DEPHASING PROCESSES AS STUDIED BY TWO PULSE PHOTON ECHOES AND PHOTOCHEMICALLY ACCUMULATED ECHOES: THE QUESTION OF SPECTRAL DIFFUSION IN A DOPED ORGANIC POLYMER MATRIX

A. REBANE [1] and D. HAARER

Physikalisches Institut and BIMF, Universität Bayreuth, D-8580 Bayreuth, Fed. Rep. Germany

Two pulse photon echoes (2PPE) and photochemically accumulated stimulated photon echoes (PASPE) were measured under identical conditions for the system octaethylporphin in a polystyrene matrix. Experiments at 1.9 K show that both echoes have a different decay behavior. Whereas the 2PPE-signal decays with a time constant of 1300 ps, the PASPE-signal decays faster with a time constant of 600 ps. The different temporal behavior of both signals is tentatively attributed to spectral diffusion.

1. Introduction

In the past decade excited state relaxation processes of molecular solids have been subject to considerable interest. It was shown in 1976 [1] that the method of photon echoes [2] can be applied to organic solids, yielding picosecond information on excited state dephasing processes. A year earlier (1975) the Fourier-related method of excited state hole burning [3] had been carried out for ruby; yet, the transient features of the excited state hole burning experiment seem to be a severe limitation for many studies and applications. This is due to the fact that excited state lifetimes of organic molecules (T_1) are typically 10^{-8} s and, hence, the experiment was, to our knowledge, only performed for the ruby R_1-bands, here the lifetime of the excited state is in the µs time regime. A breakthrough was reached through a photochemical variation of the hole burning experiment, the photochemical hole burning experiment [4,5], in which the refilling of the ground state with T_1 was blocked by a photochemical scheme, thus yielding an "infinitely" long lifetime of the photochemical hole (see for instance [6,7]).

With the photon echo experiments yielding dynamical information in the time regime $\lesssim 1$ ns and

the photochemical hole burning experiments being limited to a real time resolution of about one second, the question which remains, up to now, unanswered is the question of spectral diffusion [8], i.e. of changes occurring during the time interval between the typical time of a "instantaneous hole" as created through an excited state hole burning or echo experiment (nanoseconds) and the slow spectroscopic creation and detection of a photochemical hole (seconds). Even though this question was addressed several years ago [9,10] it is still not clear, whether or not the inverse hole burning linewidth should or should not correspond to a typical echo decay-time [11,12]. In the case of negligible spectral diffusion the echo experiment and the hole burning experiment should yield the same dynamical information. However, experiments at ultralow temperatures ($T \gtrsim 0.05$ K) [13] and recent experiments on temperature cycling of photochemical holes [14] seem to be supportive of the existence of spectral diffusion. This situation is especially given at low temperatures, since under these conditions the spectral diffusion contribution dominates the two phonon Raman processes which are believed to be responsible for the dynamical dephasing processes in the excited state [6,14]. The reason for the dominance of the spectral diffusion contribution is given by its linear temperature dependence as compared to an exponential of higher power T-dependence of the

corresponding Raman-phonon processes.

To shed light on the controversial question of spectral diffusion, one would have to perform experiments in the time regime of 1 ns $< t <$ 1 s in order to detect the contribution of spectral diffusion to the "conventional" hole burning linewidth. An attractive approach seems to be the comparison between photochemically accumulated echoes and two pulse echoes for the same sample under identical conditions. The technique of accumulated echoes, first demonstrated in ref. [15] has been shown to be rather universal and can be easily interpreted, if one uses the photochemically accumulated stimulated photon echo (PASPE) and the time domain holographic scheme as proposed in ref. [16]. This experiment corresponds to a free induction decay of an ensemble of excited states, whose inhomogeneous band exhibits a pattern of photochemical holes. The accumulation time of this echo experiment is the crucial time interval during which the spectral diffusion processes can take place and, hence, broaden and smear out a hole pattern. A direct comparison between the accumulated echo and the two pulse echo should give an immediate answer to the question of the "fast dephasing processes" (T_2) as seen in a dynamic echo and the "slow processes", as seen by an accumulated echo. Our experiments on the system octaethylporphin in polystyrene show marked differences between the two types of echo-experiments which we attribute to spectral diffusion.

2. Experimental

As laser system a Quantel PTL10 pulsed picosecond dye laser was used; it was pumped by a Quantel YG501 mode-locked YAG laser. A typical pulse duration was 25 ps; a typical pulse energy was about 400 µJ per pulse. The laser could be operated at a repetition rate of 5 Hz. Its spectral width was about 20 cm^{-1}. With the above instrument about 10 to 100 pulses were needed to produce an easily detectable photochemically accumulated stimulated photon echo (PASPE) with a conventional photodiode.

The geometry of the complete optical set-up is depicted in fig. 1. The main beam is divided into two beams by the 50%-beam splitter BS2. Beam one and two intersect at an angle of 5°; the geometrical in-
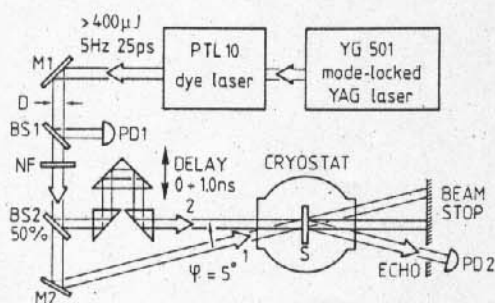

Fig. 1. Experimental setup (see text). S=sample; NF=neutral density filter; PD1=reference photodiode; PD2=signal photodiode; BS1, BS2=beam splitters, M1, M2=mirrors, D=diaphragm.

tersection point is the sample location S in the helium cryostat. One of the two beams (beam 2 in fig. 1) could be delayed by as much as 1 ns through a variable delay-line as shown in fig. 1. The pulse energy could be monitored with the photodiode PD1. The diameter of the laser spot in the cryostat was about 2 mm; a typical pulse energy, measured at the location of the sample, was 2 µJ.

The cryostat had plane windows as depicted in fig. 1; it was rigidly mounted on an optical table, together with all the optical components, to eliminate fluctuations of the optical pathlengths. The sample temperature was kept at 1.9 ± 0.3 K, to maintain the liquid helium in its superfluid state. The detection of the optical echo signals was achieved with photodiode PD2 under appropriate echo conditions (see below).

The sample was polystyrene doped with free base octaethylporphin at a concentration of about 10^{-3} to 10^{-4} M/ℓ. The sample thickness was 0.7 mm; the area of the sample which was accessible to the laser beams was about 10×10 mm.

A typical low temperature spectrum of the sample is shown in fig. 2. The maximum of the $S_1 \rightarrow S_0$ absorption is at 619 nm and had an optical density of 0.8. The experiments were carried out at 620 nm. The band located at 650 nm is due to impurities; it is absent in freshly prepared samples (dotted line) and has no measurable influences on the echo signals.

For the *echo experiments* we used the following experimental procedures:

(a) The two pulse photon echo (2PPE) occurred, when two excitation pulses (beam 1 and 2) were si-
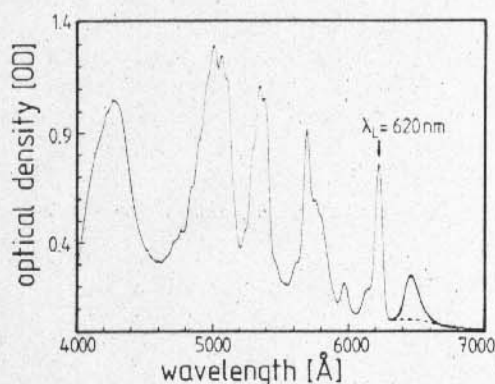
Fig. 2. Low temperature absorption spectrum (1.6 K) of free base octaethylporphin in polystyrene (see text).

multaneously applied to the sample. The 2PPE signal propagated at an angle of $5°$ with respect to the second pump pulse and, hence, could be separated geometrically via a pinhole in the beamstop (fig. 1). The intensity of the 2PPE signal was measured by a photodiode and a boxcar averager. The signal of the photodiode PD1 was used to trigger the boxcar.

(b) The *photochemically accumulated stimulated photon echo* (PASPE) occurred after the sample had been exposed to 10 to 100 excitation pulse-pairs of well defined delay. After this exposure the overall photon echo signal was a superposition of the 2PPE and the PASPE with both echo signals having identical temporal and spatial properties. The separation of the PASPE from the 2PPE could be achieved in a rather straightforward fashion: The first pump pulse was blocked and only the second pump pulse was applied to the sample. In this configuration only the PASPE was produced. This echo was generated by the photochemically stored (accumulated) spectral grating in the ground state population (i.e. modulation of the optical density). In contrast to this accumulated echo the 2PPE requires simultaneous pumping through both pulses 1 and 2 (see fig. 1).

3. Experimental procedure – discussion of results

In the following we will make a direct comparison between the 2PPE signal which reflects the fast dephasing processes in the sample ($\tau < T_1$) and the PASPE which reflects the sum of the fast dephasing processes and the slow spectral diffusion processes

($\tau \gg T_1$) during the accumulation time (typically tens of seconds). Since both experiments are carried out with the same sample and under identical experimental conditions, we believe that this experiment provides a crucial test for the presence or absence of spectral diffusion. For understanding the significance and the present limitations of the experiment, we will describe the experimental procedures in detail.

For measuring the 2PPE we had to operate in the "low exposure limit". This limit is characterized through the condition that the amplitude of the excited state grating (transient grating) is larger than the amplitude of the photochemically produced (stable) grating. For this condition to hold, we were limited to less than 50 pulses on a "virgin sample".

For measuring the intensity of the PASPE-signal the sample was exposed to 350 excitation pulse-pairs (exposure time 70 s, total exposure was 0.24 mJ per mm²) of well defined delay. After this exposure the first pulse beam was blocked and the second pulse beam produced the PASPE as described above. To reconvert the sample into its "virgin condition", one had to refill the photochemically produced hole pattern. This was achieved by illuminating the sample for 5 minutes with a 50 W tungsten lamp. This procedure has proven to be sufficient and less time consuming than going through a thermal cycle to room temperature after each PASPE data point.

The results of a series of experiments are depicted in fig. 3 (see insert). Here the decay of the two pulse echo is depicted over a delay period of 200 ps (squares). It decays slower than the corresponding PASPE-signal (triangles), indicating that the "excited state hole grating" is characterized by a narrower hole width than the corresponding "photochemical hole grating".

To check the validity of the above experiments, we have plotted the logarithm of the ratio (I_{2PPE}/I_{PASPE}) as a function of delay time from 0.4 to 1 ns (see fig. 3). If one assumes that both, the 2PPE-signal and the PASPE-signal follow monoexponential decays, one would expect a straight line, whose slope is given by the difference of the pertinent decay constants (see below).

Before discussing the data in a quantitative fashion, we would like to point to some experimental difficulties, which we could not resolve completely:
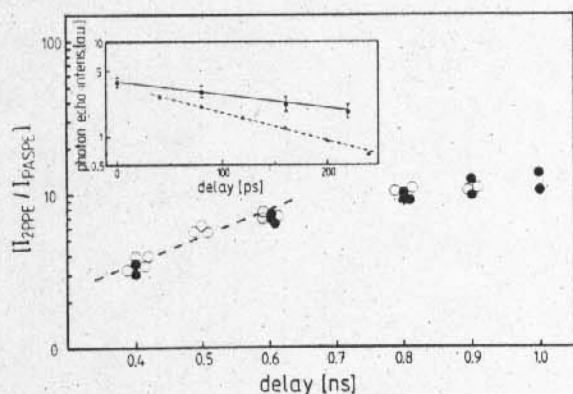
Fig. 3. Insert: Decay of the 2-pulse photon echo signal (squares) and the photochemically accumulated stimulated photon echo signal (triangles). Main figure: Ratio of the two echo signals (log plot) versus delay time (see text).

Since both, the 2PPE-signal and the PASPE-signal exhibits similar spatial and temporal properties, interference of both signals was observed, after the two pulse excitation had been applied repeatedly. At delay values of less than 0.4 ns, the PASPE-part of the echo contributed about 10% to the total echo amplitude. This was enough to disturb the measurement of the "pure" 2PPE-signal intensity. To minimize this interference effect of both signals, an offset of 0.4 ns was chosen between the first and the second excitation pulse.

A quantitative analysis of the experiments was performed, based upon data which are depicted in fig. 3. From the insert we can extrapolate the effective T_2-times according to the relation

$$I_{echo} = C \exp(-4\tau_d/\hat{T}_2) , \qquad (1)$$

where I_{echo} is the echo intensity, τ_d is the delay time between the two pulses in beam 1 and 2 respectively and C is an arbitrary constant.

Taking the data as displayed in the insert, we obtain for the faster decaying component of the echo, the PASPE-signal an effective decay time of $T_2(PASPE) = 600 \pm 80$ ps and for the slower decaying component, the dynamic two pulse echo, a decay time $T_2(2PPE) = 1300 \pm 300$ ps. Thus, the above experiments can, in our eyes, be taken as unequivocal documentation of the influence of spectral diffusion. The two T_2-times, as given above, correspond to the

slope in the plot log (I_{2PPE}/I_{PASPE}) as is given in fig. 3 (broken line). For the "bendover" of the experimental points for decay times exceeding 800 ps we have no immediate explanation. At the present time we attributed the bendover to the larger experimental error at long decay times, where both echo signals have lost considerable amplitude and thus the ratio of the respective signals is not as well defined as it is for the shorter decay times.

Eventually the curve log (I_{2PPE}/I_{PASPE}) has to bend over to a constant value at times which are characterized by τ_{SD}, the time which characterizes the dynamics of the spectral diffusion. More precise data along similar lines, however, are needed to characterize the time constant for the spectral diffusion.

A final comment should be made, concerning the order of magnitude of the above dephasing times, as compared to similar hole burning experiments. We take, for instance, the optical linewidth data of the dye molecule free base phthalocyanine in polystyrene, i.e. a different guest molecule in the same host matrix. Here, in recent interpretations of the hole burning widths [14] (of slightly less than 1 GHz, at 2 K) about one third of the linewidth was attributed to phonon scattering processes and two thirds to spectral diffusion processes [17] [1]. This is in qualitative agreement with the above data. The most promising future goals for discriminating between various processes would be the investigation of the temperature dependencies of the various echo signals below 1 K. At very low temperatures, one would expect the largest differences between the "slow" spectral diffusion processes and the "fast" dynamic dephasing processes.

[1] In ref. [17] is data presented on photochemical hole widths for the dye molecule octaethylporphine in polystyrene between 0.05 and 16 K.

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