which includes

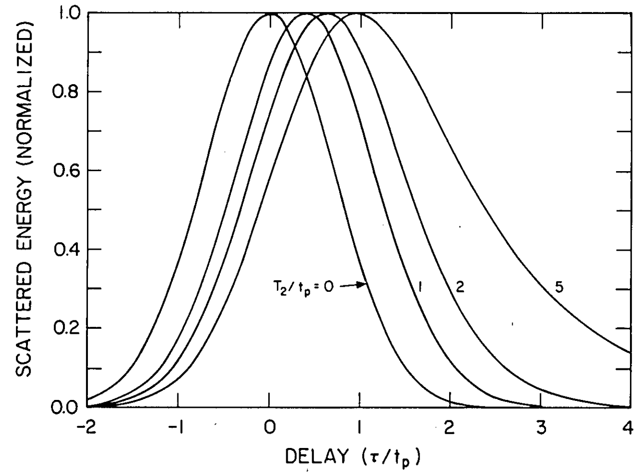

Fig. 4. Calculated scattered energy, for Gaussian pulses as a function of τ/t_p for different values of T_2/t_p in the case of wide inhomogeneous broadening.

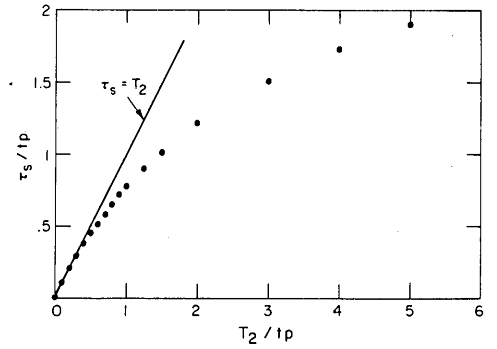

Fig. 5. Normalized peak shift τ_s/t_p as a function of the normalized dephasing time T_2/t_p.

both the homogeneous and inhomogeneous limits within its framework.

Figure 4 shows calculated curves for the scattering of Gaussian pulses into direction $\bar{k}_5$, in the case of wide inhomogeneous broadening. The characteristic exponential decay is evident only for $T_2 > 2t_p$. Even for small dephasing times, however, the rising edge and peak of these scattering curves exhibit a pronounced shift toward positive delay with increasing T_2. The normalized peak shift τ_s (defined as the total separation between the peaks of the $\bar{k}_4$ and $\bar{k}_5$ scattering curves normalized to t_p) is plotted in Fig. 5 as a function of T_2/t_p. The graph is close to linear for $T_2 < t_p$ with $\tau_s \sim T_2$. Thus τ_s can serve as a sensitive measure of dephasing times shorter than the pulse width.

As in the case of homogeneous broadening, the electric-field autocorrelation alone is sufficient to provide a reference for the three-pulse scattering. In the limit of wide inhomogeneous broadening, substitution of relation (9) into relations (3) yields after some further simplification the following:

$$\hat{P}^{(3)}_{k4}(\bar{r}, t) \sim \exp(-i\bar{k}_4 \cdot \bar{r}) \times \int dt'|h_T(t-t')|^2 q(t'-T)G^*(t-t'+\tau). \quad (14)$$

We have written $q(t'-T)$ instead of $e(t'-T)$ as previously to allow for the possibility that the shape of pulse #3 differs from that of the other two pulses. The scattered energy is evaluated using relation (14) in relation (5), with the following result:

$$U_{k_4}(\tau) \sim \iint d\tau' d\tau'' |h_T(\tau')|^2 |h_T(\tau'')|^2 Q(\tau'-\tau'')G^*(\tau + \tau')G(\tau+\tau''), \quad (15)$$

where $Q(\tau) = \int dt q(t) q^*(t+\tau)$. Relation (15) demonstrates that the scattering curves depend directly on the experimentally accessible electric-field autocorrelation functions, as claimed. Also in the case of an arbitrary inhomogeneous distribution, the scattered energy can be expressed entirely in terms of the field autocorrelation; however, the formula is rather cumbersome and is not given here.

D. Spectral Cross-Relaxation

We consider now the possibility of spectral cross-relaxation within an inhomogeneously broadened line, which arises when the resonant frequencies of individual absorbers are not fixed but can migrate within the inhomogeneous distribution. In the presence of spectral cross-relaxation, the scattering behavior is sensitive to the delay T of pulse #3. For delays longer than the characteristic spectral diffusion time ($T \gg T_3$), the rephasing discussed in connection with relation (12) can no longer occur since the various gratings are no longer distinct. There exists then only a total population grating, whose amplitude is equal to the sum of the individual complex grating amplitudes, expressed according to relation (9) and weighted by the inhomogeneous distribution, as follows:

$$\hat{\gamma}_{\mathrm{TOTAL}}(\tau) \sim \int d\omega_0 g(\omega_0)\hat{\gamma}(\tau, \Delta\omega). \quad (16)$$

This expression simplifies considerably on substitution of relation (10) for the individual complex-grating amplitudes, with the result:

$$\hat{\gamma}_{\mathrm{TOTAL}}(\tau) \sim \int d\Omega \exp(i\Omega\tau)\alpha_{\mathrm{TOTAL}}(\omega_L + \Omega)\phi(\omega_L + \Omega). \quad (17)$$

Here $\alpha_{\mathrm{TOTAL}}(\omega) = \int d\omega_0 g(\omega_0)\alpha_{\mathrm{HOM}}(\omega - \omega_0)$ is the total absorption line shape, given by the convolution of inhomogeneous distribution with the base-band homogeneous line shape function α_{HOM}. Relation (17) is exactly analogous to relation (10) for homogeneous broadening. Thus, for $T \gg T_3$, the scattered energy is a symmetric function of τ; however, the width of the scattering curve reflects the inverse absorption width rather than the actual dephasing time T_2.

We have investigated analytically the transition from asymmetric to symmetric scattering curves with increasing T/T_3 for the case of delta-function pulses and a Gaussian inhomogeneous distribution $g(\omega_0) = (1/\delta\omega\sqrt{\pi})\exp[-(\omega - \omega_0)^2/\delta\omega^2]$. The probability per unit time that an absorber initially resonant at ω_0' jumps to a new resonant frequency ω_0 is assumed to have the following simple form[23]:

$$p(\omega_0' \rightarrow \omega_0) = g(\omega_0)/T_3. \quad (18)$$

Scattering curves for direction $\bar{k}_5$ are shown in Fig. 6 as a function of τ for several values of the pulse #3 delay T/T_3, assuming that $\delta\omega T_2 = 10$ and that the ground-state recovery time T_g is much longer than the time scale of interest. As the delay of the third pulse is increased, the scattering curves become narrower but more symmetric. The scattering efficiency for $\tau = 0$ is insensitive to the spectral diffusion since all gratings are created in phase.

According to the discussion above, three-pulse scattering can yield information about spectral diffusion as well as dephasing. This is accomplished by repeating the experiment

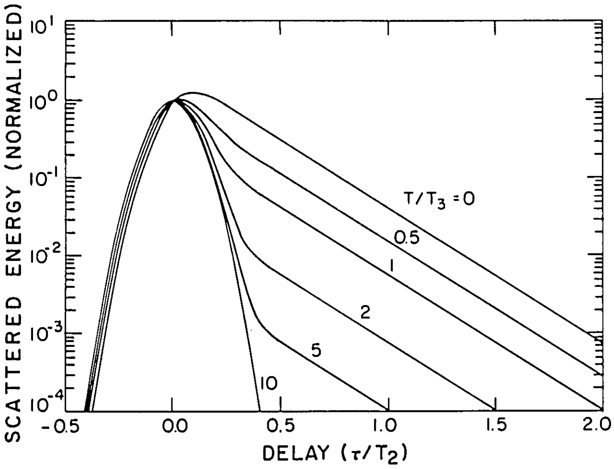

Fig. 6. Calculated scattered energy for delta-function pulses as a function of τ/T_2 for different values of T/T_3, in a inhomogeneously broadened medium with $\Delta\omega T_2 = 10$. $T_g \gg T$ is assumed.

for various settings of T and looking for a transition from asymmetric to asymmetric scattering curves. The ability to investigate spectral diffusion using our transient three-pulse technique constitutes an advantage over recently proposed techniques that use incoherent light.[24,25]

E. Multilevel Systems

We have already seen how the three-pulse scattering can be sensitive to spectral cross-relaxation. We discuss now a further potential complication that arises when a multilevel rather than a two-level energy structure is appropriate. When several transitions are excited simultaneously, interference between the various coherences leads to dephasing faster than that due to one line individually. Unlike inhomogeneous broadening, dephasing due to multiline excitation is an irreversible process.

We have considered analytically a simplified multilevel model in which the ground state is still an isolated level but in which the excited state consists of a set of discrete lines, each with its own matrix element and dephasing rate. Each individual transition is assumed homogeneously broadened. The possibility of a smooth, unresolved absorption spectrum or of a continuum is included as a special case (when the individual homogeneous linewidths exceed the level spacing). Even for a general homogeneously broadened multilevel system, we find that the scattering is still a symmetric function of τ (with the same restrictions as previously on the delay of pulse #3). The scattering curves may be calculated by relation (10) in a fashion exactly analogous to the homogeneously broadened two-level system, except that now the total absorption spectrum, rather than that due to a single line, must be used. Thus, when the individual transitions are unresolved even in the absence of any inhomogeneous broadening, three-pulse scattering yields an effective dephasing time that is the inverse of the total absorption width and that must not be considered an average dephasing time for the individual resonances.

This discussion does not preclude the possibility of observing inhomogeneous-broadening behavior in multilevel systems. For example, inhomogeneous broadening may lead to a total absorption spectrum still wider than the multilevel absorption spectrum of an individual absorber. Alternatively, inhomogeneous broadening may result in a smooth absorption spectrum even when the spectrum of a single molecule consists of discrete, resolved lines. When inhomogeneous broadening significantly influences the multilevel absorption spectrum, asymmetric scattering curves and peak shifts may be observed.

It is interesting to compare dephasing measurements performed in the time domain (three-pulse scattering) and in the frequency domain (spectral hole burning). For a two-level system these techniques yield the same dephasing time. In the case of a multilevel system or of a continuum, however, temporal and spectral measurements are no longer directly related. In a homogeneously broadened, unresolved multilevel system, three-pulse scattering measures a dephasing time that is the inverse of the total absorption bandwidth. A spectral-hole-burning experiment, however, can yield hole widths related to the linewidths of a single transition. This difference between the temporal and spectral measurement techniques must be considered when describing complex multilevel systems in terms of two-level atom concepts.

3. EXPERIMENT

As an initial application of three-pulse scattering, we used pulses from a colliding-pulse mode-locked (CPM) ring dye laser[26] to investigate the dephasing of dye molecules in solution.[4,16] Our laser produced pulses with a duration of 70 fsec FWHM at a wavelength of 620 nm and with a repetition rate of 125 MHz. In the case of parallel polarization for all three pulses, the scattering amplitude was strongly enhanced owing to the formation of a cumulative thermal grating. When thermal gratings dominate, our technique measures the total absorption width, independent of the actual dephasing time T_2; and scattering curves are always symmetric. Nevertheless, the thermal grating effect can be exploited to test the theory developed for the case of homogeneous broadening. Figure 7 shows parallel polarization scattering data for the dyes Nile blue and Rhodamine 640 in methanol. Also shown are curves calculated on the basis of relation (10), using the measured laser power spectrum and dye-absorption spectra. In the case of Nile blue, the calculated curve is indistinguishable from the squared electric-field autocorrelation, owing to the shallow curvature of the absorption spectrum at

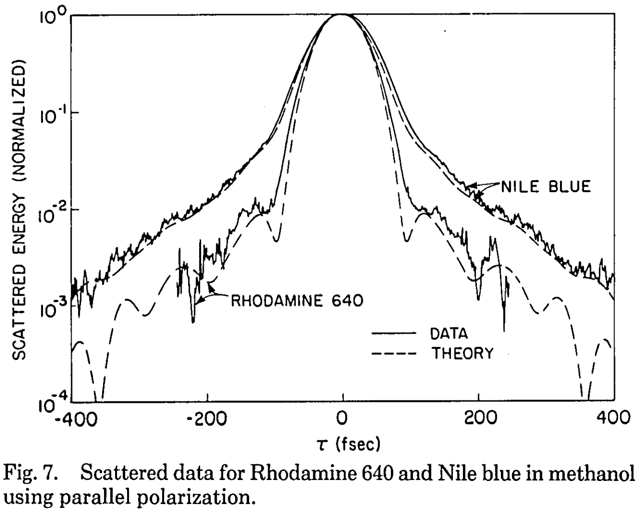

Fig. 7. Scattered data for Rhodamine 640 and Nile blue in methanol, using parallel polarization.

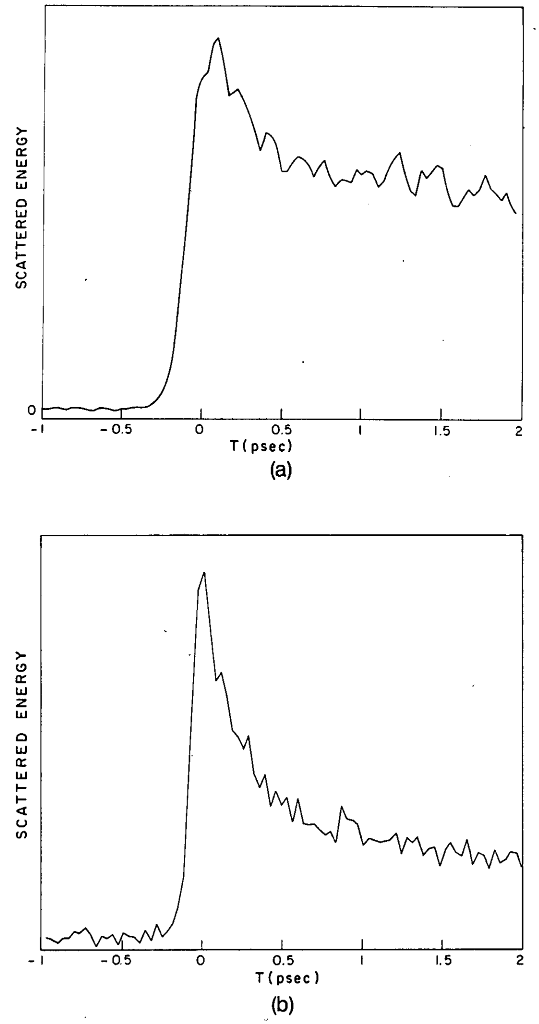

Fig. 8. Scattered energy for (a) cresyl violet and (b) oxazine 720 in PMMA at 15 K as a function of the delay T of pulse #3. Pulses #1 and #2 are set at zero relative delay.

the laser wavelength (which coincides with the absorption peak). In the case of Rhodamine 640, the excitation is shifted 50 nm to the red of the absorption peak; in this region the absorption varies sufficiently rapidly that significant departure from the instantaneous scattering response is predicted. The excellent agreement of the calculated curves with the data in Fig. 7 demonstrates the validity of our theory in the case of homogeneous broadening, for instantaneous and noninstantaneous dephasing and for resonant and off-resonant excitation. The Rhodamine 640 data substantiate our claim (see Fig. 3) that scattering curves narrower than the instantaneous response may occur.

True dephasing information can be obtained if the thermal grating is eliminated using orthogonal polarizations for pulses #1 and #2. Scattering curves for Nile blue are still symmetric and indistinguishable from the instantaneous response. This indicates homogeneous broadening with an apparent dephasing time less than the 20-fsec experimental resolution. Similar results were obtained with several other dyes. This very rapid dephasing results from the simultaneous excitation of many different states within the aborption band and does not correspond to the dephasing time of an individual transition. Our experiments do show, however, that the temporal response of these molecules in solution may be modeled as homogeneously broadened at room temperature.

We have also studied the dephasing of dye molecules in thin films of polymethyl methacrylate (PMMA) polymer[18] using amplified CPM laser pulses[27] with a duration of 75 fsec FWHM and a 10-Hz repetition rate. As a preliminary experiment, we measured the grating lifetime by scanning the delay T of pulse #3 with the delay τ between pulses #1 and #2 set to zero.[28] Data are shown in Fig. 8 for two typical dyes, cresyl violet and oxazine 720, at a temperature of 15 K. The scattering is zero when pulse #3 arrives before pulses #1 and #2; this demonstrates that no persistent grating develops. For large T the scattering approaches an almost constant level (for our 2-psec delay range) that decays on a nanosecond time scale. The large peaks near $T = 0$ are an artifact that occurs when all three beams interact coherently. The tails of the $T = 0$ peaks are evidence of intraband excited-state relaxation of the dye molecules occurring on a time scale of several hundred femtoseconds. Similar rapid excited-state relaxation has also been observed for several dyes molecules in liquid solution at room temperature.[29]

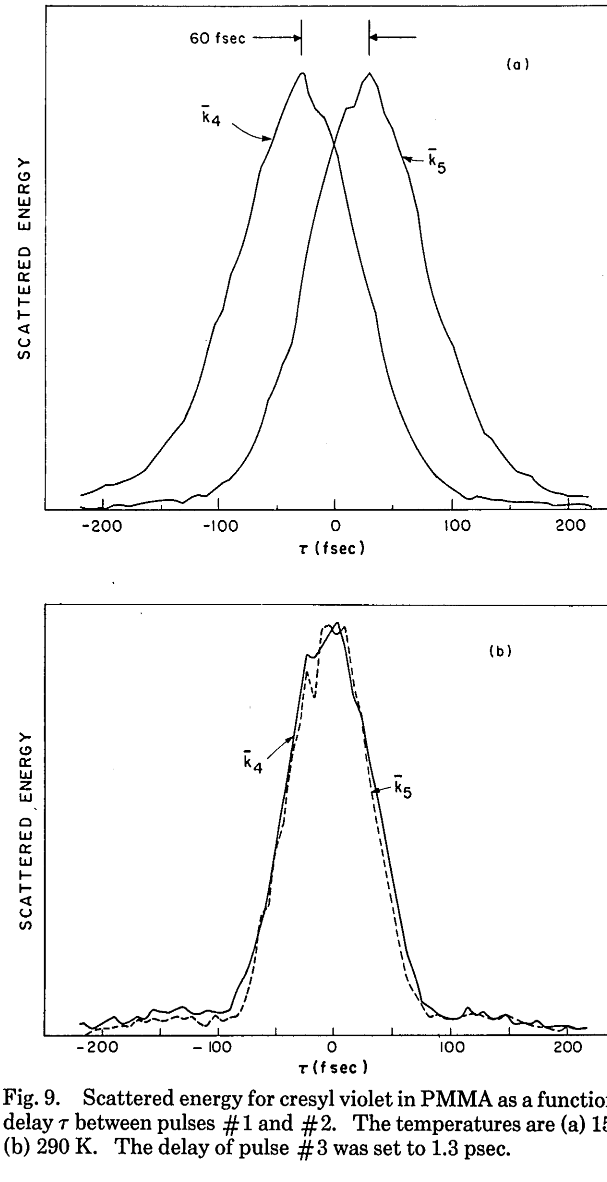

Fig. 9. Scattered energy for cresyl violet in PMMA as a function of delay τ between pulses #1 and #2. The temperatures are (a) 15 K, (b) 290 K. The delay of pulse #3 was set to 1.3 psec.

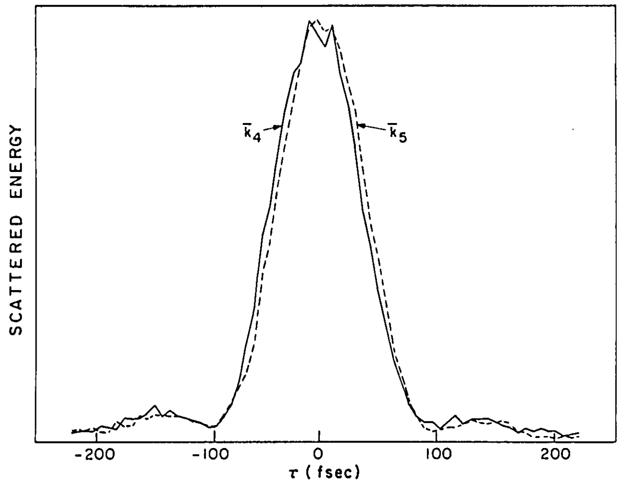

Fig. 10. Scattered energy for Nile blue in PMMA at 15 K as a function of the delay τ between pulses #1 and #2. The delay of pulse #3 was set to 1.3 psec.

We now proceed to a discussion of the dephasing measurements. Scattering curves for cresyl violet taken at a temperature of 15 K are shown in Fig. 9(a) for both scattering directions. The delay of the third pulse was set to 1.3 psec. The asymmetry of the curves, illustrated by the 60-fsec peak shift, shows that inhomogeneous broadening is present and demonstrates the ability of our technique to distinguish between homogeneous and inhomogeneous broadening. With increasing temperature the asymmetry and peak shift decrease. At room temperature the peak shift is no longer evident, as shown in the data of Fig. 9(b). At this temperature homogeneous broadening apparently dominates.

To check for spectral cross-relaxation, we repeated the dephasing measurements with the delay of the third pulse varying between 200 fsec and 200 psec. The observed peak shifts of 60 fsec at 15 K and 33 fsec at 100 K were found to be independent of the third-pulse delay. Thus spectral diffusion is not evident in this time scale and temperature range.

Despite the clearly resolved peak shifts in our low-temperature scattering data, we do not observe a pronounced tail indicative of a long T_2. According to the simple analysis of Section 2.C this would indicate dephasing on a time scale comparable to the pulse width. However, low-temperature nonphotochemical hole-burning measurements on cresyl violet in polyvinyl alcohol polymer indicate that the dephasing time should be on the order of 1 or 2 psec.[9] Our results can be explained on the basis of a multilevel rather than a two-level energy structure. From the hole-burning spectra, we infer that for our laser bandwidth several lines are indeed excited. Because the lines of a single cresyl violet molecule are well resolved at low temperature, inhomogeneous broadening still contributes to the dephasing; and a peak shift is detected. As the temperature is increased, the individual lines broaden and eventually overlap; the molecule behaves like a homogeneously broadened two-level system with a linewidth equal to the total absorption width. This explanation applies to the room-temperature data shown in Fig. 9(b) as well as to the room-temperature data for dye molecules in solution.

In addition to cresyl violet we have also investigated the dephasing of Nile blue and oxazine 720. For both dyes the scattering curves are symmetric over our entire temperature range (15 to 300 K), and no peak shifts are detected. The 15-K Nile blue data are shown in Fig. 10. The results are again explained in terms of a multilevel structure. For Nile blue and for oxazine 720, the laser photons have in each case an excess energy of several hundred reciprocal centimeters relative to the absorption onset; for cresyl violet, however, the laser frequency is coincident with the absorption edge. Therefore Nile blue and oxazine 720 should have considerably higher densities of states than does cresyl violet. Owing to higher densities of states, the individual lines may not be resolved, even at 15 K. In this case, the dephasing should appear instantaneous.

4. SUMMARY

Using a third-order density-matrix expansion, we have analyzed three-pulse scattering as a method for studying ultrafast optical dephasing. The technique provides a clear distinction between inhomogeneous and homogeneous broadening, and it does so in a way that facilitates measurement of dephasing times comparable with or shorter than the pulse width. We have also developed the theory to include the effects of spectral cross-relaxation and the behavior of a multilevel system. By varying two of the relative delays in the three-pulse geometry, we show that it is possible to monitor spectral cross-relaxation effects and to separate them from dephasing and energy relaxation phenomena. With a multilevel system, three-pulse scattering exhibits the same advantages predicted for a two-level system. Unlike dephasing in an inhomogeneous ensemble, however, dephasing due to excitation of multiple levels of the same molecule is irreversible; and its scattering signature is determined only by the input pulse and its multilevel absorption spectrum.

To illustrate the principal characteristics of three-pulse scattering, we have presented results of femtosecond dephasing experiments with dye molecules in liquid and in a polymer host. At room temperature the results indicate apparent dephasing times of less than 20 fsec and support the contention that the dye absorption bands are homogeneously broadened. At temperatures below 100 K, using cresyl violet in PMMA, we have observed asymmetric scattering due to inhomogeneous broadening. These results demonstrate the predicted sensitivity of three-pulse scattering to the two different broadening mechanisms and establish three-pulse scattering as an important tool for studies of ultrafast dephasing in condensed matter.

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(see overleaf)

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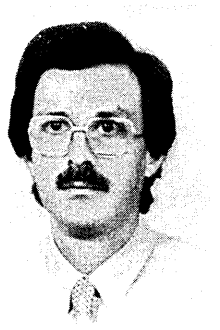

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