

HOMOGENEOUS OPTICAL DEPHASING AND LINE BROADENING PROCESSES IN AN ORGANIC GLASS: COMPARISON OF THE TEMPERATURE DEPENDENCES OF PICOSECOND PHOTON ECHO AND HOLE BURNING EXPERIMENTS

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The homogeneous optical dephasing times (T_2) and the non-photochemical hole burning (NPHB) linewidths of resorufin in glycerol glass are reported from 1.1 to 25.5 K. At low temperature, the linewidths obtained from NPHB are substantially wider than the linewidths ($1/\pi T_2$) obtained from photon echo measurements, but the two become equal at high temperatures. The extra broadening of the NPHB is found to increase as $T^{0.8}$. A model of homogeneous dephasing including both two-level system and pseudolocal mode contributions is successful over the entire temperature range.

1. Introduction

The measurement of optical dephasing of dilute chromophores has proven to be a very useful probe of dynamics in low-temperature crystals [1]. More recently, a variety of studies have attempted to extend optical dephasing measurements to the study of dynamics in low-temperature glasses, particularly the dynamics of the two-level systems (TLS) which are modes characteristic of glassy materials [2-4]. Most of the studies on organic glasses have relied on linewidths from persistent spectral hole burning experiments to derive the homogeneous dephasing times [3,5]. However, recent photon echo experiments in ethanol glass doped with resorufin have shown that spectral holes in glassy materials can be broadened by dynamic processes not involved in homogeneous dephasing [6]. These results not only called for a reinterpretation of previous hole burning experiments, but also suggested that new information on these additional dynamic processes can be obtained by a combination of hole burning and photon echo experiments. Furthermore, the photon echo experiments demonstrated new and unexpected results on the form of the dephasing decay function and the temperature dependence of the dephasing time [16].

This Letter reports an extensive comparison of photon echo and hole burning results. The system

studied was glycerol glass doped with resorufin. Hole burning measurements are again found to include extra broadening processes which do not affect photon echo measurements. Therefore the hole burning does not directly measure the homogeneous dephasing time. A comparison of data from both experiments is made over a wide temperature range, leading to the first determination of the temperature dependence of the extra hole broadening processes. In addition, the qualitative features of dephasing found in ethanol glass are shown to hold in an entirely different glassy matrix, demonstrating that they are not unusual features of a specific system. The photon echo experiments again have exponential decays. The temperature dependence of the dephasing time does not fit the simple power laws normally used to describe hole burning results. Instead a model [7] which includes dephasing by librational motion of the chromophore (or other pseudolocal modes) fits the data well. The temperature range covered in this study is 2.5 times wider than in the previous study, providing a rigorous test of this model. The importance of non-TLS motions in dephasing in glassy systems is clearly indicated.

2. Experimental procedures

Photon echo and hole burning measurements were made on a 2×10^{-4} mol/l solution of resorufin (Aldrich) in glycerol in a 1 mm spectroscopic cuvette. The sample was placed in either a liquid-helium immersion dewar or a variable temperature flow cryostat. The temperature was varied between 1.1 and 25.5 K and controlled to better than 0.05 K.

The photon echo experiments were performed with an amplified picosecond laser which produces tunable 2 μ J pulses at 700 Hz. Both the laser system and the experimental apparatus have been described elsewhere [6,8]. An instrumental time resolution of 4 ps was determined by recording the self-diffraction decay of a room temperature dye solution which has a very fast dephasing time. To excite only transitions to the vibrationally unexcited S_1 state, the photon echoes were performed at 588 nm, which is to the red of the absorption maximum at 586 nm. Previous experiments [6] indicate that there is no wavelength dependence to the dephasing times.

Hole burning of the sample caused a significant decrease of the photon echo signal during the time the echo decay was scanned (fig. 1a). To correct for this effect, the decay of the echo signal with irradiation time was recorded at a fixed pulse separation (fig. 1b) and divided into the measured echo decay. The echo decays were scanned from large to small pulse separations to maximize the signal at large separations. As a result the measured echo decay curves are highly distorted (fig. 1a), but after accounting for the hole burning effect, single-exponential decays are found (figs. 1c and 2). The decay of the echo signal with irradiation time was found to be independent of the pulse separation used. This result validates the procedure used to remove hole burning effects, and also shows that the dephasing time is independent of the extent of hole burning, as found previously for the system resorufin in ethanol [6]. It should be noted that similar experiments on resorufin in ethanol [6] required a more complicated procedure to compensate for hole burning because the burning rate of resorufin in ethanol is three times faster than in glycerol.

The total dephasing time (T_2) is four times the echo decay time and gives the homogeneous line-

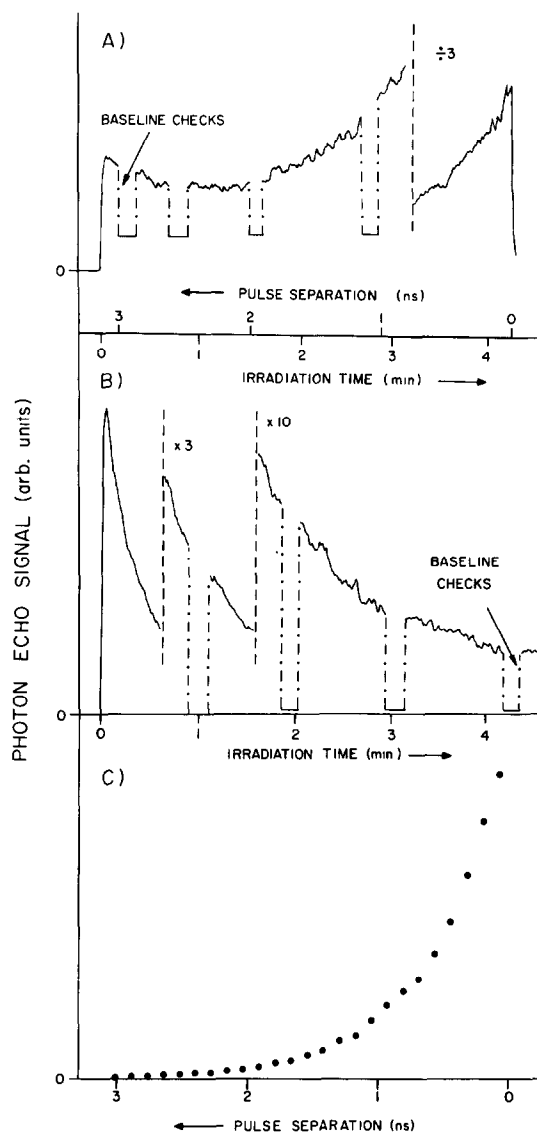


Fig. 1. Method for removing hole burning effects from photon echo decay for resorufin/glycerol glass. (A) The photon echo decay recorded by continuously varying the pulse separation from long to short separations (upper x-axis). The photon echo signal decreases with irradiation time (lower x-axis) because of hole burning, resulting in a distorted echo decay. (B) The photon echo signal recorded as a function of irradiation time for fixed pulse separation. (C) Curve (B) divided into curve (A), resulting in the echo signal as a function of pulse separation, free from hole burning effects. The dash-dotted lines indicate blockage of excitation beams to measure the contribution to the signal by scattered light. The dashed lines indicate scale changes. If a portion of either curve (A) or (B) is missing due to baseline checks, a reasonable interpolation is made. These data were recorded at 3.15 K.

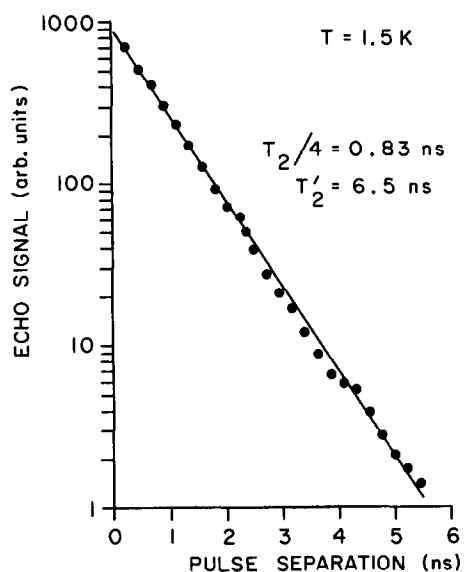


Fig. 2. Semi-log plot of photon echo decay of resorufin in glycerol glass at 1.5 K as a function of pulse separation. The decay is exponential over 6.2 lifetimes (see fig. 1). The dephasing time, T_2 , is four times the decay time. The pure dephasing time, T_2' , has the excited state lifetime contribution to the decay time removed.

width ($\Gamma_{\text{HOM}} = 1/\pi T_2$). The pure dephasing time (T_2') and corrected homogeneous linewidth ($\Gamma'_{\text{HOM}} = 1/\pi T_2'$) are found by removing the fluorescence lifetime (T_1) contribution ($1/T_2' = 1/T_2 - 1/2T_1$). For this purpose, the fluorescence lifetime of a 2×10^{-6} mol/l solution of resorufin in glycerol in a 1 mm path length cell was measured. The sample was excited at 2 Hz with 4 ps pulses with energies ranging from 0.1 to 10 nJ. Fluorescence was collected at 90° , passed through filters to eliminate laser light, and detected with a Hamamatsu R1645U multichannel plate photomultiplier connected to a Tektronix R7912 transient digitizer. The response time of the system was 1.1 ns. The lifetime was measured at 1.5 K with excitation wavelengths from 580 to 600 nm. Great care was taken to avoid artificially increasing the measured decay time by absorption and re-emission of the fluorescence. A very low optical density sample was used and the fluorescence decay time did not change with excitation wavelength, demonstrating that fluorescence re-emission was negligible. The measured lifetime of 3.4 ± 0.2 ns is comparable to measurements in other solvents [9],

but is a factor of two shorter than the time reported by Thijssen and Völker [10].

Temperature-dependent hole burning experiments were carried out over the range 1.7–25.5 K. A Coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to burn and detect the holes as described in ref. [6]. All hole burning was carried out near 590 nm. Burn fluences ranged from $12 \mu\text{J}/\text{cm}^2$ at 1.7 K to $7.5 \text{ mJ}/\text{cm}^2$ at 25.5 K, and holes were detected with 0.02 – $0.2 \mu\text{W}/\text{cm}^2$. A range of hole depths, including holes as shallow as 1%, were measured at all temperatures. The hole width was independent of hole depth for shallow holes at all temperatures. Linewidths were found by taking one half of the fwhm of the shallow holes.

3. Results and discussion

Photon echo decays from resorufin in glycerol glass were measured from 1.1 to 21 K. The decays were single exponentials at all temperatures within the experimental signal to noise (see fig. 2). The corresponding homogeneous linewidths are shown in figs. 3 and 4. An exponential decay extending over 6.2 lifetimes is shown in fig. 2. Exponential decays have also been observed for resorufin in ethanol glass [6] and for the inorganic glass $\text{Nd}^{3+}:\text{SiO}_2$ [11]. This is a significant result since a large number of chromophores from a variety of microscopic environments contribute to the photon echo signal. If the different environments produced different dephasing rates, the total echo decay would be highly non-exponential. Within a model proposed by Huber, Broer and Golding an exponential echo decay occurs only if the solute and solvent are coupled by long-range dipole-dipole interactions [12].

Hole burning linewidths ($\Gamma_{\text{HB}} = \frac{1}{2}$ fwhm) were measured over the temperature range 1.7–25.5 K and are shown in fig. 3 with the contribution from the lifetime removed. As in the previous study of resorufin in ethanol, the linewidths from NPHB low temperatures are significantly wider than the homogeneous linewidths. At 1.7 K, $\Gamma_{\text{HB}} = 3.6 \Gamma_{\text{HOM}}$. If Γ_0 is removed from both linewidths, $\Gamma'_{\text{HB}} = 5.7 \Gamma'_{\text{HOM}}$. However, the current measurements extend to much higher temperatures, and show that the two widths coalesce when the homogeneous width becomes suf-

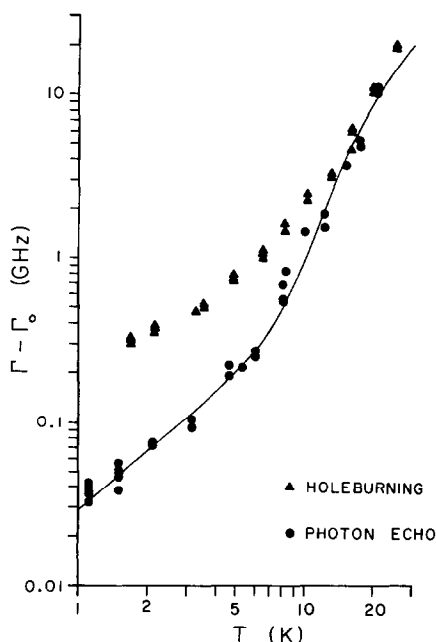


Fig. 3. Log-log plot of the temperature dependences of the line-widths measured by photon echoes and by hole burning. $\Gamma_{\text{HOM}} = 1/\pi T_2$ for photon echo measurements; $\Gamma_{\text{HB}} = \frac{1}{2}$ fwhm for hole burning measurements. The excited state lifetime contribution, $\Gamma_0 = 1/2\pi T_1$, where T_1 is the excited state fluorescence lifetime, has been removed. Neither photon echo nor hole burning data are well described by a single power law. The solid line is the best fit of the photon echo data to eq. (2).

ficiently large. Fig. 3 clearly shows that neither the photon echo nor the hole burning data can be described by a single-power law.

The failure of hole burning measurements to measure the homogeneous dephasing time is not entirely surprising. Any ground state spectral diffusion process which changes the transition frequency of the chromophore on a timescale between the dephasing time and the minute timescale on which the hole burning experiment is done will not affect the photon echo measurement, but will cause the hole to broaden [6]. This effect has been demonstrated in a crystalline system, although the underlying mechanism is different for that case [13]. Evidence for ground state spectral diffusion on a microsecond timescale has been found in the inorganic glass $\text{Nd}^{3+}:\text{SiO}_2$ with a stimulated photon echo [14] and on the minutes to days [15] and microsecond [16] timescales in organic glasses using hole burning. Putikka and Huber have numerically calculated the

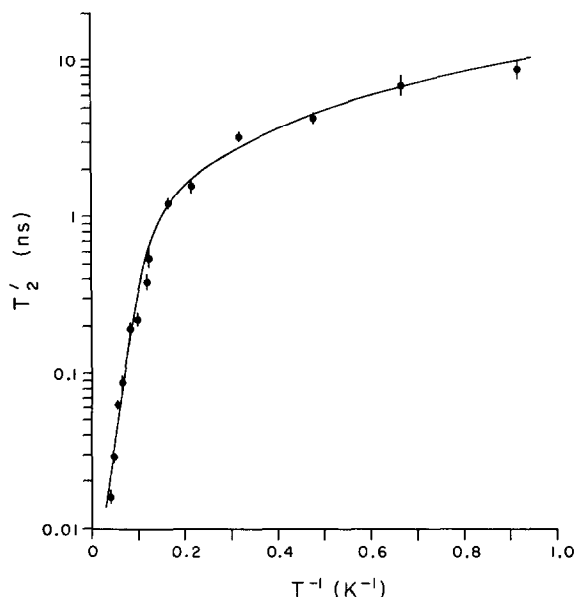


Fig. 4. Arrhenius plot of the temperature dependence of the pure dephasing times (T_2) of resorufin in glycerol glass from photon echo measurements (see also fig. 3). The linear behavior at high temperatures (left-hand side of the plot) is characteristic of dephasing by the chromophore's libration or by other pseudolocal modes. The point for each temperature is the average of several measurements. The solid line is the best fit to eq. (2).

difference between photon echo decays and optical lineshapes in $\text{Nd}^{3+}:\text{SiO}_2$, and shown that the long relaxation times in the glass cause large differences in the two measurements [17].

It should also be noted that in both the previous [6] and the current comparisons of hole burning and photon echoes, the hole burning occurs through a non-photochemical process. The mechanism for non-photochemical hole burning is poorly understood and it is possible that the hole burning process can cause additional broadening [18]. It has already been shown that NPHB linewidths display a large sensitivity to experimental conditions [19,20].

The holes measured at all temperatures were well fit by Lorentzians. Lorentzian lineshapes are often assumed to indicate homogeneous broadening, but there are well known cases where Lorentzian lines arise from inhomogeneous broadening [21]. Because both the homogeneous and hole burning lineshapes are Lorentzian, the contribution of the homogeneous linewidth to the hole can be removed by simply subtracting the widths,

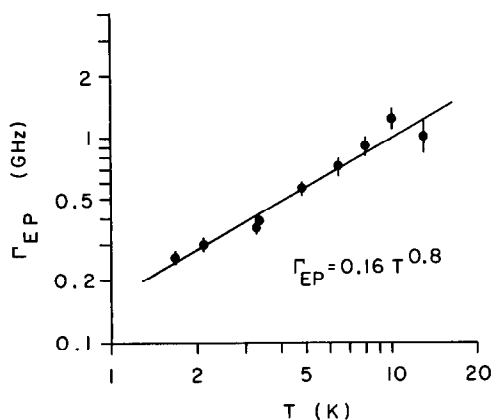


Fig. 5. Temperature dependence of Γ_{EP} , the extra line broadening process observed in NPHB measurements. $\Gamma_{EP}(T) = \Gamma_{HB}(T) - \Gamma_{HOM}(T)$, where Γ_{HB} is the linewidth obtained from NPHB, and Γ_{HOM} is the homogeneous linewidth obtained from photon echo measurements.

$$\Gamma_{EP}(T) = \Gamma_{HB}(T) - \Gamma_{HOM}(T), \quad (1)$$

where $\Gamma_{EP}(T)$ refers to the contribution to the hole burning linewidth by the extra broadening process, and $\Gamma_{HB}(T)$ is the hole burning linewidth and $\Gamma_{HOM}(T) = 1/\pi T_2$. The temperature dependence of the extra process is shown on a log-log plot in fig. 5. The temperature dependence follows a power law with an exponent of 0.8 ± 0.1 ($\Gamma_{EP} = 0.16 \text{ GHz } T^{0.8}$). Similar results are obtained for resorufin in ethanol, but with an exponent of 1.2 [22]. Temperature-dependent hole burning results for resorufin in ethanol over a narrow temperature range [10] were described by a power law with the same exponent as the power law describing the temperature dependence of photon echoes [6]. Jankowiak et al. have discussed the implications of this result [18]. The current results in glycerol show distinct differences in the power law exponents describing the low-temperature hole burning and photon echo results (fig. 3). It is apparent that since Γ_{EP} and Γ_{HOM} are described by different power laws, the hole width, which is the sum of Γ_{EP} and Γ_{HOM} , has a temperature dependence which is different from the temperature dependence of Γ_{HOM} .

If the extra process is assumed to be ground state spectral diffusion, there are two possible sources for the temperature dependence of Γ_{EP} . It could be that the range of the frequency excursion which chro-

mophores undergo is increasing with temperature. Alternatively, it could be that spectral diffusion occurs on timescales ranging from shorter than the time of hole burning experiments to times longer than hole burning experiments. As the temperature increases, the entire range could shift to shorter times, so that more of the spectral diffusion is observed by the hole burning experiment.

Traditionally, the temperature dependence of optical dephasing in glasses has been described by a T^α temperature dependence, where $1 \leq \alpha \leq 2$ [4,5]. This weak temperature dependence is characteristic of glasses and has been attributed to the interaction of the chromophore with TLS present in the host. However, the homogeneous dephasing times of resorufin in ethanol glass do not follow a simple power law temperature dependence [6]. Instead the temperature dependence was interpreted as a combination of dephasing due to TLS motion and dephasing due to a second process such as librational motion of the chromophore or some other pseudolocal phonon mode [6,7]. The net dephasing rate is then

$$1/T_2 = aT^\alpha + b \exp(-\Delta E/kT), \quad (2)$$

where T_2 is the pure homogeneous dephasing time, ΔE is the librational (pseudolocal mode) frequency, and $1/b$ is related to the librational lifetime. The first term arises from the TLS dephasing and the second term from a libration or pseudolocal phonon dephasing.

The current data in glycerol extend over a much wider temperature range and thus provide a much more rigorous test of eq. (2) than the ethanol study. Fig. 3 shows that the deviation from a power law is severe. The Arrhenius plot in fig. 4 emphasizes the activated behavior of the dephasing times at high temperatures. A good fit to eq. (2) is found with the parameters $a = 0.9 \times 10^{-4} \text{ ps}^{-1} \text{ K}^{-\alpha}$, $\alpha = 1.2$, $b = 0.33 \text{ ps}^{-1}$, and $\Delta E = 37 \text{ cm}^{-1}$ (figs. 3 and 4). Values of α between 1.0 and 1.4 are also consistent with the data, if the other parameters are changed somewhat [22]. The pseudolocal mode parameters are very similar to those found for resorufin in ethanol [6,22]. It would be expected that the librational motion of the same chromophore in different matrices would be similar, although not identical. (It should be noted

that the remeasurement of T_1 has changed the results stated in ref. [6] slightly [22].)

4. Concluding remarks

In conclusion, a detailed comparison of photon echo and non-photochemical hole burning results has been made over a wide temperature range. This has allowed the measurement of the weak, but non-zero temperature dependence of the extra broadening process which contributes to the hole burning measurements. In addition the conclusions regarding the exponentiality of the echo decay and the importance of pseudolocal modes associated with the chromophore as well as two-level system dynamics in optical dephasing in glasses have been reconfirmed in a second organic glass. This demonstrates that these effects are not unique to one particular glass, but may apply to a wide range of glasses.

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