TWO-COLOR PICOSECOND STIMULATED PHOTON ECHOES IN SOLIDS

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We report a novel type of photon echo, the relaxed two-color stimulated echo, in the molecular mixed crystal of pentacene in naphthalene. A prerequisite to observation of this type of echo is that the inhomogeneous broadening on the selected transitions be correlated. The echo is used to study the picosecond vibrational deactivation of some excited-state vibrations of pentacene. Evidence for intermediate levels in the relaxation pathway is presented.

The three-pulse stimulated echo, long known in magnetic resonance [1], has more recently been demonstrated in optical transitions [2]. In multilevel systems with bottleneck states, the population grating left by the first two excitation pulses in the optically connected levels, need only persist in one of the levels for the stimulated echo to be elicited by the third pulse [3]. A corollary is that the echo may be stimulated at some entirely different frequency \( \omega_2 \) than the one, \( \omega_1 \), at which the grating was prepared. It has been realized [4] that, after redistribution of the initially excited population grating, the echo, in fact, may be stimulated from any state into which the grating has relaxed. We report here the first observation of such a relaxed two-color stimulated echo (R2CSE) which can be seen as the optical analog of the NOE effect in 2-D NMR [5]. The rise of this echo is used to probe the rate of vibrational population filling into the vibrationless level, subsequent to excitation of various vibrational levels in the \( S_1 \) manifold of pentacene doped into naphthalene. By comparing this rate with the relaxation rate of the initial level, as measured by a connected two-color stimulated echo (C2CSE) [6], evidence was obtained for short-living intermediate levels in the relaxation route.

The apparatus used in the experiments consists of two synchronously pumped picosecond dye lasers. A Nd–YAG laser, at 10 Hz, is used to amplify the output pulses to single pulse energies of \( \approx 10 \mu J \) in pulses of 6 ps duration. For a detailed description of the apparatus we refer to ref. [7].

Consider now fig. 1 which contains the appropriate level scheme for the photon echo experiments on pentacene in naphthalene. Here, |a\rangle stands for the ground state and |c\rangle for the electronically excited state of pentacene, while |b\rangle and |d\rangle represent vibrational levels in the ground and excited states respectively. In fig. 1B the level |i\rangle in the upper electronic state stands for the intermediate level structure in the vibrationless level. 

![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.](image-url)
functional relaxation process. In both stimulated echo experiments the preparation stage is the same: the first two excitation pulses at \( \omega_1 \) create an ordered population (grating in frequency space) in the ground and excited states as follows:

\[
\rho_{dd}(t_{12}^+) = \frac{1}{2} \left[ 1 - \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \right] \times \exp\left(-t_{12}/T_{2d}^{ad}\right) \cos(\Delta t_{12} - k_{12} \cdot r + \phi_{12}) ,
\]

\[
\rho_{dd}(t_{12}^+) = 1 - \rho_{dd}(t_{12}^-) .
\]  

where \( t_{12}^+ \) is the time immediately after application of the second pulse and \( \theta_j \) is the rotation angle of the Bloch vector induced by the \( j \)th excitation pulse. \( \Delta \) is the detuning due to the inhomogeneous width, and \( t_{12}, k_{12} \) and \( \phi_{12} \) are the time, \( k \)-vector and phase difference between the excitation pulses. The last term in the expression for \( \rho_{dd}(t_{12}^+) \) is responsible for the sinusoidal modulation of the population as a function of \( \Delta \).

Furthermore, from this expression it is clear that the amplitude of the grating contains optical phase information which under proper conditions may be recalled as an echo, as we will see.

In the case of the C2CSE, the probe pulse transforms the ordered population from state \( |d\rangle \) into a polarization at frequency \( \omega_{db} \). The polarization near \( \omega_{db} \) is proportional to the off-diagonal density matrix element \( \rho_{bd} \) which at the time of the echo may be written, with the phase factor dropped, as

\[
\rho_{bd}(t_{12}, \tau) = f(\theta_1, \theta_2, \theta_3) \times \exp(-t_{12}/T_{2d}^{ad}) \exp(-\Gamma_{d} \tau) \exp(-\kappa t_{12}/T_{2}^{bd}) ,
\]

where \( f(\theta_1, \theta_2, \theta_3) = \sin \theta_1 \sin \theta_2 \sin \theta_3 \), \( \Gamma_{d}^{-1} \) is the lifetime of state \( |d\rangle \) and \( \tau \) the separation between the second and third pulse which is varied in the experiment. \( T_{2d}^{ad} \) and \( T_{2}^{bd} \) are dephasing constants of the transitions at \( \omega_{da} \) and \( \omega_{db} \) respectively, and are known from previous CARS [7] and photon-echo [8] experiments. The inhomogeneous broadening is absent from eq. (2) since we have assumed that the dephasing occurring during the first interval \( t_{12} \) is just cancelled by rephasing during the last interval \( \kappa t_{12} \) before the echo maximum. The assumption here is perfect correlation of the inhomogeneous distributions centered at \( \omega_{da} \) and \( \omega_{db} \). The scale factor \( \kappa = \omega_{da}/\omega_{db} \) leads in principle to a retardation of the echo by \( (\kappa - 1)t_{12} \), but this delay is much less than the echo width and so we can set \( \kappa \approx 1 \) in practice. A typical example of a C2CSE decay obtained, after tuning \( \omega_1 \) to a vibronic transition of pentacene at 17335 cm\(^{-1} \) (747 cm\(^{-1} \) above the origin) and \( \omega_2 \) to \( \omega_{db} \) at 16579 cm\(^{-1} \), is shown in scan A of fig. 2. The stimulated echo was observed by optical mixing of the echo with a time-coincident probe pulse at \( \omega_1 \) in a KDP crystal [6]. The echo clearly exhibits single-exponential decay, as predicted by eq. (2), with a time constant of 33 \( \pm \) 1 ps which is in perfect agreement with the results of an earlier one-color stimulated echo experiment on the vibronic transition at \( \omega_{da} \) [8].

In the second echo (R2CSE) experiment, outlined in fig. 1B, the third excitation pulse is applied to the transition at \( \omega_{cb} \), where at \( t_{12}^+ \) neither of these levels is populated. In the process of vibrational relaxation, the ordered population from level \( |d\rangle \) is, possibly via some intermediate levels, transferred to the vibrationless level \( |c\rangle \). Again if the inhomogeneous distributions at \( \omega_{da} \) and \( \omega_{cb} \) are correlated, the macroscopic polarization at \( \omega_{cb} \) will rephase at a time \( \xi t_{12} \) after the third pulse through the off-diagonal density matrix element \( \rho_{bc} \) which at the echo time may be written as

\[
\rho_{bc}(t_{12}, \tau) = f(\theta_1, \theta_2, \theta_3) \times \exp(-t_{12}/T_{2d}^{ad}) F(\Gamma_{d}, \Gamma_{c}, \tau) \exp(-\xi t_{12}/T_{2}^{bc}) ,
\]

where \( \xi \) again is a scale factor, \( \xi = \omega_{da}/\omega_{cb} \), and \( F(\Gamma_{d}, \Gamma_{c}, \tau) \) is a function depending on the lifetime of level \( |d\rangle \), and on the lifetimes of possible intermediate
states. In scan B of fig. 2 we show the result of a \( \text{RZCSE} \) experiment, again after exciting the same transition at 17335 cm\(^{-1}\), but now with the probe tuned to the \( \omega_{cb} \) resonance at 15832 cm\(^{-1}\). The first noteworthy thing is, as expected, that the echo intensity starts at zero and then quickly rises on a 100 ps timescale to a plateau which persists on the timescale of the experiment. On a longer time scale this plateau should exhibit exponential decay with the 20 ns lifetime [8] of state \( |c\rangle \). The second thing to note is the initial sigmoid curvature of the echo intensity, indicative of a consecutive relaxation process that leads to the echo formation. Indeed by assuming that the initial population of \( |d\rangle \) directly decays into level \( |c\rangle \), the dotted curve in fig. 2 is predicted, which is not in agreement with our observation. For this case the function \( F(d, c, \tau) = 1 - \exp(-\Gamma_d \tau) \). We therefore must conclude that the vibrational relaxation from level \( |d\rangle \) down to \( |c\rangle \) proceeds in steps. To evaluate the data we have chosen the simplest relevant model, namely the presence of one intermediate level \( |i\rangle \). For this case, see fig. 1B, we obtain:

\[
F(d, c, \tau) = 1 + |\Gamma_i/(\Gamma_d - \Gamma_i)| \exp(-\Gamma_d \tau) - \left[\Gamma_d/(\Gamma_d - \Gamma_i)\right] \exp(-\Gamma_i \tau).
\]

(4)

With this expression the echo intensity, being proportional to \(|\text{Tr}[\rho_{dc}(\tau)]|^2\), is fitted with \( \Gamma_i \) as a parameter. The best fit is obtained with a lifetime of the intermediate level of 16 \pm 2 ps. This short lifetime of the intermediate “level” comes as a surprise as there any many longer-lived modes observed and expected [8] below the 747 cm\(^{-1}\) mode. If dissipation of vibrational energy proceeds through a sequence of one-phonon emission events, at least five intermediate states must be involved, all with a lifetime less than the 16 ps obtained with the model in eq. (4). If direct decay from \( |d\rangle \) to \( |c\rangle \) 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.

Similar R2CSE experiments were performed with vibrational levels at 597 and 609 cm\(^{-1}\) above the vibrationless transition. These levels have vibrational lifetimes of 19 and 59 ps respectively [8]. We also find for these levels, within experimental accuracy, the same lifetime for the intermediate “state”. It would be extremely interesting to locate these intermediate levels by attempting to generate R2CSE from transitions with these states as final levels.

To avoid distortion of the echo decays, the experiments reported were performed with small-angle excitation pulses. In the case of C2CSE, stimulated emission at \( \omega_{dp} \), induced by the probe pulse, can lead to an artificial lengthening (\( \theta_2 > \pi/2 \)) or shortening (\( \theta_2 < \pi/2 \)) of the echo decay. For the R2CSE under these conditions, spontaneous amplified emission at \( \omega_{ca} \) leads to a reduction of the echo signal on a longer timescale. In both experiments, therefore, the intensity of the grating forming beams (at \( \omega_{da} \)) was attenuated such that these effects were absent and the echo decay or rise was unaffected by further lowering the intensity of the beams.

There is another point of the C2CSE generation that needs to be discussed. In the description of the rephasing effect we have not only assumed that the inhomogeneous broadenings on the selected transitions are correlated but also, implicitly, that they are identical, when expressed as a fraction (\( \delta_{ij} = \Delta \omega_{ij} / \omega_{ij} \)) of their center frequencies. Here \( \Delta \omega_{ij} \) is the inhomogeneous width of the transition at \( \omega_{ij} \). This is substantiated by the appearance of the echo at the time predicted by eqs. (2) and (3). If the inhomogeneous widths were different, \( \kappa \) and \( \xi \) in eqs. (2) and (3) would have to be replaced by \( \kappa' = (\delta_{da}/\delta_{db})\kappa \) and \( \xi' = (\delta_{da}/\delta_{cb})\xi \) respectively. The fact that two-color echoes can be generated in this mixed crystal shows that the inhomogeneous broadenings at the selected transitions are correlated. A more quantitative measure for this correlation could be obtained from a study of the echo intensity (compared to the one-color case) and temporal shape as a function of delay between the grating-forming excitation pulses. A more convenient way of probing this correlation is by performing time-resolved four-wave mixing experiments. In a recent such study [9] on the same system it was found that the vibrational dispersion was immeasurably small compared to the homogeneous width of the Raman transitions, which presents the fundamental limit in establishing spectral correlations.

We end this letter by noting that the relaxed two-color stimulated echo provides information on the vibrational dynamics, which in principle can also be obtained from time-resolved fluorescence experiments using either gating [10] or streak camera [11] techniques. The echo has the advantages of all coherent
techniques, such as high sensitivity and spectral resolution, but is limited to low temperature, since finite electronic $T_2$'s are a prerequisite. The idea obviously can be extended to the study of vibrational relaxation on the ground-state potential energy surface by labeling the initial state by a coherent Raman process or infrared excitation. As such it is a viable alternative to spontaneous Raman scattering [12] or vibrational grating experiments [13].

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References