Coherent coupling effects in pump–probe measurements with collinear, copropagating beams

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Received April 17, 1984; accepted May 29, 1984

We demonstrate the existence of coherent coupling effects in pump–probe measurements with collinear, copropagating beams, despite the absence of any induced spatial gratings in this geometry. The coherent interaction, which is found to be similar but not identical to that for crossed beams, must be taken into account in analyzing relaxation processes occurring on the time scale of the laser pulse. These coherent effects cannot generally be eliminated by detecting the total change in energy in both the pump and probe beams.

Pump–probe measurements in which the pump and probe pulses originate from the same laser constitute a standard means of performing time-resolved measurements of relaxation processes on the picosecond and subpicosecond time scale. When the two light pulses are well separated in time, the variation in the probe signal as a function of delay time can be interpreted in terms of the material response function and the pulse intensity envelope. When the pulses overlap in time, however, their mutual coherence affects the observed signal.[1–4] The coherent coupling between the pump and the probe beams crossing at an angle in the sample can be described in the following manner. When both pulses are simultaneously present, they interfere and produce a spatial modulation in the optical properties of the sample. Light from the pump beam is then scattered off this induced grating in the probe direction and is detected as part of the probe signal. On the basis of this model, it has been suggested that for collinear, copropagating pump and probe beams, for which the spatial grating disappears, the coherent coupling should vanish as well.[2] The conclusion of this Letter is that the coherent interaction is present even in this degenerate geometry. Also, in contrast to what might be suggested by the grating picture, we find that the coherent interaction will in general increase or decrease the transmitted intensity of both the pump and the probe rather than simply exchanging energy between them. These results bear directly on the interpretation of several recent studies of ultrafast relaxation processes.[5–7]

The basic physics of the coherent interaction between collinear pump and probe beams can be understood strictly in terms of the nonlinear response in a small volume of the sample. We consider first how the nonlinear polarization in the medium varies in time and then how this polarization alters the transmitted probe energy. For a system with rapid dephasing, the nonlinear polarization is proportional to the electric-field strength at time t and a factor associated with population changes caused by the action of the fields at previous times t' (Ref. 4):

$$P_i^{(3)}(t) = iE_j(t) \int_{-\infty}^{\infty} dt' E_k^*(t') E_l(t') A_{ijkl}(t - t'). \tag{1}$$

Here $\mathbf{P}^{(3)}(t)$ and $\mathbf{E}(t)$ are the slowly varying envelopes of the nonlinear polarization and of the total electric for an implicit $e^{-i\omega t}$ time dependence. It has been assumed that measurements are performed in a regime for which the response can be described by a third-order nonlinearity. Directly on resonance, the components of the nonlinear susceptibility should be predominantly imaginery or, equivalently, the response functions A_{ijkl} in Eq. (1) should be real.

The rate at which energy is lost from the probe beam in the presence of the nonlinear polarization is proportional to $\mathrm{Im}[E'_i{}^*(t) P_i^{(3)}(t)]$, where $\mathbf{E}'(t)$ is the electric-field envelope of the probe pulse. Consequently, the total change in energy induced in the probe is obtained by integrating over all times t and is proportional to

$$S = \mathrm{Re} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' E'_i{}^*(t) \times E_j(t) E_k^*(t') E_l(t') A_{ijkl}(t - t'). \tag{2}$$

Since for collinear, copropagating beams all phases are constant across a transverse plane, this expression, although derived only for a small volume element, applies directly to the experimentally measured signal for an optically thin sample.

We now evaluate Eq. (2) when the probe pulse is a copy of the pump delayed by time τ. We consider here only orthogonally polarized beams, for which we can distinguish between light from the pump and that from

0146-9592/84/080359-03$2.00/0

the probe with an analyzer after the sample. If we denote the complex field envelope of the pump by $\hat{y}E(t)$, the envelope of the probe becomes $\hat{x}E(t-\tau)e^{i\omega\tau}$. We then find for an isotropic medium that the change in the transmitted probe energy induced by the pump is given by

$$S(\tau) = \beta(\tau) + \beta'(\tau) + \gamma(\tau), \tag{3}$$

with

$$\beta(\tau) = \mathrm{Re}\left[\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' E^*(t-\tau)E(t)E^*(t') \times E(t'-\tau)A_{xyyx}(t-t')\right], \tag{3a}$$

$$\beta'(\tau) = \mathrm{Re}\left[e^{-2i\omega\tau}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' E^*(t-\tau)E(t) \times E^*(t'-\tau)E(t')A_{xyxy}(t-t')\right], \tag{3b}$$

$$\gamma(\tau) = \mathrm{Re}\left[\int_{-\infty}^{\infty} dt A_{xxyy}(\tau-t) \times \int_{-\infty}^{\infty} dt' |E(t')|^2 |E(t'-t)|^2\right]. \tag{3c}$$

We see that in the present case the signal contains not only the incoherent term $\gamma(\tau)$ representing the convolution of the material response with the pulse intensity autocorrelation but also terms $\beta(\tau)$ and $\beta'(\tau)$ arising from the coherent interaction between the pump and the probe pulses. The contribution of $\beta(\tau)$, which is identical with that found for the crossed-beam geometry,[3,4] will depend in general on the detailed form of the electric-field envelope and the response function. In the limit of a slow relaxation, modeled as a step function, $\beta(\tau)$ varies as the square of the electric-field autocorrelation function $|\rho_E(\tau)|^2$, whereas the incoherent term builds up with the integral of the intensity autocorrelation function $\rho_I(\tau)$. The $\beta'(\tau)$ term oscillates as a function of delay time with a frequency 2ω and will therefore not contribute to the measured signal unless the delay is scanned slowly. The origin of this contribution is the interference between the forward-traveling phase-conjugate wave[4] and the probe beam, an effect arising only in the fully degenerate geometry. The relative strength of the coherent and incoherent terms depends, of course, on the nature of the relevant response functions. For the case of isotropically distributed molecules having a well-defined transition dipole moment and a fixed orientation on the time scale of interest, we find that $A_{xxyy} = A_{xyyx} = A_{xyxy}$. All three terms in Eqs. (3) then contribute equally at zero delay time. For other systems, such as semiconductors[4,6] and solutions with molecules undergoing rapid orientational diffusion,[2] the coherent interaction may be much less important.

We have studied the coherent interaction between pump and probe pulses experimentally for collinear, copropagating beams in an optically thin jet of cresyl violet dye dissolved in ethylene glycol. Pulses of light with a 7-psec FWHM were obtained from a synchronously pumped dye laser operating at 590 nm (near the center of the absorption band in our sample). Pump and probe pulses of orthogonal polarization were produced by dividing the incident laser beam in two, passing one part through a polarization rotator and variable delay line, and recombining the beams in a Glan polarizer. The resulting beams after focusing to ~25 μm on the sample were collinear to better than 3 mrad. With the pump chopped, the modulation induced in the probe was detected with a photodiode after the pump was blocked in a polarizer. The intensity of the light was kept sufficiently low to induce only a weak bleaching in the sample.

To highlight the contribution of the coherent interaction, we have measured the induced transmission of the sample with pulses having different coherence properties. The dotted curves in Fig. 1 show the probe signal [averaged over the oscillations in $\beta'(\tau)$] as a function of delay with respect to the pump. The data in Fig. 1(a) were obtained by using the nearly transform-limited pulses from the dye laser, and those of Fig. 1(b) were obtained by using chirped pulses produced by passing the output of the dye laser through an optical fiber. This procedure broadened the spectrum of the pulses by about a factor of 10 without appreciably increasing their duration.

The marked difference between the results in Figs. 1(a) and 1(b) can be explained by the theory outlined above. Since in the cresyl violet solution all relaxation processes are either extremely fast (vibrational) or slow (orientational, electronic) on the relevant time scale, we can approximate $A_{xxyy} = A_{xyxy}$ by a step function. The incoherent contribution $\gamma(\tau)$ should then vary as the integral of the intensity autocorrelation of the pulse. In Figs. 1(a) and 1(b), the solid lines show these integrals calculated from the experimentally determined intensity autocorrelation functions. The difference between these solid curves and the observed probe transmission can be attributed to the coherent contribution $\beta(\tau)$, the shape of which should be given by $|\rho_E(\tau)|^2$. For the

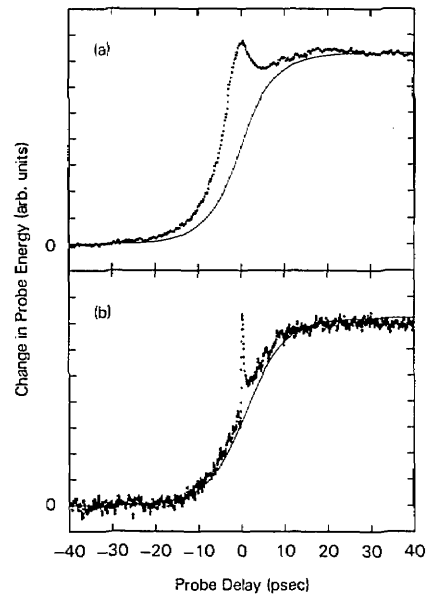

Fig. 1. Induced probe transmission in cresyl violet obtained with (a) nearly transform-limited pulses and (b) pulses that were spectrally broadened in an optical fiber. Solid lines are the integrals of the experimentally measured intensity autocorrelation functions.

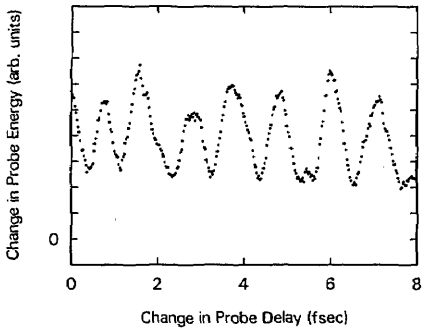

Fig. 2. Induced probe transmission in cresyl violet as a function of change in delay time near zero delay showing fringes at twice the optical frequency ($2\pi/\omega$ = 1.97 fsec).

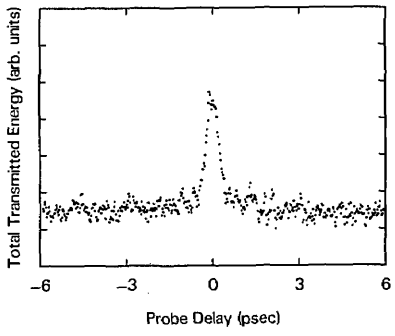

Fig. 3. Total transmitted intensity in cresyl violet using spectrally broadened pulses of equal intensity. The pulse duration in these measurements was 7 psec (FWHM).

nearly transform-limited pulses, this implies a width for $\beta(\tau)$ comparable with the pulse length, in agreement with the results of Fig. 1(a). The width of the coherent signal for the chirped pulses is reduced substantially and agrees reasonably well with the coherence time of 0.7 psec estimated from the pulse bandwidth.

We have demonstrated experimentally the influence of the forward-traveling phase-conjugate wave in measurements with collinear beams. The oscillations in the probe transmission exhibited in Fig. 2 were obtained by scanning the delay time slowly near $\tau = 0$. They are characterized by a frequency twice that of the direct interference fringes obtained by leaking a little pump light onto the photodiode. This doubled frequency clearly indicates that the origin of these fringes lies in the nonlinear mixing process. We note also that the peak-to-peak modulation of the fringes is approximately equal to the signal averaged over the fringes, as expected from Eqs. (3) with $A_{xxyy} = A_{xyyx} = A_{xyyx}$.

Our discussion up to this point has shown that the coherent interaction has an important influence on the probe signal for measurements with collinear beams. It might, however, be argued that the coherent terms could be eliminated by detecting the net change in energy in both the pump and the probe beams: This quantity would not be sensitive to the transfer of energy between the two beams induced by the coherent interaction. We have tested this conjecture directly by experiment. In Fig. 3 we show the total transmitted energy measured with chirped pump and probe pulses of equal intensity. The feature centered at $\tau = 0$, being far narrower than the intensity autocorrelation, must be attributed to the coherent interaction between the pulses. Physically, the origin of the increase in transmitted energy lies in the fact that when the pump and the probe pulses are mutually coherent, the polarization of the total electric field will be approximately constant in time. Then, as this radiation propagates through the sample, it will in general interact preferentially with molecules in the solution having certain orientations and induce a strong, anisotropic bleaching. When the two pulses are separated in time by more than their coherence length, this cooperative bleaching effect will vanish, and more energy will be absorbed from both pulses. Analytically, the expected change in the total transmitted energy of two equal pulses is given by $S(\tau) + S(-\tau)$, the first term corresponding to the modulation of the probe intensity and the second to that of the pump (which acts as a probe for negative delay). For a step-function material response, the variation in the signal will be due entirely to the coherent term and should be proportional to $|\rho_E(\tau)|^2$. The symmetrical peak in Fig. 3, with a width corresponding to the coherence length of the chirped pulses, agrees with this prediction.

In conclusion, we have seen that coherent coupling effects can occur in pump–probe measurements with collinear, copropagating beams, despite the absence of any induced spatial gratings in this geometry. Although the detailed form of the coherent term was found to differ somewhat from that for crossed pump and probe beams, its contribution must still generally be considered in interpreting relaxation processes on the time scale of the laser pulse. Intuitively, we may view the coherent interaction for a resonant system not as a scattering process but rather as a cooperative bleaching of the sample while the pump and probe pulses are mutually coherent. It is then clear why the coherent interaction is present for collinear, copropagating beams and, furthermore, why this interaction is not eliminated by detecting the total transmitted energy in both the pump and the probe beams.

The authors acknowledge valuable discussions with D. R. Grischkowsky and J.-M. Halbout. This research was partially supported by the U.S. Office of Naval Research. K. B. Eisenthal acknowledges the support of the National Science Foundation, the U.S. Air Force Office of Scientific Research, and the Joint Services Electronics Program.

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