Picosecond Photon Echoes Stimulated from an Accumulated Grating

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measured in the experiment—is obtained. Since the quantity M_D containing the complex sublevel-population amplitudes of the $2p^2\,{}^1D$ state is known from an earlier independent measurement (see Table I of Ref. 2), the only free parameter in the calculation is the relative phase δ. The best fit to the experimental curve is obtained for $\delta = \frac{1}{2}\pi$. The distribution calculated with this values is shown in Fig. 1 as the solid line. In order to demonstrate that the result $\delta = \frac{1}{2}\pi$ is significant we show also the result of a calculation assuming a value of $\delta = 0$ (dashed line, Fig. 1).

Since our experimental angular resolution of approximately $\Delta\vartheta = \pm 1^\circ$ is comparable with the width of the observed structure we convoluted the calculated curve with a corresponding Gaussian. The result is shown in Fig. 2, where the whole $2p^2\,{}^1D$ angular distribution in the scattering plane is given in a polar plot to demonstrate more clearly the unique interference phenomenon. The asymmetric structure caused by the value $\frac{1}{2}\pi$ of the phase angle δ we ascribe to the fact that the two situations—target excited, or projectile excited—differ by the process of charge exchange.

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Picosecond Photon Echoes Stimulated from an Accumulated Grating

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It is shown that in optical transitions with a bottleneck, a mode-locked cw dye laser may be used to generate and heterodyne detect picosecond photon echoes. These echoes are stimulated from an accumulated grating in the electronic ground state formed by a train of twin excitation pulses of constant phase difference. In the zero-phonon transition of pentacene in naphthalene at 6026.8 Å the bottleneck is identified and these echoes are used to determine the dominant dephasing process.

The measurement of optical phase-relaxation processes on a picosecond time scale has recently become of considerable interest.[1,2] New information on optical exciton[3] and polariton[4] scattering and pseudolocal phonon-induced dephasing[5] indeed can only be obtained by picosecond coherence-decay measurements. Progress in this field, however, has been hampered by the complexity of the experimental setup needed in the currently employed techniques.[1,2]

In contrast to phase relaxation, population relaxation on a picosecond time scale can easily be measured with pump-probe techniques employing mode-locked cw dye lasers.[6] In a recent attempt by us to use this technique to study population relaxation in the zero-phonon transition at 6026.8 Å of pentacene in napthalene, we observed, instead of the expected absorption recovery signals, intense optical coherent transients. The reason that such signals have gone unnoticed so far we attribute to the fact that all previous experiments of this sort were done under conditions where the pump-probe time separation far exceeds optical T_2.

In this Letter we will show that these coherent transients are photon echoes stimulated from an *accumulated* grating in the electronic ground state. By a grating we mean here a periodic population-versus-frequency distribution. The accumulation will be shown to be caused by a bottleneck in the optical pumping cycle. We will further demonstrate that the formation of these echoes requires a train of excitation pulses of constant phase difference. Finally, the observed echo decay will be used to study optical dephasing in the zero-phonon line of the lowest transition of pentacene in napthalene.

Photon echoes stimulated from ground-state

gratings have previously been observed in Na vapor[7] and in triphenylmethyl (as guest in triphenylamine).[8] What not has been realized so far[9] and will be exploited in this paper is that gratings in the ground state can be *built up* by an excitation pulse cycle short compared to the bottleneck lifetime.

Consider Fig. 1 which has been shown to represent adequately the optical pumping cycle in the zero-phonon line of pentacene in napthalene.[10,11] At times short compared to the upper-state lifetime the system behaves as a two-level system, and it can easily be shown that immediately after the first two excitation pulses (at time t_{12}^{+}) the lower- and upper-state density-matrix elements in a small sample ($<\lambda^3$) have become

$$\rho_{11}(t_{12}^{+}) = \tfrac{1}{2}[1+\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\exp(-t_{12}/T_2)\cos(\Delta t_{12}+\varphi_{12})],$$

$$\rho_{22}(t_{12}^{+}) = 1-\rho_{11}(t_{12}^{+}),$$

where $\theta_i = (\mu_{12}E_0/\hbar)\delta t_i$ is the rotation angle of the Bloch vector induced by the ith excitation pulse, Δ the off-resonance frequency, and t_{12} and φ_{12} the time duration and phase difference between the excitation pulses. Equation (1) shows that two excitation pulses produce a grating $[\cos(\Delta t_{12}+\varphi_{12})]$ in *both* the ground and the excited states from which a third pulse, independently, may stimulate an echo.[7,8] Notice that each grating contains, via the amplitude factor $\exp(-t_{12}/T_2)$, information on the optical phase loss in the time between the excitation pulses. As time proceeds a fraction of the molecules in the upper state (ca 2%)[11] decays into the triplet state. Therefore at a time that the upper state effectively is depleted, but the triplet state not, $\rho_{11}(t) = 1-\rho_{33}(t)$. By applying a train of twin excitation pulses with a separation between the pulses short compared to the triplet lifetime one can easily imagine that the modulated part of ρ_{11} *builds up* in time to a steady-state value far exceeding the initial one, the precise value of ρ_{11} of course being determined by the pump rate and all parameters of the pumping cycle. At this point it is important to realize that a grating in the ground state can only grow provided that the phase difference between consecutive twin excitation pulses in the pulse train remains constant in the preparation stage. This is clear from Eq. (1) where a random phase difference in this period, $\langle\cos(\Delta t_{12}+\varphi_{12})\rangle_{\rm av}=0$, wipes out the grating. This phase stability requirement is similar to the one encountered in optical Ramsey fringe experiments.[12]

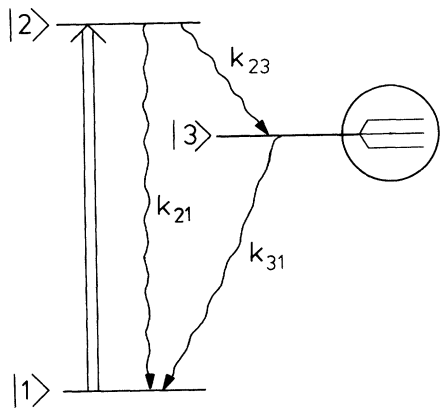

FIG. 1. Level system for the zero-phonon line of pentacene in naphthalene. The wavy arrows indicate decay channels of the various states. |1> is the ground state, |2> the excited singlet state, and |3> the triplet state. The part within the circle has a greatly magnified ($\sim 10^4$) energy scale. $k_{21}=5.1\times10^7$ sec^{-1}; $k_{23}=\cong 10^6$ sec^{-1}; k_{31} unknown.

A further point to note is that in a macroscopic sample the stimulated echo is radiated in a direction determined by the phase-match condition $\vec{k}_e = \vec{k}_3+\vec{k}_2-\vec{k}_1$.[13] The photon-echo intensity can be shown to be proportional to $A(\sin^2\theta_3)\exp(-4t_{12}/T_2)$, where A is the steady-state grating intensity and $\sin^2\theta_3$ is proportional to the probe intensity. Details on the calculation of A will be published in a forthcoming paper. This expression shows that by variation of the separation between first and second excitation pulses, optical T_2 can be measured. A last point to note is that, after termination of the excitation pulses, the accumulated grating is expected only to decay with the bottleneck lifetime, as the ground singlet state is infinitely stable.

In the experiments we used the entire intensity-stabilized[14] pulse train of a synchronously pumped, mode-locked Rhodamine-6G dye laser at a repetition rate of 82 MHz.[2] The dye-laser pulses had a width of $\simeq 3$ ps as determined in an autocorrelation experiment [Fig. 2(d)]. The beam was split into a pump and a probe of which one could be delayed. Two different experimental schemes were employed depending on whether the probe pulse (1) followed or (2) preceded the pump pulse (Fig. 2.). In both cases the parallel but noncollinear pump and probe beams were focused in the sam-

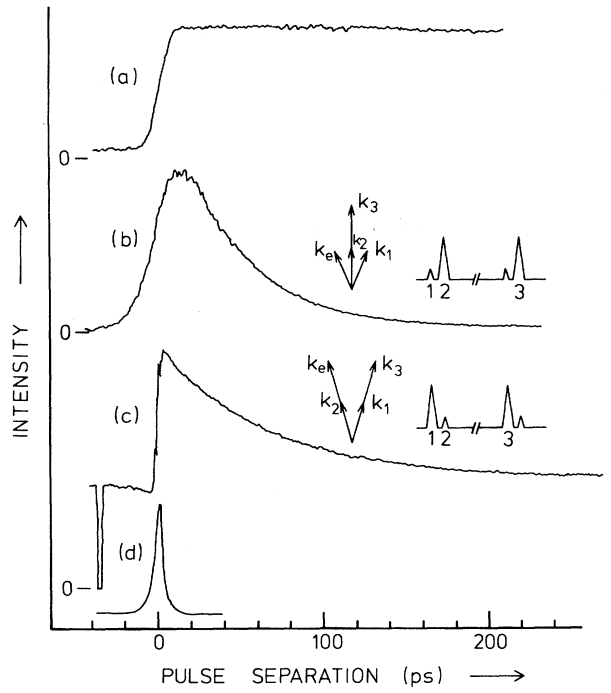

FIG. 2. Optical coherent transients observed in pentacene in a pump-probe experiment for phase-match conditions and pulse sequence indicated (a) at 1.3 K for the phase-match condition shown for (b) and (c) at 7.2 K; (d) pump-probe cross correlation marking zero pulse separation.

ple at an angle of about 1.5°. In setup (1) the pump beam was modulated at 300 Hz and the echo was phase-sensitive detected in the direction of the probe beam ($\vec{k}_e = \vec{k}_2$; $\vec{k}_1 = \vec{k}_3$). Note that this setup is identical to the one used by Ippen, Shank, and Bergman[6] for measurement of absorption recovery. In setup (2) the probe beam was modulated and the echo detected in the direction $\vec{k}_e = 2\vec{k}_2 - \vec{k}_1$ ($\vec{k}_2 = \vec{k}_3$).

Compared to the measurements of picosecond dephasing with low-repetition-rate amplified pulses, as previously employed,[2] this new method has several advantages. In the first place only one picosecond dye laser is used without amplification, which simplifies the setup appreciably. Furthermore, heterodyne detection of the echo is straightforward, as it results from the chosen pulse sequence [Fig. 2(c)]. Because of the quasi-continuous echo signal, lockin detection techniques can be used, resulting in an improvement of signal-to-noise ratio by a factor of $\simeq 10$. A final important point is the increased time resolution, which is now only limited by the excitation pulse width, so that in principle even subpicosecond phase relaxation may be studied.

Typical coherent transients observed in the zero-phonon line at 6026.8 Å of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of pentacene in naphthalene[9] are shown in Fig. 2. In this experiment ca 300 μW was used in the pump and 30 μW in the probe beam. Figure 2(a) shows, as expected,[15] that at 2 K, on a picosecond time scale, there is no decay. At higher temperature, however, decay is observed, but as Figs. 2(b) and 2(c) show for the different phase-match conditions, the observed decay at the same temperature differs, in fact, precisely by a factor of 2.

This effect has an interesting, though straightforward, interpretation. As argued earlier, the probe pulse can only effectively stimulate an echo from the grating if the grating is "phase locked" to the probe pulse. This implies that the echo that is stimulated *is also in phase* with the probe beam. As a consequence, for the phase-match condition $\vec{k}_e = \vec{k}_2$, the echo constructively interferes with the probe beam at the (quadratic) detector. With a probe beam far more intense than the echo beam, the coherent transient will have an amplitude proportional to $E_e E_p$, where E_e and E_p are the amplitudes of the echo and probe pulse field, respectively. The echo amplitude decays with $\exp(-2t_{12}/T_2)$ as is well known. For the phase-match condition $\vec{k}_e = 2\vec{k}_2 - \vec{k}_1$, no interference can occur and the signal at the detector is proportional to the echo *intensity*, which decays with a factor of $\exp(-4t_{12}/T_2)$.

The origin of these transients as echoes stimulated from an accumulated grating in the ground state of pentacene was further revealed as follows. First, the crystal was exposed to a train of twin pump pulses, split by 60 psec. Then suddenly excitation was stopped by a shutter with a rise time of 2 μsec. The decay of the grating was then followed through observation of the stimulated echo induced by a weak probe beam. The chosen phase-match condition in this experiment and the results obtained are shown in Fig. 3. The figure shows that the echo decay exhibits a short decay component of 15 ± 3 μsec and a long one, measured on an appropriate time scale, of 2.3 $\pm$ 0.5 msec. We interpret this observation by assuming that in the optical pumping cycle, two triplet spin sublevels are active, one with a 15-μsec and the other with a 2.3-msec lifetime.

We now continue by presenting and discussing the new information obtained on the mechanism of dephasing in the zero-phonon line by measur-

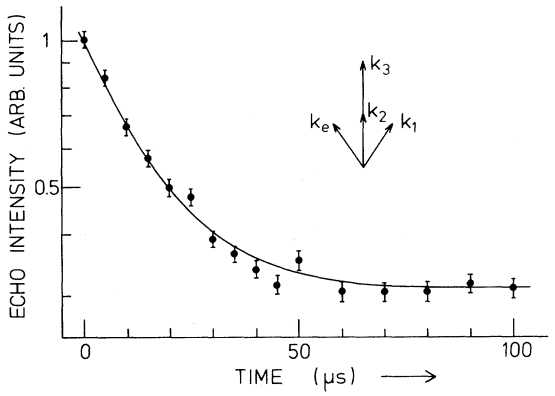

FIG. 3. Intensity of the stimulated echo after interruption of the twin-excitation-pulse train, as probed by pulse three for the indicated phase-match condition.

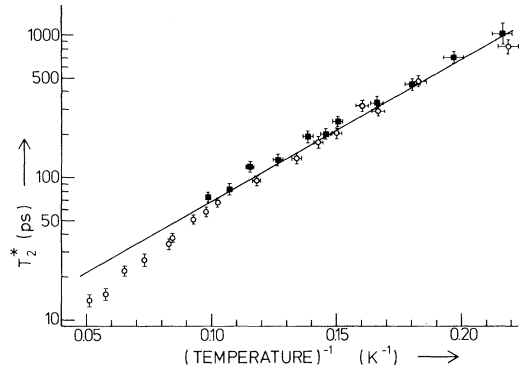

FIG. 4. Plot of the measured pure dephasing times (T_2^*) vs the inverse temperature obtained using the conventional two-pulse echo (squares) and "phase-locked" stimulated echo (circles). The solid line is a fit to the data below 10 K.

ing the echo decay as a function of temperature. In Fig. 4 we present the results and also include data obtained from conventional two-pulse echo-decay measurements. The 19.5-ns lifetime (T_1) of the S_1 state is taken into account:

$$(T_2)^{-1} = (2T_1)^{-1} + (T_2^*)^{-1}.$$

From the excellent agreement between the results obtained by both methods we conclude that the new technique provides a reliable measurement of optical T_2. From a physical point of view the data are also very interesting as they show that up to 12 K, optical dephasing is exponentially activated. The solid line in Fig. 4 is a best fit to the photon echo results with $T_2^*(T) = T_2^*(\infty) \times \exp(+\Delta E/kT)$, from which $\Delta E = 16 \pm 1$ cm^{-1} and $T_2^*(\infty) = 7 \pm 2$ ps. The measurement of a well-defined activation energy over an extended temperature range supports the idea[15] that this transition is dephased by a pseudolocal phonon. The nature of this phonon and the cause of the deviation from exponential activation of T_2 above 12 K is a point of further investigation.

Summarizing, we note that we have shown that a train of twin excitation pulses may generate an accumulated grating in the electronic ground state, from which a probe beam may stimulate a photon echo. We have demonstrated that these echoes may be used to measure picosecond coherence-decay times. A prerequisite to apply this technique is the presence of a bottleneck in the optical pumping cycle. In most optical transitions bottlenecks do occur, but we emphasize that even in a two-level system the upper state, through a long lifetime, could function as a bottleneck.

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