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# PICOSECOND PULSE SPECTROSCOPY IN SOLID STATE PHYSICS

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It is shown that picosecond coherence experiments can be used to study optical dynamics in doped semiconductors and molecular solids. In the system GaP:N, picosecond photon echoes are used to study exciton relaxation and detrapping into the free exciton band. In the molecular mixed crystal of pentacene in naphthalene, two-color stimulated photon echoes are employed as a probe for vibrational deactivation.

## 1. Introduction

In recent years tremendous strides have been made in the generation of ultrashort light pulses. For the shortest pulses presently obtainable the coherence bandwidth can be as large as $1000\,\mathrm{cm}^{-1}$, enabling coherent excitation of a large part of the optical spectrum of an absorbing centre. It is no surprise then, that an active branch of optical spectroscopy is concerned with the application of pulse techniques, most of these well known in the field of magnetic resonance, to the study of optical dynamics.

In this paper we will report results of photon echo studies on selected optical transitions in doped semiconductors and molecular crystals. The doped semiconductor is the system GaP:N in which we study relaxation and detrapping into the band of the nitrogen bound exciton. The mixed crystal of pentacene in naphthalene is taken as an example to demonstrate the application of two-color stimulated echoes to the study of vibrational dynamics in molecular solids.

### 1.1. *Theoretical background*

In order to understand the experiments presented in this paper it is instructive to consider the effect of two optical pulses on the population distribution as a function of detuning in the ground and excited state of a two-level system. After two resonant excitation pulses the diagonal elements of the density matrix in the ground state level $|1\rangle$ and excited state level $|2\rangle$ take the following form:

$$\rho_{11}(t_{12}^{+}) = \tfrac{1}{2}[1+\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2 e^{-t_{12}/T_2}\cos(\Delta t_{12} - \boldsymbol{k}_{12}\cdot\boldsymbol{r}+\phi_{12})],$$
$$\rho_{22}(t_{12}^{+}) = 1-\rho_{11}(t_{12}^{+}). \quad (1)$$

Here $t_{12}^{+}$ is the time immediately after application of the second pulse and $\theta_j$ the rotation angle of the Bloch vector induced by the $j$th excitation pulse. $\Delta$ is the detuning due to the inhomogeneous width, and $t_{12}$, $\boldsymbol{k}_{12}$ and $\varphi_{12}$ are the time, $k$-vector and phase difference between the excitation pulses. $T_2$ is the optical dephasing constant [1] which can be decomposed in the following form:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^{*}}. \quad (2)$$

Here $T_1$ is the population relaxation time and $T_2^{*}$ the pure dephasing time due to interaction of the two-level system with the other (bath) levels in the system. Eq. (2) shows that in situations where pure dephasing processes are absent, the optical dephasing time constant is only determined by population relaxation dynamics.

Returning now to eq. (1), we note that the last term in the expression of $\rho_{11}$ (or $\rho_{22}$) is responsible for a sinusoidal modulation of the population as a function of detuning in the ground and excited state. From hereon we will call this ordered population a 'grating in frequency space',

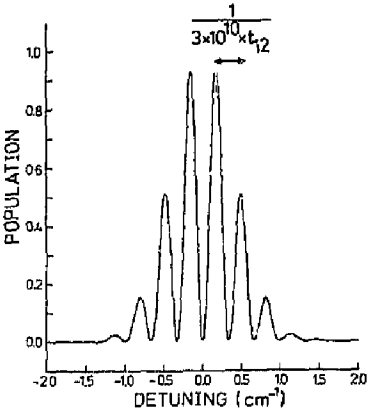


Fig. 1. Ground state population versus detuning from the line center after two resonant $\pi/2$ pulses separated by 100 ps. In the text this population distribution is referred to as 'grating in frequency space'.

which only exists when $t_{12} \leq T_2$. Eq. (1) also shows that the amplitude of this grating contains the optical phase information which, through eq. (2), may be related to the system's dynamics. In fig. 1 we show such a grating after the application of two $\pi/2$ pulses on a transition with an inhomogeneous linewidth of 1 $cm^{-1}$.

It is known that a third excitation pulse is able to recall the optical phase information stored in this grating in the form of an echo, the so-called stimulated echo [2]. In the time between the 2nd and 3rd pulse the amplitude of the grating only decays through population relaxation processes ($T_1$). It is not so surprising then that the usage of this echo effect is generally confined to measurement of $T_1$. The stimulated echo may however also be used to obtain information on $T_2$ but then the intensity of the echo must be measured as a function of the separation between the first and second pulse.

The concept of 'grating in frequency space' or just 'frequency grating' as basis for the generation of a stimulated echo leads to an easy understanding of the two photon echo effects which are described in this paper: the accumulated [3] and the two-color echo [4]. For both these echo effects it is fundamental that a stimulated echo may be generated from a transition in which only one state needs to carry a frequency grating. In the accumulated photon echo effect [3] it is usually the ground state in which a grating is built up through repetitive excitation with twin excitation pulses because part of the excited state population leaks away to a long-lived state, the bottleneck in the optical pump cycle. In the quasi steady state stimulated echoes may be generated from this frequency grating, which can be used to measure $T_2$. In the case of a two-color stimulated photon echo [4] the echo is generated at an entirely different frequency $\omega_2$ than the one $\omega_1$ at which the grating was prepared. A necessary prerequisite to observation of such echoes is that the inhomogeneous broadenings at the selected transitions are correlated. Only then a frequency grating formed at one transition can be transferred, e.g. by population relaxation, to another at which the echo is stimulated.

## 2. Results

### 2.1. Exciton dynamics in the system GaP:N

We present in this section the results of accumulated photon echo experiments on the system GaP:N, with $[N] = 1.3 \times 10^{16}$ $cm^{-3}$.

In the last decade the spectroscopy of this system has been studied in great detail [5]. The first photon echo measurements on this system were reported by Hu et al. [6]. In a short note on the subject they reported the effect of the N-dopant concentration on the echo relaxation time. At the lowest doping level of the N-traps an echo lifetime of 200 ps was measured. Fig. 2 shows the accepted level scheme of the nitrogen-bound exciton and its optical absorption spectrum in the region of interest. Important to this presentation is the fact that only the A-state ($J = 1$) is optically allowed from the ground state ($J = 0$), while the lower B-state ($J = 2$) is optically forbidden and can only be observed in emission. The lifetime of the B-state was reported to be 4 $\mu$s [7]. Considering the previous discussion, we expected that the B-state could function as a bottleneck in the optical

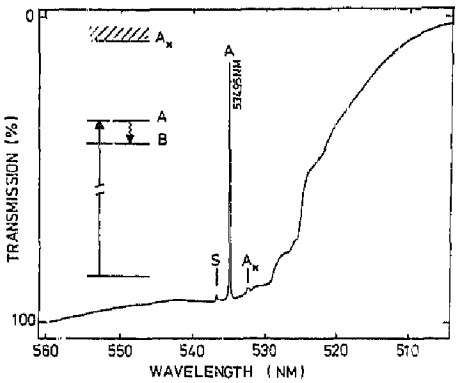


Fig. 2. Level scheme and optical absorption spectrum at 1.5 K of the nitrogen bound exciton in GaP. The N-concentration is $1.3\times10^{16}$ cm$^{-3}$. The line in the optical spectrum denoted by S is due to an exciton absorption bound to a sulphur impurity in the crystal.

pump cycle involving the A-state. We therefore decided to perform an accumulated echo experiment on this transition, employing a psec synchronously pumped dye-laser at a 100 MHz rep rate. For a further discussion of the setup we refer to ref. 3. A typical low-temperature (1.5 K) trace of the accumulated echo is shown in fig. 3. In the lower part of the figure a log plot of the echo intensity is given, from which a low-temperature decay time of 25.5 ps may be deduced. This lifetime is interpreted as the exciton relaxation time from the A to the B state. We note that the relaxation time we measure is substantially different from the ones reported by Hu et al. [6]. This difference is as yet unexplained but may be related to strain in the crystal which could depend on the method of sample preparation. This is a point of further investigation.

Although from the absence of the A-line in the low-temperature emission spectrum one could already conclude that the relaxation from the A-state into the B-state is ultrafast, a relaxation time of 25 ps suggests a strong coupling between the A and B state. This is surprising, particularly in view of the fact that a direct phonon relaxation process is spin-forbidden. The

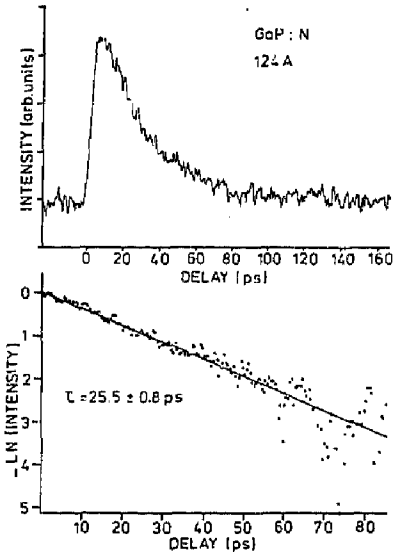


Fig. 3. Decay of the accumulated photon echo at 1.5 K in the system GaP:N.

relaxation mechanism therefore must involve spin-orbit phononic coupling. When the temperature is raised, the echo decay time becomes shorter. Above 20 K the echo decay time is too short to measure with the presently available pulses. Fig. 4 shows a log versus $1/T$ plot of the temperature induced optical dephasing, whereby it is noted that the points above 20 K were obtained from the homogeneous lineshape of the optical absorption. The curve clearly shows a quasi-biexponential activation of the dephasing, suggestive of two distinct processes that modulate the frequency of the optical transition. The solid line through the experimental points is obtained with the following expression:

$$T_2^{-1}(T) - T_2^{-1}(0) = \tfrac{1}{2}\tau_A^{-1} n(\omega_{AB}) + \tfrac{1}{2}\tau_{A,}^{-1} n(\omega_{A,A}), \tag{3}$$

where $n(\omega_{AB})$ stands for the Bose-Einstein occupation number for phonons of energy $\omega_{AB}$, and with the following values for the constants $\tau_A = 25.5$ ps, $\omega_{AB} = 7.1$ cm$^{-1}$, $\tau_{A,} = 72$ fs and

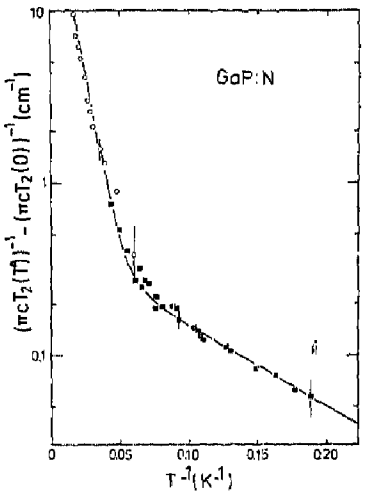


Fig. 4. Log-versus-$1/T$ plot of the pure dephasing contribution to the homogeneous linewidth of the A-transition in the system GaP:N. The solid squares were obtained from accumulated photon echo experiments, while the data designated by open circles, were deduced from the optical lineshape deconvoluted with the low-temperature inhomogeneous linewidth of 1.7 $cm^{-1}$.

$\omega_{A,A} = 83\ cm^{-1}$. The first term in eq. (3) represents the dephasing by inverse Orbach processes [8], involving the lower E state. While the lifetime of the A state remains constant, the rate out of A, which determines the dephasing, is increased by stimulated phonon processes. The second term in eq. (3) represents the process of phonon-assisted detrapping of the exciton, localized at nitrogen, into the free exciton band. From the pre-exponential constant of this term we infer that trapping of a free exciton at nitrogen occurs in 144 fs. It would be very interesting to study exciton dephasing in this system systematically as a function of nitrogen dopant concentration. We hope to be able to perform such a study in the near future.

### 2.2. *Vibrational deactivation in the system pentacene in naphthalene*

The second part of this paper deals with usage of the stimulated echo as a probe for vibrational

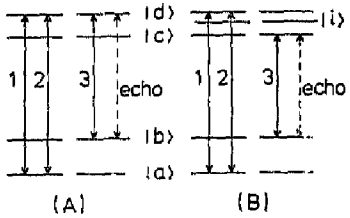


Fig. 5. Level schemes for the two different types of two-color stimulated echoes described in this note. Consult the text for a characterization of the level symbols. The time separation between the first two excitation pulses is 60 ps in both cases. The break in the center indicates that the probe pulse is applied at a variable delay after the second pulse.

deactivation processes in molecular solids [4]. To provide a framework for the following discussion consider fig. 5. In (A) of this figure, a four level scheme is depicted in which at certain time intervals, laser fields are applied at different transitions. In this figure |a⟩ is the ground state, |c⟩ the electronically excited state, |b⟩ a vibrational level in the ground state and |d⟩ a vibrational level in the excited state. With the first two excitation pulses a grating is generated at the transition |a⟩ to |d⟩, while a probe pulse is applied at the transition |d⟩ to |b⟩. If the inhomogeneous broadenings at these transitions are correlated then the third pulse will generate an echo at the latter frequency. The decay time of this echo, as a function of delay between the second and third pulse probes the population decay of state |d⟩. The result of such an experiment on vibronic transitions in the molecular system pentacene in naphthalene is given in curve (A) of fig. 6. The solid line is a fit to an exponential decay with a lifetime of 33 psec. In fig. 5B an experiment is described where the probe pulse is applied at an entirely different frequency, namely |c⟩ to |b⟩, than the excitation pulses. If however in the time lapse between the second and third excitation pulse population is transferred from |d⟩ to |c⟩, *and* the inhomogeneous broadenings at these transitions are correlated, then again an echo may be generated at the transition |c⟩ to |b⟩. The build-up of the echo intensity as a function of the delay between the second and third pulse will yield information on the dynamics of vibrational

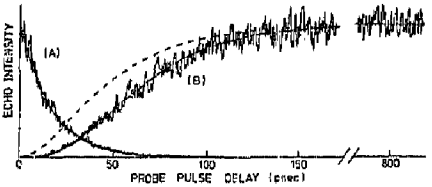


Fig. 6. Stimulated echo intensity as a function of delay between the second and third pulse. Scan (A) presents the decay of the echo intensity for the pulse sequence displayed in fig. 5A. Scan (B) shows the rise of echo intensity described by the pulse sequence of fig. 5B. The finite width of the excitation and probe pulses was taken into account by convoluting the echo intensity rise with the cross-correlation width of 11 ps. The dotted line in (B) is the predicted rise in intensity of the signal, in the absence of the intermediate level |i⟩.

deactivation. Curve (B) in fig. 6 shows the result of such an experiment on the same system. The dashed line in fig. 6 shows the expected echo intensity rise if direct relaxation would occur from state |d⟩ to |c⟩. The difference between this curve and the measured one shows that at least part of the population from level |d⟩ relaxes via intermediate levels |i⟩ to |c⟩. The solid line in curve B presents a fit to the data using a simple model with one intermediate level. In this model the lifetime of the intermediate state is found to be 16 ps. If direct decay from |d⟩ to |c⟩ is retained as a separate possibility (this process involves the simultaneous emission of at least six phonons), an upper limit of 22 ps is found for the decay time of a single intermediate level. It would be extremely interesting to locate these intermediate levels by attempting to generate two color stimulated photon echoes from transitions involving these levels.

## 3. Summary

We have shown in this paper that picosecond optical coherence measurements can provide interesting information on the dynamics of optical excitations in doped molecular solids and semiconductors. In particular we have reported dynamical information on the system GaP:N and on the pentacene-in-naphthalene mixed crystal. We expect that in the coming years picosecond optical coherence experiments will continue to provide new and interesting data concerning dynamical processes of optical transitions in the solid state.

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