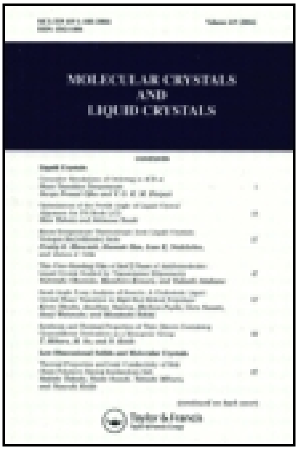

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Contributions of The Different Line Broadening Mechanisms in Photon Echoes and Single Molecule Spectra in Amorphous Solids

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CONTRIBUTIONS OF THE DIFFERENT LINE BROADENING MECHANISMS IN PHOTON ECHOES AND SINGLE MOLECULE SPECTRA IN AMORPHOUS SOLIDS

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Abstract Experimental data on Photon Echoes (PE) in the system terrylene/poly(isobutylene) in the temperature range 0.4-8K are presented and compared with Single Molecule Spectroscopy (SMS) results. From this comparison we conclude that the linewidth distribution in SMS is caused mainly by a large T_2-dispersion (but not slow spectral diffusion). The temperature line broadening is discussed.

INTRODUCTION

Spectroscopic studies of the dynamical processes in doped amorphous systems are usually based on homogeneous linewidth measurements. In contrast to crystals there are two specific important and ill-known features in the dynamics of disordered solids which make these investigations more complicated. The first one is Spectral Diffusion (SD) which takes place in a very broad time range. The second one is the large dispersion of the dynamical parameters of individual impurity centers in amorphous hosts. It leads (as discovered recently) to a broad distribution of "homogeneous" linewidths in an ensemble of identical impurity molecules [1-5]. Experimental methods for "homogeneous" linewidth measurements, namely Hole Burning (HB), Photon Echoes (PE) and Single Molecule Spectroscopy (SMS) are characterized by different ways of averaging over the ensemble of molecules and over time intervals. Therefore, these methods yield different values for the linewidth. It means that neither method alone can give reliable information concerning true dynamical parameters and their distribution.

In order to better understand the dynamics of amorphous solids and to obtain information about the distribution of dynamical parameters over time and molecular ensemble it is necessary to investigate the same systems using different methods and to compare the results. Up to now there are very few data of this kind. In the paper [6] essential differences in the linewidths measured by HB and PE methods (for resorufin in ethanol glasses) have been obtained and explained by the strong influence of SD on the HB data. In the papers [7,8] authors compared the results obtained by different kinds of PE measurements and concluded that SD takes place even in the nanosecond range. In these few studies one deals only with different temporal averaging without any possibility to get information about the ensemble distribution of the investigated dynamical parameters. Such possibility appeared only recently after development of SMS We believe that complex comparative investigations of amorphous solids using different spectroscopic methods (including SMS) are very promising.

This paper presents the results of PE-measurements and a comparative analysis of experimental PE and SMS data for terrylene in a polymer matrix. First results of that work were presented in [9,10]. In these papers the comparative analysis was performed for molecules in a polyethylene matrix which does not form a true glass. In this work we performed a more precise investigation of a perfect amorphous system: tetra-*tert*-butylterrylene (TBT) in poly(isobutylene) (PIB) in a more wide low temperature range (0.4-8K). We have used two different versions of PE method: two pulse picosecond PE (2PPE) and incoherent PE (IPE). Our experimental results on PE were analyzed together with literature data on SMS for exactly the same system [4,5]

EXPERIMENTAL

The samples for the PE experiments were prepared as a film of PIB of approximately 300μm thickness doped with TBT with a concentration $1x10^{-4}M$. The optical density of the sample measured at room temperature was 0.8-1.0 at the excitation wavelengths. The absorption spectrum of the sample is shown in Fig. 1.

The 2PPE experiments were performed with the set-up developed at the University of Bayreuth. This set-up consists of a picosecond dye laser, an optical system with optical delay for excitation of the sample, a He-3 cryostat, which allows to perform measurements down to 0.4K, and a PE-signals registration system. The laser emits pulses with a repetition rate of 10Hz, 2-3ps pulse duration and an energy ≤ 10μJ $pulse^{-1}$ In 2PPE measurements on TBT/PIB the laser wavelength was equal to 573nm. A more comprehensive description of this set-up will be given elsewhere [11]

The IPE measurements were performed at the Institute of Spectroscopy on the

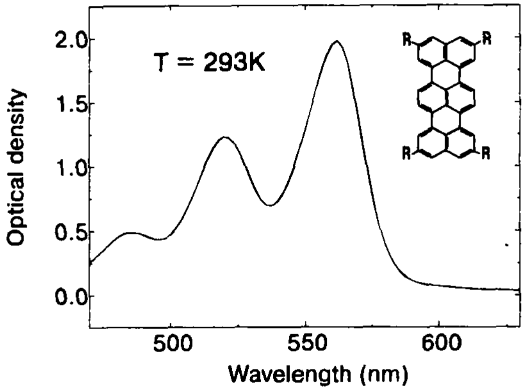

FIGURE 1 Absorption spectrum of TBT in PIB. (The R in the structure formula is a tert-butyl group)

set-up described previously [12] The main parameters of the set-up: the laser spectrum width is about 100cm^{-1} (λ=573÷576nm), pulse duration 12-15ns, energy $\leq$1mJ, repetition rate 3Hz.

The first set-up was suitable for low temperature measurements. The IPE set-up was used for measurements at higher temperatures due to its higher temporal resolution (up to 25 - 30fs). The exciting beam intensities were $\approx 10^{-5}$•J•cm^{-2}•pulse^{-1} in 2PPE and $\approx 5 \cdot 10^{-4}$•J•cm^{-2}•pulse^{-1} in IPE experiments. The control experiments showed that at these intensities the measured dephasing times were practically independent of the exciting light intensity.

RESULTS AND DISCUSSION

The main experimental results of our PE measurements for TBT/PIB in the temperature region 0.4-8K are presented in Fig.2. In this figure the $\Gamma_o = 1/2\pi T_1$ value for this system (measured by us using three pulse PE) is also shown. At the temperature T = 1.4K the experimental points obtained by the two PE methods practically coincide. All experimental points for TBT/PIB lie on a smooth curve and represent the temperature behaviour of the linewidth due to interaction with two level systems (TLS) and a local mode (see below).

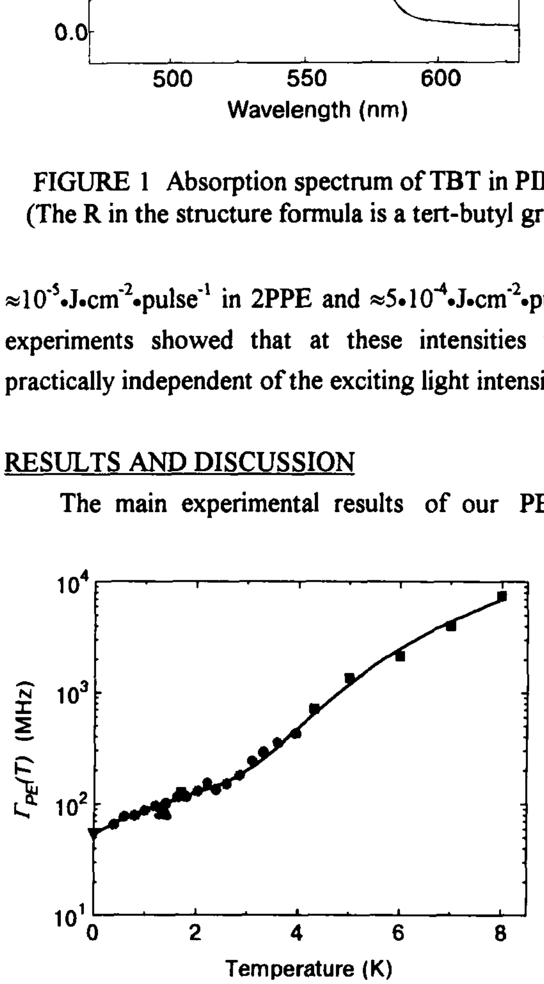

FIGURE 2 T-dependence of the linewidths of TBT/PIB. ● - 2PPE data; ■ - IPE-data; ▼ - Γ_o value, ▲ - the linewidth value calculated under assumption that the line-width distribution in Fig.3 is caused by T_2 dispersion. (The solid line represents a fit with equation(1)).

1. Comparison of PE and SMS Data.

At first let us consider the temperature region near 1.4K, where the linewidth distribution for TBT/PIB has been measured via SMS [4,5]. This distribution is presented in Fig.3. From our experimental data (Fig.2) at 1.4K the linewidth value $\Gamma_{PE} \approx 100$MHz. How to compare this value with data in Fig.3? As it was shown in previous papers [9,10] on the base of model calculations, in the case of a broad distribution of the homogeneous linewidth PE-measurements give some weighted average value Γ_{ef}, which does not coincide either with the maximum or with the gravity center of the distribution function and is influenced by the form of the linewidth distribution.

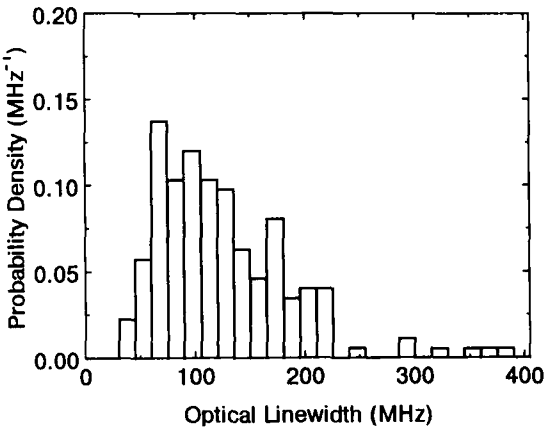

FIGURE 3 Histogram for the distribution of linewidths in TBT/PIB measured via SMS-method for 173 single molecules at 1.4K (adapted from [5]).

Using the histogram in Fig.3 we can calculate the “effective” value of the linewidth which should be obtained by PE in this case and compare it with experimental results. (The method of such model calculations was described in [9,10]). It is necessary to stress that the result of these calculations depends on the nature of the distribution and will be different whether this distribution is caused by SD or by homogeneous linewidth dispersion. If the line width distribution in Fig.3 would be caused mainly by slow SD, PE-measurements should obtain a linewidth near the minimum of the histogram (~40MHz). The value Γ_{ef} calculated under the assumption that the distribution in Fig.3 is caused only by homogeneous linewidth dispersion (without SD) is shown In Fig.2 by the symbol ▲. This calculated value is equal to 86MHz. Our experiment gives 100MHz which is close (or in the frame of experimental errors is equal) to the calculated value for the case of homogeneous linewidth dispersion. This fact leads us to the conclusion that the distribution in Fig.3 is mainly caused by a dispersion of the dephasing times T_2 (but not slow SD). This result seems important for the theoretical analysis of the low temperature optical dephasing due to interaction of impurity molecules with TLS. In particular, the large dispersion of the dephasing times T_2 can be related to the fact that every impurity center interacts with a relatively small number of TLS.

2. Temperature Dependence of the Linewidth

In recent SMS experiments on TBT/PIB and on the similar system TBT/polyethylene it was discovered that different single molecules show a different temperature behaviour of the linewidth. In the work [3] three different molecules of TBT/polyethylene demonstrate different temperature line broadening: linear, cubic, and exponential. In another SMS study [13] on the system TBT/PIB temperature dependencies of the linewidths of 10 single molecules have been measured. The temperature behaviour for all molecules was successfully described as a result of the interaction with TLS and a local mode ($\Gamma(T) \propto b{\bullet}T^{\alpha} + c{\bullet}exp(-E/kT)$), but with very different parameters. The value of α was ranging from 0.8 to 1.3 and the value of E - from 14cm^{-1} up to 35cm^{-1}. The question appears: what can we expect for the PE measurements of the temperature line broadening? It is obvious that due to the molecular ensemble averaging the PE method should give some "effective" temperature behaviour which is influenced by the distribution of the dynamical parameters of different molecules.

Our PE measurements have been performed in the temperature range 0.4-8K (to our knowledge, these are the first PE measurements on organic glasses below 1K). Experimental data for $\Gamma_{PE}(T)$ (Fig.2) look typical for organic glasses. They are very well described by a relation which takes into account the interaction with TLS and a local mode:

$$\Gamma(T) = \Gamma_0 + b{\bullet}T^{\alpha} + c{\bullet}exp(-E/kT) \,/\, [1 - exp(-E/kT)]^2, \qquad (1)$$

where $\alpha = 1.07$ and $E = 17\text{cm}^{-1}$, ($b = 34.3\text{MHz}{\bullet}K^{-\alpha}$, $c = 1.28{\bullet}10^5\text{MHz}$).

These results show that even in the case when different single molecules demonstrate essentially different temperature line broadening, the PE method (quite the same as HB) gives the typical for organic glasses temperature dependence with typical values of the parameters. From these averaged parameters it is hardly possible to obtain some detailed information concerning the system dynamics.

The investigated system is one of the conventional organic amorphous solids. For this reason we believe that the above regularities have more general nature and should be true for other systems. Consequently, for a correct study of the amorphous system dynamics one needs to perform complex investigations using different techniques.

CONCLUSIONS

1. In the present PE study we investigated the true amorphous terrylene/poly(isobutylene) system and compared the results with SMS data for the same system. The main reason for this is the possibility to obtain additional information on dynamics of the system from comparison of the data provided by the two different

methods with the different ways of averaging over the molecular ensemble and over the time.

2. The study shows that in this system the broad distribution of the linewidths which was found in SMS is mainly caused by a large dispersion of the T_2-dephasing time (but not slow SD).

3. The temperature line broadening measured in the PE-experiment presents some "effective" behaviour which looks typical for glasses. But this dependence is a result of an averaging over a large number of molecules with very different individual behaviour.

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