Novel transient scattering technique for femtosecond dephasing measurements

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A novel transient scattering technique is proposed for femtosecond dephasing time measurements. This technique provides several advantages compared with existing techniques for time-domain dephasing measurements, including resolution below the pulse width, insensitivity to rapid energy relaxation, and clear demarcation between homogeneous and inhomogeneous broadening. We report experimental results for the dye Nile blue in solution; the dephasing time T_2 is determined to be less than 20 fsec.

Transient four-wave mixing techniques have recently been developed for the investigation of ultrafast dephasing in condensed matter.[1–3] These experiments involve self-diffraction of two noncollinear pulses from an optically induced absorption grating. In this Letter we report an improved scheme utilizing three separate input pulses. Similar three-pulse transient-grating experiments have been applied to study a wide variety of processes in condensed matter, including thermal diffusion,[4] orientational relaxation in dye solutions,[5] and hot-electron relaxation in semiconductors[6]; but the applicability of three-pulse scattering to the study of dephasing had not previously been recognized. The development of the colliding-pulse mode-locked (CPM) dye laser[7] with pulse widths of about 70 fsec, coupled with the improved temporal resolution of our three-pulse-scattering technique, may now make it feasible for the first time to make direct time-domain measurements of femtosecond dephasing of electronic transitions in condensed matter.

Compared with two-pulse scattering, our three-pulse experiment offers several advantages that facilitate the measurement of ultrafast dephasing times comparable with or shorter than the pulse width. These include the following:

(1) The three-pulse-scattering technique is sensitive only to the transverse relaxation time T_2; the two-pulse technique depends not only on T_2 but also on the longitudinal relaxation time T_1. In the case of rapid longitudinal relaxation [such as vibrational relaxation within excited states of organic dye molecules, which may occur in a time less than 0.2 psec (Ref. 8)], it will be hard to distinguish T_1 effects from the T_2 effects.

(2) The $T_2 = 0$ response curve for three-pulse scattering can be experimentally determined by an independent measurement; the $T_2 = 0$ curve for the two-pulse scattering cannot be readily obtained.

(3) The three-pulse method plainly distinguishes between homogeneous and inhomogeneous broadening. The two-pulse method does not make this distinction unless the dephasing is so clearly resolved that accurate comparison with the spectral data is possible.

Our three-pulse-scattering geometry is shown in Fig. 1. The method relies on an optically induced grating, formed by the interference of pulses #1 and #2. When these two pulses are separated temporally, a grating can still be formed, provided that the dephasing time T_2 is sufficiently long. Therefore, by measuring the grating amplitude as a function of the delay τ between pulses #1 and #2, one can measure the dephasing time. This is accomplished using pulse #3 as a probe to scatter off the grating into directions $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$. The delay T of pulse #3 is fixed and is chosen to meet the following criteria: (1) $T \gg t_p$, i.e., pulse #3 arrives several pulse widths after pulses #1 and #2 when the formation of the grating is complete. (2) $T \gg T_{\text{vibrational}}$, i.e., pulse #3 arrives after all fast population-relaxation processes have taken their course. (3) $T \ll T_1$, i.e., pulse #3 arrives before interband relaxation erases the grating.

We now analyze three-pulse scattering in an optically thin medium, assuming that the induced grating is sufficiently small that a third-order density-matrix expansion is justified. For δ-function pulses ($t_p \ll T_2$), the scattered energy U is

$$U_{\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)} \sim \exp(-2|\tau|/T_2),$$
$$U_{\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)} \sim \exp(-4|\tau|/T_2) u(\mp\tau), \qquad (1)$$

for homogeneous and inhomogeneous broadening, respectively. The delay τ is positive when pulse #1 precedes pulse #2, and $u(\tau)$ is the unit step function.

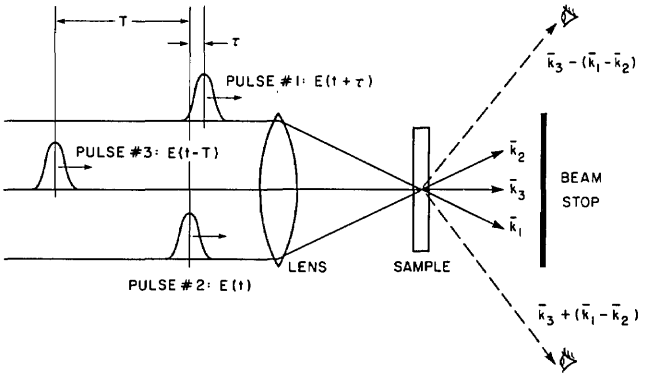

Fig. 1. Experimental geometry for dephasing measurements by the three-pulse-scattering technique.

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For a homogeneously broadened transition, the scattered energy is always a symmetric function of delay. The asymmetry of the inhomogeneous case provides a simple criterion for differentiating between the two types of line broadening. This result holds assuming that the delay T of pulse #3 is less than the spectral-diffusion time. Note that, in the inhomogeneous case, the three-pulse scattering is formally equivalent to the stimulated photon echo[9] in the low-field limit. We wish to emphasize, however, that the stimulated photon echo is only a special case of the more generally applicable three-pulse-scattering technique.

In the long-pulse limit ($t_p \gg T_2$), the expression for the scattered energy is simply the envelope of the electric-field autocorrelation squared for both homogeneous and inhomogeneous broadening:

$$U_{\mathbf{k}_3\pm(\mathbf{k}_1-\mathbf{k}_2)} \sim \left| \int \mathrm{d}t E(t) E^*(t+\tau) \right|^2. \quad (2)$$

This property has been utilized by Eichler *et al.*[10] to measure the coherence of mode-locked Nd:YAG-laser pulses. Because the electric-field autocorrelation function is readily measured, the $T_2 = 0$ limit can be determined experimentally. Therefore fast dephasing times can be resolved by looking for small differences between the scattering data and the $T_2 = 0$ limit.

Even for arbitrary pulse widths, the scattered energy depends only on the electric-field autocorrelation and not on the pulse shape itself. For a homogeneously broadened transition, the scattered energy is the square of a symmetrized convolution between the dephasing function $h_T(\tau)$ and the electric-field autocorrelation $r(\tau)$, where $h_T(\tau)$ and $r(\tau)$ both include optical frequency carrier terms:

$$U_{\mathbf{k}_3\pm(\mathbf{k}_1-\mathbf{k}_2)} \sim \left| \int_{-\infty}^{\infty} \mathrm{d}\tau' h_T(\tau'+\tau)\, r^*(\tau) + \int_{-\infty}^{\infty} \mathrm{d}\tau' h_T^*(\tau'-\tau)\, r(\tau') \right|^2. \quad (3)$$

For an inhomogeneously broadened transition, the field autocorrelation function is still sufficient to characterize the scattering experiment; the resulting expression is rather cumbersome, however, and is not given here.

The homogeneous broadening formula (3) can be expressed entirely in terms of the frequency domain by utilizing the Fourier-transform relationship between the dephasing function and the absorption spectrum. The Fourier transform of the grating amplitude $g(\tau)$ defined as the quantity within the absolute-value sign in expression (3) can be written as the product of the absorption spectrum $\alpha(\omega)$ and the laser power spectrum $\phi(\omega)$:

$$G(\Omega) \sim \alpha(\omega_L + \Omega)\phi(\omega_L + \Omega), \quad (4)$$

where ω_L is the laser carrier frequency and $\Omega = \omega - \omega_L$. To obtain the scattered energy, one calculates the inverse Fourier transform of expression (4) and squares its absolute value.

We have used pulses from a CPM ring dye laser[7] to perform both two- and three-pulse-scattering experiments on a variety of organic dye solutions in thin cells. Our CPM laser produces two pulse trains at 625 nm, each with an 8-nsec repetition period and an average power of 15 mW. We have observed pulses as short as 55 fsec FWHM, assuming a sech pulse shape, although 70 fsec is more typical. Pulses #1 and #2 are obtained from a single pulse train by means of a beam splitter and a mechanical delay line. For pulse #3 we have used the second pulse train, which in our laser is synchronized to within 10 fsec with the first. For our actual three-pulse experiment a folded boxcars[11] configuration (not shown in Fig. 1) was chosen to achieve exact phase matching for one of the scattered beams; the two-pulse experiment, on the other hand, is inherently unmatched.

In experiments using parallel polarization for all pulses, the two- and three-pulse-scattering curves appeared essentially identical. The scattering peak occurred at $\tau = 0$, not unreasonable for three-pulse scattering but surprising for two-pulse scattering in which a peak shift of the order of 24 fsec is anticipated because of the long ground-state recovery time. The lack of a peak shift in two-pulse scattering has been noted by Yajima *et al.*[2] for several dye samples. These initially puzzling results can be attributed to the formation of a cumulative thermal grating whose lifetime greatly exceeds the pulse-repetition period. This explanation was verified by observing the three-pulse scattering as the delay T of pulse #3 was varied; the scattered energy did not change, even when pulse #3 arrived before pulses #1 and #2. When a cumulative grating dominates, the two-pulse experiment becomes formally equivalent to the three-pulse experiment; they both depend only on the inverse absorption bandwidth, independently of the actual dephasing time T_2.

Fortunately, the thermal-grating effect can be eliminated by using orthogonal polarizations for pulses #1 and #2. In this case only an orientational grating and not a concentration grating is formed. By varying the delay of pulse #3, we have verified that the grating no longer has a cumulative character. When orthogonal polarizations are used, the peak shift reappears for two-pulse scattering, as shown in Fig. 2.

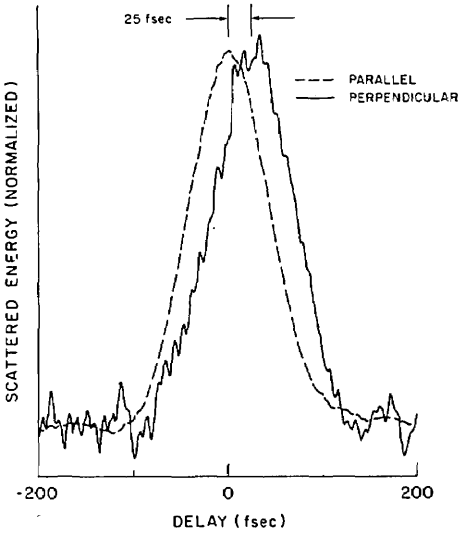

Fig. 2. Two-pulse-scattering data for Nile blue dye in methanol, for both parallel (— — —) and perpendicular (—) polarizations.

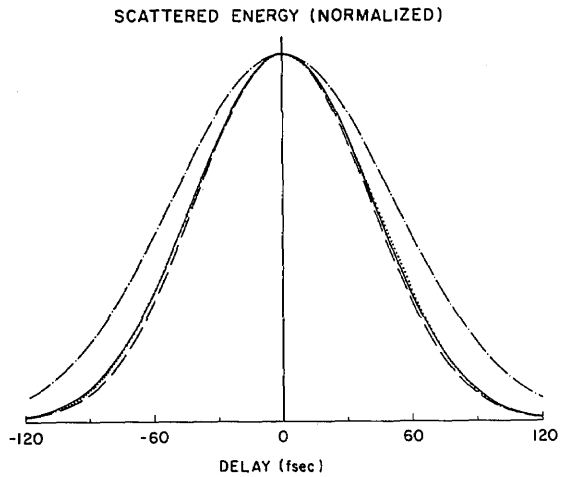

Fig. 3. Three-pulse-scattering data for Nile blue dye in ethylene glycol, for both parallel (—) and perpendicular (· · · ·) polarizations. Also shown are two reference curves, calculated by expression (4) assuming a homogeneously broadened transition. Curve A (— — —) uses the measured absorption spectrum, whereas Curve B (—·—·—) assumes a Lorentzian line peaked at 625 nm with T_2 = 50 fsec. Both curves A and B utilize the actual laser spectrum.

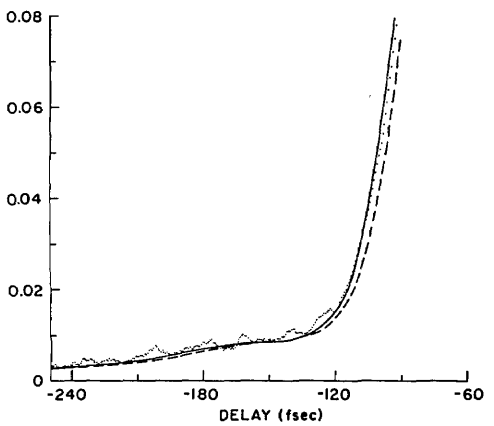

Fig. 4. Same as in Fig. 3 but expanded in scale and extended to longer time delays. Reference curve B is not shown.

Three-pulse-scattering data for Nile blue dye in ethylene glycol are shown in Figs. 3 and 4. Figure 4 depicts the same data as Fig. 3 but with an expanded vertical scale to illustrate the excellent signal-to-noise ratio achieved. The delay T of pulse #3 is set at 5.2 psec. The data for parallel polarization (thermal) and perpendicular polarization (nonthermal) agree almost perfectly; both exhibit a slight broadening of a ~4-fsec FWHM compared with reference curve A (Fig. 3, long-dashed curve), which is calculated on the basis of expression (4) using the measured laser power spectrum and the dye absorption spectrum. This slight broadening is presumably caused by the small geometrical dispersion inherent in the noncollinear experimental configuration. We note that reference curve A is virtually indistinguishable from the electric-field autocorrelation squared, as expected because of the shallow curvature of the Nile blue absorption spectrum at the laser wavelength. A second reference curve B (Fig. 3, dotted–dashed curve), calculated using the actual laser spectrum but assuming a Lorentzian absorption line peaked at 625 nm with T_2 = 50 fsec, is also provided for comparison. To eliminate any possible ambiguity, we verified that the shapes of the power spectra measured before and after the dye cell were essentially identical. On the basis of Fig. 3, we conclude that the dephasing time of Nile blue dye in ethylene glycol is less than the experimental resolution of 20 fsec. From the Fourier transform of the absorption spectrum, on the other hand, one obtains a 9-fsec lower limit for the dephasing time (at the $1/e$ point). These considerations support the contention that the homogeneous width of electronic transitions in dye molecules is essentially the same as the absorption width.[12]

In summary, we have proposed a novel transient four-wave mixing technique for measuring ultrafast dephasing times in condensed matter. The advantages of this technique include an improved resolution, a clear distinction between homogeneous and inhomogeneous broadening, an insensitivity to fast longitudinal relaxation, and the possibility of a phase-matched geometry. We have applied this method to observe dephasing of Nile blue dye in ethylene glycol and have determined T_2 to be less than 20 fsec. Our three-pulse-scattering technique should prove useful for further investigations of electronic dephasing in liquid and solid-state materials. The advantages of this technique, including its potential sensitivity to inhomogeneous versus homogeneous broadening, may also be extended to coherent Raman studies.

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