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Equal-pulse correlation technique for measuring femtosecond excited state relaxation times

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A new technique for measuring extremely fast excited state relaxation times, on the order of or less than the laser pulse width, in the presence of a longer relaxation time is described. The difficulties involved in using the conventional pump-and-probe technique and the corresponding advantages of the new technique are illustrated with numerical examples for specific three-level systems. Qualitative experimental results on semiconductors and organic dye molecules substantiating the results are shown.

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A standard method for measuring the ultrashort lifetimes of the excited states of atoms, molecules, or solids using subpicosecond laser pulses is the so-called pump-and-probe technique.[1] In this technique, the populations of the relevant states are first altered with a strong pump pulse and the subsequent population change in the states is probed by a suitably delayed weak probe pulse that does not significantly perturb the population change being measured. In the case when the relaxation of the population is not governed by a single exponential process but by, for example, a fast process superimposed on a much slower process, there are real difficulties involved using the pump-and-probe technique to measure the faster component. The problems involved will be explained and illustrated in detail with numerical examples below. In this letter we describe a technique, which we call the equal-pulse correlation technique, that has been successfully used to observe the femtosecond relaxation of hot electrons in the conduction band of semiconductors[2,3] and the vibrational-rotational levels of the excited electronic states of organic dye molecules.[4] In both cases, the states excited are high above the bottom of a band of excited states. The relaxation time out of the photoexcited states is shorter than 100 fs and extremely fast compared to the band-to-band transition. Because presently available lasers are limited to about 0.1 ps, without using the technique described below, these ultrafast processes would be difficult to observe.

The comparison between the pump-and-probe and the equal-pulse correlation techniques can best be illustrated with the three-level system shown in Fig. 1. (The problems described below do not occur in two-level systems, where there is only one population relaxation time.) The purpose of the experiment is to measure the relaxation time T_{32}, which is assumed to be on the order of or shorter than the available laser pulse length and much shorter than the relaxation times T_{31} and T_{21}. The laser frequency is equal to the transition frequency ν_{31} between levels 1 and 3. It is also assumed that the transition energies between the levels are all much greater than the thermal energy kT so that thermal excitations from the lower levels to the upper levels are negligible. On a time scale long compared to all the relevant transverse relaxation times, the dynamics of the system are described by the following rate equations for the densities of the three levels:

$$dn_1/dt = -S(t)(n_1 - n_3) + n_3/T_{31} + n_2/T_{21}, \quad (1)$$

$$dn_3/dt = -S(t)(n_3 - n_1) - n_3/T_{32} - n_3/T_{31}, \quad (2)$$

$$n_1 + n_2 + n_3 = 1, \quad (3)$$

where n_1, n_2, and n_3 are the fractional density of absorbing centers in states 1, 2, and 3. $S(t) = \sigma_{31} I(t)/h\nu_{31}$, where σ_{31} is the cross section for the transition 1 to 3 and $I(t)$ is the intensity of the pulse. We further define an intensity parameter $S_0 = \int S(t)\, dt$, which is the cross section times the number of photons/area in a pulse.

In one version of the pump-and-probe experiment, one

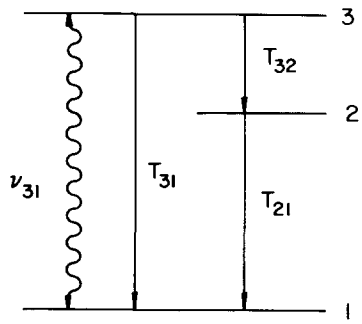

FIG. 1. Schematic diagram for a three-level system.

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measures the effect of a strong pulse $I_1(t)$ on the transmission of the weak pulse $I_2(t)$ by the system. Assuming that the pulses are orthogonally polarized and have the same pulse shape $f(t)$ but are shifted in time from each other by τ:

$$I(t) = I_1(t) + I_2(t) = I_1 f(t) + I_2 f(t-\tau). \tag{4}$$

To be specific, let us assume also that the pulses are Gaussian of the form

$$f(t) \propto \exp[-8 \ln 2(t/T_p)^2], \tag{5}$$

where T_p is the full width half-maximum (FWHM) of the autocorrelation of the pulse.

For an optically thin sample ($\sigma_{31} L N_0 \ll 1$, where L is the sample thickness and N_0 is the total density of absorbing centers), the response of the system can be obtained by solving Eqs. (1)–(3) with the intensity given by Eqs. (4) and (5). In the pump-and-probe experiment, one measures changes in the transmitted probe beam power ΔT_{probe} as a function of τ; the signal is then proportional to

$$\Delta T_{\text{probe}} \propto \int_{-\infty}^{\infty} I_2 f(t-\tau)[n_1(t) - n_3(t)]dt. \tag{6}$$

In Fig. 2(a), we show numerical examples of the shape of the expected signal ΔT_{probe} for various ratios of T_{32}/T_p from the numerical solutions of Eqs. (1)–(6). It is apparent first of all that it is not always easy to ascertain whether there is a fast relaxation component corresponding to T_{32} present, especially when $T_{32} \ll T_p$, such as the case corresponding to $T_{32}/T_p = 0.1$ in Fig. 2(a). Even if such a component can be identified, it would be difficult to deduce the value of T_{32} from signals of the form shown in Fig. 2(a), as will be discussed in more detail below.

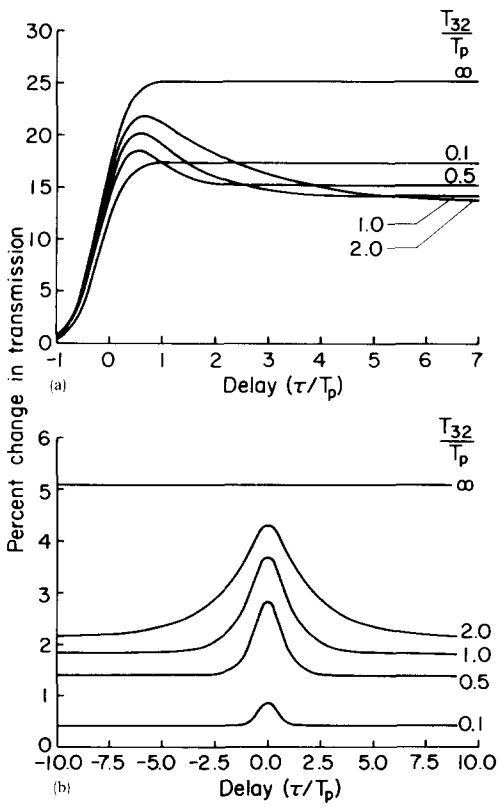

FIG. 2. Calculated values of the change in transmission as a function of delay for $T_{32}/T_p = 0.1, 0.5, 1, 2$, and ∞ using (a) the pump-and-probe technique and (b) the equal-pulse correlation technique. In both cases $T_{21}/T_p = T_{31}/T_p = 2000$, $\sigma_{31} N_0 L = 0.2$, and $S_0 = 1$. The delay is in units of the autocorrelation width T_p. The change in transmission corresponds to percentage change from the $T_{32} = 0$ case in the limit $\tau = -\infty$. In (b), the baseline actually corresponds to the case $T_{32} = 0$.

For comparison, consider now the equal-pulse correlation experiment. In this case, $I_1 = I_2 = I$ in Eq. (4), and instead of just the probe beam, the change in the transmitted total power of both beams, ΔT_{total} is measured. The corresponding expected signal is proportional to

$$\Delta T_{\text{total}} \propto \int_{-\infty}^{\infty} I[f(t) + f(t-\tau)][n_1(t,\tau) - n_3(t,\tau)]dt. \tag{7}$$

Figure 2(b) shows the calculated forms of the signals corresponding to the cases shown in Fig. 2(a). In this case the presence of the fast component will always be revealed as an unmistakable peak in the measured total transmitted power as a function of the pulse separation τ, even for $T_{32} \ll T_p$, as long as $T_{32} \ll T_{31}$ and T_{21}.

In addition, the value of T_{32} can be easily determined from the width of this correlation peak and the autocorrelation width of the incident light pulse through a straightforward deconvolution process. This is illustrated through the numerical examples shown in Fig. 3. The results show that the convolution of the autocorrelation of the pulse and a double-sided single exponential with the time constant equal to T_{32} gives an identical peak shape as that from the exact numerical solution based on Eqs. (1)–(5) and (7), as long as the intensity is not too high ($S_0 < 1$). This, therefore, provides a simple procedure for extracting the numerical value of the fast time constant T_{32} from the equal-pulse correlation result, requiring only the autocorrelation of the pulse.

By contrast, the analysis is more complicated with the pump-and-probe technique for three-level systems. In this

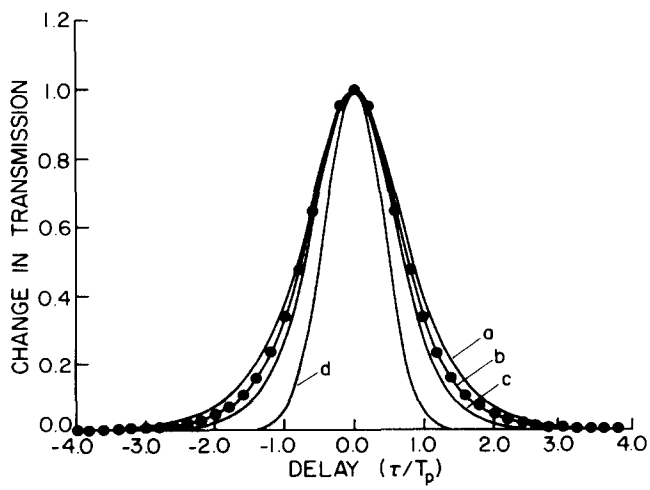

FIG. 3. Comparison between rate equation solution and convolution results. Curves a, b, and c are convolutions of the autocorrelation of the pulse and a double-sided single exponential with decay time $T_{\text{decay}}/T_p = 0.6, 0.5$, and 0.4, respectively. The dotted line is the solution to Eqs. (1)–(5) and (7) with $T_{32}/T_p = 0.5$, $T_{21}/T_p = T_{31}/T_p = 2000$, and $S_0 = 0.2$. This demonstrates the relaxation time can be extracted by fitting the convolution to the experimental data. Curve d is the autocorrelation of the pulse. All curves are normalized to the same peak height of 1 in arbitrary units.

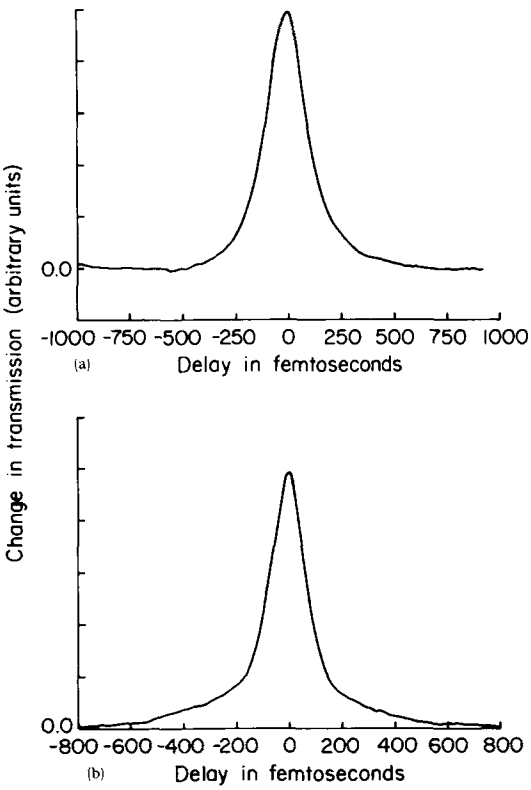

FIG. 4. Equal-pulse correlation signals for (a) GaAs and (b) cresyl violet dissolved in ethylene glycol.

case, the step in the signal due to only the long relaxation time component must first be subtracted from the data. Only then can the residual be deconvolved to yield the fast relaxation time. However, in general, there is no simple way to determine the exact shape of the step to be subtracted.

Physically, the difference in the two cases is that in the pump-and-probe case: because T_{21} is long, the saturation effect on the weak pulse induced by the strong pulse persists a long time relative to the relaxation time T_{32} after the passage of the strong pulse. This leads to a step in the measured power of the transmitted beam. The presence of the fast relaxation component modifies the shape of the rise of the step but cannot be easily isolated from the effect due to the long relaxation component. On the other hand, in the equal-pulse correlation experiment, the saturation effects of the two beams on each other are symmetrical. On a time scale short compared to the long relaxation time, but longer than the short relaxation time, the total transmitted powers of both beams are, therefore, essentially independent of the pulse separation time τ. On a time scale comparable to the fast relaxation time, the short relaxation time will then show up as an unmistakable peak, even in the case of T_{32}/T_p as small as, for example, 0.1, as demonstrated by the numerical examples shown in Fig. 2(b). *Thus, the presence of a peak on this time scale implies the existence of a fast relaxation process.* But, the smaller the ratio T_{32}/T_p is, the smaller the amplitude of the peak is. Note that as long as the time-averaged total power is measured and T_{32}/T_p is finite, there will be a peak even when the two pulses are not of equal intensity. However, the peak height is maximum when the two pulses are of equal intensity.

The basic features of these results have also been substantiated experimentally. In Fig. 4, we show examples of experimental results obtained on GaAs (Ref. 2 and 3) and the organic dye cresyl violet[4] in ethylene glycol. In the experiment, an Ar-ion laser pumped passively mode-locked Rh6G dye ring laser produces pulses having approximately a 150-fs FWHM autocorrelation width at a 10^8 Hz repetition rate. The pulse train is separated into two arms of orthogonal polarizations and recombined collinearly with one arm delayed with respect to the other by a time τ. Note that because the two pulses are orthogonally polarized and propagating collinearly in the same direction, there cannot be any coherence effect.[5] The combined pulse train is then focused onto the sample, either a thin layer of GaAs, or a jet of cresyl violet dye dissolved in ethylene glycol. Light transmitted through the sample is detected and plotted versus τ. In both cases, a sharp peak is seen in the total transmitted power as a function of delay time τ as shown in Fig. 4, indicating the presence of an extremely fast relaxation component. The details of the experiments are more complicated than can be described here and will be reported elsewhere. The purpose here is to point out that the type of sharp peaks shown in Fig. 2(b) has indeed been observed experimentally.

It should also be pointed out that a two-pulse correlation technique has been used by von der Linde *et al.*[6] to study the decay of hot electrons in GaAs at low temperatures. His technique is based on the nonlinear luminescence effect due to bimolecular recombination of hot electrons. The technique is useful mainly in the picosecond regime. In the femtosecond time domain, the hot luminescence is usually too weak for the technique to be usable.

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