

## Section 2. Optical Hole Burning

# PICOSECOND PHOTON ECHO AND OPTICAL HOLE BURNING STUDIES OF CHROMOPHORES IN ORGANIC GLASSES

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The range of relaxation rates present in amorphous systems is shown to affect the results of optical dephasing measurements. The interpretation of these experiments in terms of four-time correlation functions is introduced. Photon echo and hole burning results are shown for resorufin in three glass hosts: ethanol, *d*-ethanol, and glycerol. The hole burning data are shown to be affected by slow relaxation processes whereas the echo results are not. The implications of a slowest relaxation rate in amorphous systems are also considered.

## 1. Introduction

The study of the optical dephasing of molecules in condensed matter systems can give valuable information about the dynamics of such systems. In recent years, a variety of different dephasing experiments have increased our knowledge about the interactions present in both crystalline and amorphous systems [1]. An isolated molecule in a mixed crystal is surrounded by an ordered host matrix and can interact with the bulk modes of the lattice, the acoustic and optical phonons. In addition, the solute molecule itself can undergo motions which are referred to as pseudo-local modes. By contrast, molecules in a glass experience a wide range of local environments because of the variety of structures of the solvent shells around each molecule.

The local structures associated with a glassy system are not static even at very low temperatures (1.5 K). In organic glasses, small potential barriers separate different local mechanical configurations. Tunneling and thermal activation result in constantly changing solvent structures. This is in contrast with a crystal in which phonon-induced fluctuations occur about a single equilibrium lattice structure.

The constantly changing local structures in a glass cause the heat capacities of glasses to be markedly different at low temperatures than those of crystals [2]. Anderson and co-workers and Phillips independently proposed a model based on the two-level system (TLS) to explain these differences [3,4]. TLS represent extra degrees of freedom characteristic of the glassy state and they contribute a term approximately linear in temperature to the temperature dependence of the heat capacity of a glass. Briefly, a TLS is composed of two local potential minima separated by a barrier. Changes in local glass structure are modelled as transitions between the two potential minima. There is a

wide distribution of energy differences of the TLS potential minima and a wide distribution of tunneling parameters which are responsible for transitions between local configurations. Thus there is a very wide range of time scales associated with the dynamics of the TLS. For example, this is manifested in the time dependence of the heat capacities of glasses [5].

In addition to direct phonon induced fluctuations, the changes in the local configuration of a glass can modulate the transition energies of a solute chromophore. If the solute were not coupled to the environment, an absorption spectrum would reveal a line broadened only by the electronic excited state lifetime ( $T_1$ ). Since the chromophore is coupled to environment the energy levels fluctuate yielding a broader linewidth (frequency domain description) or alternately a shorter dephasing time (time domain description). However, an absorption spectrum of a chromophore in a glass is dominated by inhomogeneous broadening. Inhomogeneous broadening is a result of the wide variety of static solvent configurations found in glasses. To extract dynamical information from the dephasing of electronically excited chromophores, it is necessary to obtain lineshape information with inhomogeneous broadening removed.

## 2. Brief description of the theory of dephasing experiments

The optical transition energies of chromophores in a glass will be affected by processes in the medium which occur on a wide variety of time scales. The time scales will range from extremely fast fluctuations to much slower configurational changes, and finally to totally static inhomogeneities. It is therefore necessary to carefully consider the sensitivity of various spectroscopic observables to the distribution of time scales.

Dephasing experiments have traditionally been treated with optical absorption formalisms. That is, the lineshape is related to the Fourier transform of a two-time dipole-moment correlation function [6]:

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$$\langle \mu(\tau)\mu^*(0) \rangle \Rightarrow \left\langle \exp i \int_0^\tau \Delta(t') dt' \right\rangle. \quad (1)$$

$\mu$  is the dipole moment operator at times 0 and  $t$ , and  $\Delta$  represents environmental energy perturbations including static terms describing inhomogeneous broadening and dynamic terms arising from motions in the glass. The optical absorption experiment is the Fourier transform of the optical free induction decay. It is sensitive to all time scales from the fastest fluctuations to the static inhomogeneities. In a glass, the inhomogeneous broadening will mask the dynamical information of interest. The two-time correlation function is not an appropriate description for line narrowing experiments such as photon echoes or hole burning experiments which are actually performed in chromophore-glass systems.

We have recently developed an appropriate formulation for interpreting line narrowing experiments used to study glassy systems [7]. Using the formalism of Mukamel [8] and Mukamel and Loring [9], we have been able to derive the correct four-time correlation functions which properly describe the line narrowing experiments. The correlation function for the photon echo experiment is [10,11]

$$\langle \mu^*(2\tau)\mu(\tau)\mu(\tau)\mu^*(0) \rangle \Rightarrow \left\langle \exp i \left[ \int_\tau^{2\tau} \Delta(t') dt' - \int_0^\tau \Delta(t') dt' \right] \right\rangle. \quad (2)$$

In this experiment, a pulse of light resonant with the optical transition of the chromophore excites the sample at time  $t=0$ . A second pulse excites the sample at time  $t=\tau$ . The echo, a coherent pulse of light, emerges from the sample at  $t=2\tau$  and its intensity is measured as a function of the pulse separation,  $\tau$ . Consider a situation in which there is only static inhomogeneity. The integral from 0 to  $\tau$  will be identical to the integral from  $\tau$  to  $2\tau$ , and the two terms will cancel. In this manner, the echo pulse sequence removes static inhomogeneity from the optical dephasing measurement. However, in a real system, there will also be random fluctuations in energy in addition to the static inhomogeneity. The random fluctuations will not be identical in the intervals 0 to  $\tau$  and  $\tau$  to  $2\tau$ . Therefore the terms will not exactly cancel and will measure the optical dephasing induced by random fluctuations on the time scale of  $\tau$ .

It was also proven in ref. [7] that the correlation function which describes hole burning and other such experiments, is the same as that which describes the stimulated photon echo. In fact hole burning is the Fourier transform of the stimulated echo which is a three-pulse sequence originally developed in magnetic resonance to measure spectral diffusion [12]. Its correlation function is

$$\langle \mu^*(2\tau + T_w)\mu(\tau + T_w)\mu(\tau)\mu^*(0) \rangle \Rightarrow$$

$$\left\langle \exp i \left[ \int_{T_w+\tau}^{T_w+2\tau} \Delta(t') dt' - \int_0^\tau \Delta(t') dt' \right] \right\rangle. \quad (3)$$

There are two time scales evident in eq. (3). The first is  $\tau$ , as in the photon echo experiment. The second is a much longer time,  $T_w$ . Experiments describable in terms of eq. (3) will eliminate static inhomogeneous broadening, but will be sensitive to slow dynamics on the time scales out to the time  $T_w$ . Equation (3) is the basis of describing fluorescence line narrowing, phosphorescence line narrowing, accumulated grating echoes, and hole burning experiments. For fluorescence line narrowing,  $T_w$  is on the order of the fluorescence lifetime. For phosphorescence line narrowing and accumulated grating echoes,  $T_w$  is on the order of the triplet state lifetime. In a hole burning experiment,  $T_w$  is on the time scale required to perform the experiment, i.e. write and read the hole, typically 100 s. The photon echo experiment is the limit of all four-time correlation function experiments in which  $T_w$  goes to zero. Therefore the echo experiment, in a system such as a glass in which there exists a wide distribution of time scales, will yield the narrowest spectroscopic line. It is sensitive to only the fastest dynamics on the time scale of  $\tau$ .

The important point is that each of the four-time correlation function experiments is sensitive to dynamics on a different time scale. Since glass systems exhibit a wide distribution of time scales for dynamics and therefore optical dephasing, a combination of the echo experiment, which measures the homogeneous dephasing, and experiments such as hole burning, in which  $T_w$  is not zero, which measure homogeneous dephasing and slower spectral diffusion processes, can provide a detailed picture of the multitime scale dynamics in glasses.

### 3. Experimental results and discussion

We report the results of temperature-dependent hole burning and photon echo experiments on resorufin in ethanol, *d*-ethanol, and glycerol glasses. The details of the picosecond laser system used for the echo experiments and the narrow-band dye laser used for the hole burning experiments have been described extensively elsewhere [13]. Solutions of resorufin in the various solvents (all were  $\sim 2 \times 10^{-4}$  M) were placed in 1 mm spectroscopic cuvettes and were immersed in either a liquid helium cryostat or a variable temperature flow cryostat. The temperature was varied between 1.5 and 11 K for the ethanol and *d*-ethanol samples and between 1.1 and 25.5 K for the glycerol samples. Temperature regulation was better than 0.05 K. The experiments were performed well to the red of the absorption maxima in all samples in order to eliminate contributions from vibronic states of resorufin. The echo decays and hole widths were found to be independent of wavelength. The echo experiments were tested for optical density, concentration, sample heating,

and power-dependent effects [7,13]. The echo data were collected in a manner to remove the effect of hole burning during the echo decay measurements. The procedures have been described in detail previously [7,13,14]. In all cases the echo results were consistent and free of artifacts. The hole burning experiments were carefully performed to avoid broadening of the holes by excessive power, burn time or hole depth. In the resorufin ethanol glass discussed below, hole widths agreed perfectly with those from another laboratory [15,16].

It is well known that ethanol can form two different glass-like phases depending on the cooling rate of the sample [17]. A cooling rate of  $<0.5$  K/s has been shown to produce a glassy plastic-crystal phase whereas a rate of  $\sim 1$  K/s produces a truly amorphous phase. In all cases, the cooling rate of the samples exceeded 1 K/s. A variety of cooling rates considerably faster than 1 K/s gave identical results. The echo and hole burning experiments were performed on samples cooled in an identical manner. Hence the results presented are characteristic of the true glass phase of ethanol, and there is no possibility that they were performed on the plastic crystal phase.

Glycerol is very hygroscopic and water content can affect parameters such as the TLS structure. Therefore, experiments performed on samples not identically prepared cannot be meaningfully compared. All of the photon echo and hole burning data presented here were obtained on identical samples. In order to isolate pure dephasing from lifetime effects, the fluorescence lifetimes of the chromophore were measured in each solvent. Great care was taken to avoid reabsorption and other experimental problems which can produce inaccurate lifetimes [7].

A typical hole and echo decay are shown in fig. 1. All of the holes were Lorentzian and all of the echo decays were exponential. Note that the echo decay is single exponential over many factors of  $e$ . The temperature dependences of the echo and hole burning experiments for resorufin in ethanol glass are shown in fig. 2. Hole burning data on this same system taken in another laboratory are also shown [15,16]. At the temperatures in which holes were measured in both laboratories, the data are identical. The temperature dependences of the echo and hole burning data for resorufin in glycerol are shown in fig. 3(a).

The most important feature of figs. 2 and 3(a) is that the echo experiment measures a dephasing time which is slower than the dephasing times from hole burning experiments for  $T < 10$  K. In ethanol, the hole burning dephasing time is approximately a factor of 4 faster than the homogeneous dephasing time at 1.5 K. As discussed in connection with the proper four-time correlation function descriptions of these experiments, this is to be expected. The echo is sensitive to the homogeneous dephasing of the chromophore-glass system. The hole burning experiment, being essentially the Fourier transform of a stimulated echo experiment, is sensitive to homogeneous dephasing and spectral diffusion, i.e. slow dynamics which occur on time scales out to the time  $T_{\infty}$ .

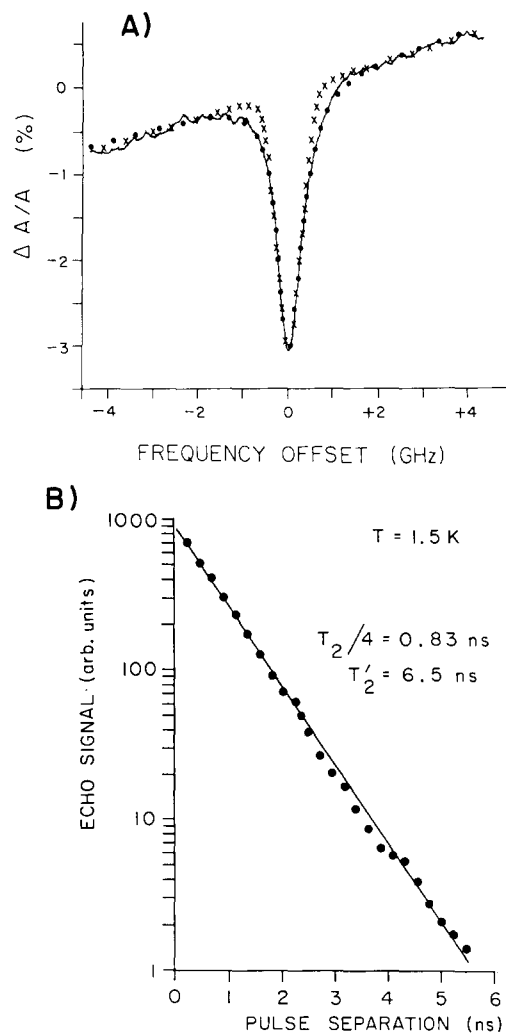


Fig. 1. (A) Spectrum of hole burned in the resorufin/glycerol system at 1.7 K. A Lorentzian fit to the experimental hole shape is indicated by the solid black circles. An attempt to fit the hole with a Gaussian is also shown ( $\times$ ). Similar results were found for all hole depths in all samples. (B) A semilog plot of the photon echo signal in resorufin in glycerol glass at 1.5 K as a function of pulse separation. The decay is exponential over 6.2 lifetimes. Similar results were found in all samples.

Since the hole burning experiments operate on a time scale about twelve orders of magnitude longer than the echo experiments, the holes are broadened by very slow configurational changes in the glass, which appear static to and are rephased by the echo experiment. The observed differences between hole burning and echo experiments do not imply that either experiment is in error. Rather the differences are due to the broad distribution of time scales for dynamics in glasses and the inherent differences in the correlation functions measured by each experiment. The agreement between the two experiments for  $T > 10$  K does not imply that spectral diffusion has stopped. It is due to the onset of pseudolocal mode dephasing. This is an acti-

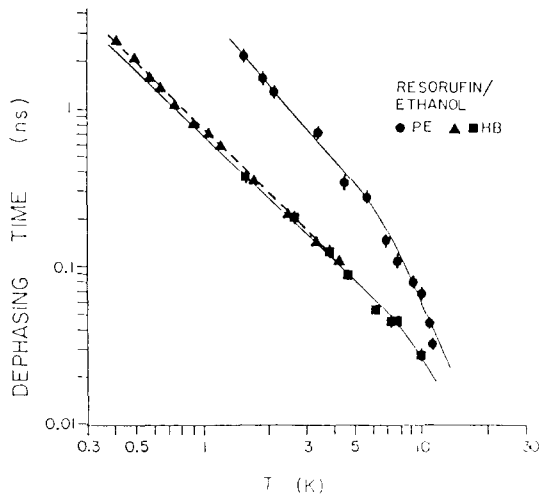


Fig. 2. Log-log plot of temperature dependent hole burning dephasing times [ $2/\pi(\text{FWHM})$ ] (■) compared to photon echo dephasing times ( $\bullet$ ) for resorufin in ethanol glass. The hole burning data of Van den Berg and Völker [15,16] are also shown ( $\blacktriangle$ ). The fluorescence lifetime contributions have been removed from all measurements. The hole burning and photon echo measurements give different results at low temperature where spectral diffusion dominates the hole width. The solid lines are the best fits of our data to eqs. (4) and (5). The dashed line results from slight adjustment of spectral diffusion parameters for the best agreement with the low temperature data of Van den Berg and Völker.

vated process and has a much steeper temperature dependence than the slow spectral diffusion and dominates dephasing at high temperatures.

Figure 3(b) shows a comparison of echo and hole burning results obtained for ethanol and *d*-ethanol (-OH group replaced by -OD) glasses. Again different dephasing times are measured with echo and hole burning experiments at low temperature, but the two measurements coalesce at high temperatures. The deuteration of the hydroxyl proton slowed the hole burning rate dramatically but it did not affect the dephasing dynamics [7].

The formal theoretical evaluation of the correlation functions briefly described in sect. 2 yields a simple procedure for combining echo and hole burning data to obtain a separation of information on fast and slow dynamical processes in glasses. The formal treatment shows that subtracting the homogeneous linewidth determined by the echo experiment from the linewidth determined from hole burning experiments on the same sample at the same temperature provides a direct measure of the spectral diffusion. We call this difference in widths  $\Gamma_{SD}$ , where the SD stands for spectral diffusion. The temperature dependences of the measurements of  $\Gamma_{SD}$  in ethanol and glycerol are shown in fig. 4.

The total temperature dependence of the echo decays is determined by the homogeneous dephasing from TLS dynamics, pseudo-local mode dephasing and the excited state lifetime contribution. Excluding the excited state

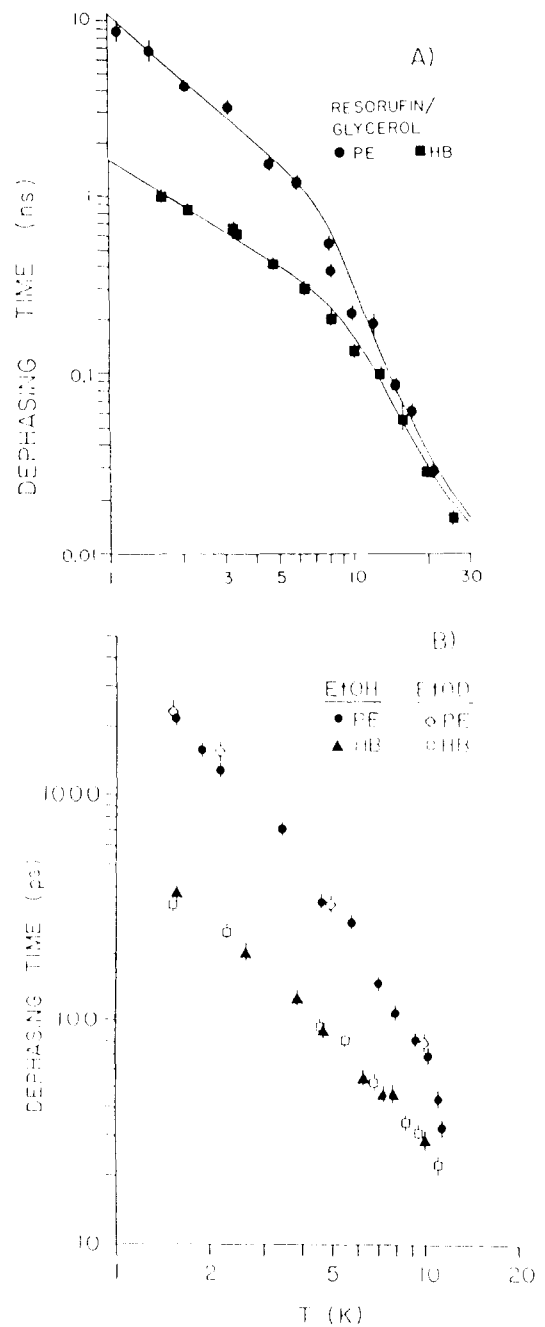


Fig. 3. (A) Log-log plot of photon echo ( $\bullet$ ) and hole burning ( $\blacksquare$ ) dephasing times for resorufin in glycerol. Solid lines are the best fits to eqs. (4) and (5). Although slow spectral diffusion causes the hole burning and photon echo measurements to give different dephasing times at low temperatures as in resorufin/ethanol (see fig. 2), the two measurements coalesce at high temperatures where pseudolocal mode dephasing dominates. (B) Effect of deuteration of the glass matrix on photon echo and hole burning dephasing times. The temperature-dependent pure dephasing times are shown on a log-log plot.  $\bullet$ , photon echo, ethanol;  $\diamond$ , photon echo, *d*-ethanol;  $\blacktriangle$ , hole burning, ethanol;  $\square$ , hole burning, *d*-ethanol. There are no differences between the deuterated and protonated glasses which are larger than the experimental error.

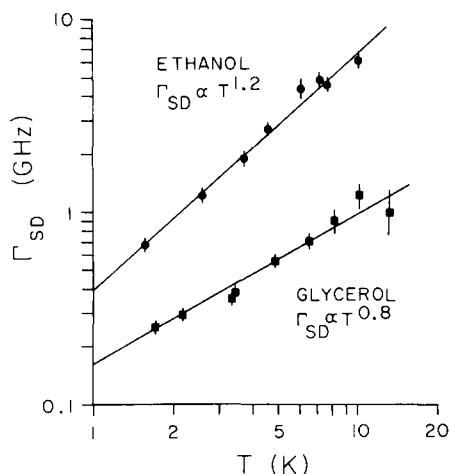


Fig. 4. Log-log plot of the temperature dependence of the spectral diffusion linewidth  $\Gamma_{SD}$  defined as the difference of the photon echo and hole burning linewidths. Data are shown for resorufin in two glasses: ●, ethanol, and ■, glycerol. Both sets of data are well fit by a power law  $\Gamma_{SD} \propto T^\beta$ .

lifetime decay contribution, the echo dephasing rate as a function of temperature is given by [7,13]

$$1/T_{\text{hom}} = aT^\alpha + ce^{-E/kT}, \quad (4)$$

where the first term is the homogeneous dephasing caused by the TLS dynamics and the second term comes from pseudo-local mode dephasing. The dephasing rate measured by hole burning is given by (excluding the lifetime contribution)

$$1/T_{\text{HB}} = aT^\alpha + bT^\beta + ce^{-E/kT}, \quad (5)$$

where the first term is the TLS induced homogeneous dephasing, the second term is the TLS induced spectral diffusion, and the third term is the pseudo-local mode dephasing. The second term in eq. (5) is responsible for the extra width measured in hole burning experiments and is plotted from the experiments as a function of temperature in fig. 4.

The pseudo-local mode activation energy of resorufin,  $\Delta E$ , is  $35 \text{ cm}^{-1}$  in both ethanol and glycerol glasses. The  $\alpha$ 's are 1.6 and 1.2 in ethanol and glycerol, respectively. The  $\beta$ 's are 1.25 and 0.80 in ethanol and glycerol, respectively. Plots of eqs. (4) and (5) using these parameters are shown in figs. 2 and 3a. These parameters for ethanol were determined from our echo and hole burning measurements. The solid line through the hole burning data in fig. 2 used these parameters. Additional low-temperature hole burning data [16] were not used in the original fits. The dashed line through the data is the best fit including the additional low-temperature data. All the parameters are identical with the exception that  $\beta$  has been changed from 1.25 to 1.30. This is within the original experimental error in the determination of  $\beta$  [7]. Therefore all available data are consistent with the theoretical de-

scription of optical dephasing experiments in glasses briefly outlined in this paper.

#### 4. Conclusions

Dephasing processes in glasses occur on a wide range of time scales. We have presented temperature-dependent photon echo and hole burning data on three amorphous systems. The photon echo experiments were shown to measure the homogeneous dephasing time of the solute in the glass whereas the hole burning data include additional contributions from slow spectral diffusion. The material discussed briefly above demonstrates that experiments on a variety of time scales can give a more complete picture of glass dynamics than can any one technique. The theoretical descriptions of glasses which account for the gradual temperature dependences associated with TLS dephasing are based on the existence of a wide range of time scales for the rates of dynamics of the TLS. This same range of time scales makes experiments operating on different time scales inherently different. Theories of TLS-induced dephasing have generally taken the rates of processes in the glass to range from extremely fast to infinitely slow. This picture implies that the longer the time scale of an experiment, the wider the optical linewidth that will be measured. It is important to point out that in real glass systems there may be a slowest dynamical rate. Experiments performed on time scales long compared to the inverse of this slowest rate and then on increasingly long time scales will show no additional broadening. For experiments to be sensitive to the distribution of rates in glasses, the experimental time must vary in a range of times associated with the range of the inverse of the rates.

All optical experiments performed to date are describable in terms of appropriate four-time correlation functions. Attempts to describe the experiments in terms of two-time correlation functions mask the important distinctions among experiments. Combining echo experiments which provide a measure of the fast fluctuations with slower time scale experiments, such as hole burning, which are sensitive to the slow dynamics of structural rearrangements in addition to fast fluctuations, will provide detailed insights into the dynamics in amorphous systems.

#### Acknowledgements

This work was supported by the National Science Foundation, Division of Materials Research (#DMR84-16343). Additional support was provided by the Office of Naval Research, Physics Division (#N00014-85-K-0409). LRN would like to thank the Fannie and John Hertz Foundation for a Graduate Fellowship.

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