

TIME EVOLUTION OF NON-PHOTOCHEMICAL HOLE BURNING LINEWIDTHS: OBSERVATION OF SPECTRAL DIFFUSION AT LONG TIMES

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Received 27 February 1989; in final form 18 April 1989

Time-dependent non-photochemical hole burning linewidths for cresyl violet in ethanol glass are reported from 100 ms to 3000 s at 1.3 K. The linewidth increases by nearly a factor of two in this region, changing most rapidly in the range around 20 s. The increase in linewidth is directly related to the broad rate distribution of dynamic processes in the glass. Using the results of a theoretical analysis based on the four-point correlation function description of optical dephasing experiments, the fluctuation rate distribution is calculated. In the experimental time range, the distribution is characterized by a Gaussian function on a $\ln R$ scale centered at $R_0 = 0.4 \text{ s}^{-1}$.

1. Introduction

In this paper we present a study of the optical dephasing (hole linewidth) as a function of the experimental time scale for cresyl violet molecules in ethanol glass. From the results we are able to extract detailed information on the rates of the dynamic processes occurring in the glass.

The term optical dephasing refers to the decay of an optically induced polarization due to fluctuations in the electronic state energies. In condensed matter systems, bulk molecular dynamics are known to couple to the electronic states of embedded optical centers, greatly influencing the rate of optical dephasing [1]. The bulk dynamics occur on a wide range of time scales. In simple crystals, the dynamics are fast phonon fluctuations about the equilibrium crystal structure [2]. In complex systems such as glasses, the dynamics are both fast and slow, having a wide distribution of rates spanning a range from subpicoseconds to thousands of seconds or longer [3].

Questions about rate distributions and how they influence observable properties such as optical dephasing have been the focus of many experimental and theoretical studies [2-11]. There exists a variety of experimental techniques used to measure optical dephasing in glasses e.g. hole burning [12], two-pulse photon echo (PE) [13], and stimulated pho-

ton echo (SPE) [14]. Berg et al. [7] analyzed the various methods and showed each to be sensitive to a different region of the fluctuation rate distribution, $P(R)$. Two-pulse photon echoes are influenced predominantly by fluctuations on the order of $1/\tau$ where τ is the delay between the excitation pulses (typically hundreds of picoseconds). Hole burning and stimulated photon echoes, on the other hand, were shown to be sensitive to fluctuations with a rate from $\approx 1/\tau$ to $\approx 1/T_w$, where T_w is the delay between the second and third pulses in SPE or the delay between burning and reading in hole burning (see fig. 1). This concept of a waiting time, T_w , was shown to be characteristic of all optical line narrowing experiments. It was proven that the four-time correlation function which describes optical hole burning is the Fourier transform of the stimulated echo correlation function. Therefore, unlike PE where τ is limited by what is operationally called the homogeneous dephasing time [7], T_w for a hole burning experiment may be varied over an extremely wide range. This permits the examination of $P(R)$, the fluctuation rate distribution, for rates $\ll 1/\tau$.

The temporal dependence of dephasing experiments in glasses at long times ($T_w \gg \tau$), commonly referred to as spectral diffusion, has been hypothesized and in some cases observed [8,15]. Breinl et al. [8] reported a 30% change in the holewidth of

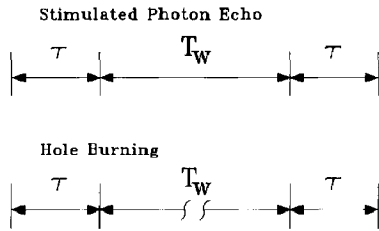


Fig. 1. Time orderings for both stimulated photon echo and hole burning experiments. For the case of SPE τ and T_w are defined as the delays between the first and second pulses and the second and third pulses respectively. The signal is generated at a time τ after the third pulse. In the case of hole burning, τ has a slightly different meaning. It is essentially the lifetime of the coherent polarization induced during the burning and reading pulses. The lifetime is of the order τ . T_w is the delay between the burning event and its detection, which is many orders of magnitude larger than τ .

quinizarin doped in a mixed alcohol glass by means of photochemical hole burning when the waiting time was varied from tens of minutes to days. Berg et al. [7] compared non-photochemical hole burning data in various organic glasses to PE data taken on the same samples and noted dramatic differences in the dephasing rates measured by the two techniques. The linewidth was observed to change by a factor of 6 between the time scales of the two experiments. Recently PE results and hole burning results with $T_w \approx 100$ s were reported for cresyl violet in ethanol glass [9], the system studied here, and again a large difference in the dephasing time was observed. The linewidth increased by a factor of 8 in going from PE to hole burning. (These PE results are used in the calculations of section 4.)

Recent theoretical work by Bai and Fayer has produced a powerful method by which the fluctuation rate distribution can be recovered from experimental observations [16]. After a brief summary of the theoretical considerations, we present the results of a waiting-time-dependent hole burning study and the fluctuation rate distribution function calculations.

2. Summary of theory

The specific nature of molecular dynamics responsible for optical dephasing in glasses is still not well understood. However, these dynamics have been

well described by the two-level system (TLS) model of amorphous systems [17]. In this model local configurational changes are characterized by transitions between two levels of a TLS. The rates of these transitions are determined by the parameters of the TLS. It is the TLS which couples to the optical centers. The molecular dynamics have also been characterized by Gaussian fluctuations about a local configurational minimum [7,10]. Together these two models represent the two extremes describing the dynamics of glassy systems. In this paper we use the results of a sudden jump TLS model [16]. The information which is extracted is virtually insensitive to the choice of model [16].

It has been shown that any standard four-wave mixing experiment, including PE, SPE, and hole burning, may be described in terms of a four-point correlation function [18]. It has also been shown that the correlation functions for the individual experiments are all variations of the SPE correlation function [7,10]. Thus by analyzing the correlation function for SPE one describes the response of all standard optical dephasing experiments. This analysis has been presented in detail elsewhere [16] and will only be briefly outlined here. The SPE correlation function for a large number of statistically independent TLS is given by [11,16]

$$C(\tau, T_w, \tau) = \exp\{-N\langle 1 - \exp[i\varphi(\tau, T_w)] \rangle_{H,r,\lambda}\}, \quad (1)$$

$$\varphi(\tau, T_w) = \int_0^\tau \Delta\omega(t) dt - \int_{T_w+\tau}^{T_w+2\tau} \Delta\omega(t) dt. \quad (1a)$$

The four times in the correlation function are the four limits in the two integrals (see fig. 1). The averages H , r , and λ are over the random history path of the perturbation $\Delta\omega(t)$ due to the TLS, and over the spatial distribution and internal parameters of the TLS. By averaging over the history path first, one obtains a solution which is independent of the coupling or internal parameters of the TLS and is, therefore, more generally applicable. The solution is of the form

$$\begin{aligned} \langle 1 - \exp(i\varphi) \rangle_H &= F_1(R\tau, \Delta\omega\tau, x) \\ &+ F_2(R\tau, \Delta\omega\tau, x) [1 - \exp(-RT_w)], \quad (2) \\ x &= E/2kT, \end{aligned}$$

where F_1 and F_2 are integral functions. Examining this solution one notes that in the limit of $T_w=0$ (PE experiment) only F_1 remains non-zero. Thus this term describes the behavior of the two-pulse echo. It can be shown that F_1 goes to zero at $R \gg 1/\tau$ and $R \ll 1/\tau$. This is consistent with the idea that only TLS with a fluctuation rate $R \approx 1/\tau$ will affect the PE observed dephasing.

The second term in the solution determines the additional dephasing (spectral diffusion) introduced when $T_w > 0$, i.e. in the SPE or hole burning experiment. The function F_2 is independent of T_w and determines only the functional form of the echo decay (line shape for hole burning) arising from spectral diffusion, whereas the rate of decay (linewidth) is determined by the factor $1 - \exp(-RT_w)$. The function F_2 , behaves differently from F_1 . It falls to zero sharply at $\approx 1/\tau$ and approaches a constant value for $R \ll 1/\tau$. Thus, including the factor $1 - \exp(-RT_w)$, the second term in the solution is a constant between the limits $1/\tau > R > 1/T_w$ whereupon it falls steeply to zero. The window like behavior of this term makes it possible to quantitatively study aspects of spectral diffusion. Simply by varying T_w , one selects the type of TLS that contribute to optical dephasing.

Letting $1/T_w, R \ll 1/\tau$, i.e. the long waiting time limit, one may calculate the history average explicitly [11,16]. The result is

$$C(\tau, T_w, \tau) = \exp\{-N \langle \sin^2(\Delta\omega\tau) \operatorname{sech}^2(E/2kT) \times [1 - \exp(-RT_w)] \rangle_{r,\lambda}\}, \quad (3)$$

where R is the fluctuation rate and E is the energy splitting of the TLS. In organic glasses such as cresyl violet in ethanol, the consistent observation of exponential echo decays and Lorentzian hole shapes [9,19,20] suggests that the TLS/chromophore coupling is dipole-dipole. The TLS are not strongly influenced by the presence of the optical centers, or equivalently, r and R are independent variables. Thus the average over r may be performed independent of R . In general one can always convert the average over λ to an average over R by first averaging over the energy separation of the TLS [10,16,21]. Thus we have

$$\begin{aligned} & \langle \sin^2[\Delta\omega(r)\tau] \\ & \times \operatorname{sech}^2(E/2kT) [1 - \exp(-RT_w)] \rangle_{r,\lambda} \\ & = \langle \sin^2[\Delta\omega(r)\tau] \rangle_r \\ & \times \langle \operatorname{sech}^2(E/2kT) [1 - \exp(-RT_w)] \rangle_{E,R}. \quad (4) \end{aligned}$$

This along with the relation of the correlation function to the optical dephasing observable leads directly to an expression for the T_w dependence of the hole burning linewidth,

$$\begin{aligned} \Delta\nu_H \propto & - \int dR P(R) [1 - \exp(-RT_w)] \\ & + T_w\text{-independent contributions} \\ & \text{of fast fluctuations.} \quad (5) \end{aligned}$$

In this context the fluctuation rate distribution

$$P(R) \propto A \int dE P(E, R) \operatorname{sech}^2(E/2kT) \quad (6)$$

is defined such that it is the average of the thermally accessible TLS, i.e. those actually influencing the behavior of optical dephasing at a given temperature T . With eq. (5), we now have the necessary tool to analyze the results of T_w -dependent line narrowing studies such as hole burning and to calculate $P(R)$. For a detailed development of the average and interpretation of the results, the reader is directed to ref. [16]. An analysis is forthcoming in which the validity of the treatment is demonstrated when it is specifically applied to the system cresyl violet in glassy ethanol [21].

3. Experimental procedure

Glasses for study were prepared by placing a solution of approximately 2×10^{-4} M cresyl violet 670 perchlorate (Exciton) in anhydrous ethanol in a 1 mm spectroscopic cuvette which in turn was placed in a liquid helium bath cryostat precooled to approximately 150 K. The cryostat was then filled, quickly cooling the sample to 4.2 K. Pumping on the helium cooled the sample further to 1.30 K, the temperature at which data were recorded. The sample temperatures were measured to within ± 0.002 K by means of a germanium resistance thermometer di-

rectly attached to the sample and also by monitoring the vapor pressure of the helium bath. Regulation was good to within ± 0.006 K over 8 h.

Holes were burned and detected at 620.5 nm using a Coherent model 599-21 scanning single mode dye laser (2 MHz bandwidth) under computer control. The samples had ODs of ≈ 0.60 at this wavelength being somewhat to the red of the absorption maximum at 610 nm [9]. Burning times and fluences ranged from 5 to 40 ms and from 20 to 160 $\mu\text{J}/\text{cm}^2$ respectively. The spot size was 250 μm . The burn times and powers were regulated by means of two acousto-optic variable beam attenuators working in tandem with a mechanical shutter. Once burned, the holes were scanned after various waiting times (T_w 's).

For each waiting time less than 20 s, the dye laser was scanned once at a rate of ≈ 100 MHz/ms. Scan times were typically 100 ms. This introduced a slight temporal uncertainty when the waiting time was on the order of the scan time. For waiting times longer than 20 s, five sweeps were averaged to increase the signal to noise ratio. One concern when repeatedly scanning is that each scan in fact burns additional chromophores possibly distorting the line shape. To minimize this effect, the detection beam was attenuated by a factor of 3000 relative to the burning intensity. As a check, long time measurements were made with many preceding short time measurements and compared to a single long time reading with no preceding readings. The results were identical.

The holes were detected in transmission using a cooled photomultiplier tube. The transmitted signal was normalized for laser intensity fluctuations using an analog divide circuit referenced to a pickoff placed immediately before the cryostat. The divided signal was then digitized by a transient recorder and stored.

Artificial hole broadening [22,23] was eliminated by burning shallow holes. Hole depths varied from 5% to 1% depending on burn fluence and waiting time. A burning fluence of 40 $\mu\text{J}/\text{cm}^2$ produced a 2% hole at a waiting time of 100 s. These fluences are consistent with holes burned with lower powers over a longer time [9]. Hole area was in general conserved. Therefore, as the hole width increased, the depth decreased in inverse proportion.

4. Results and discussion

Fig. 2 shows a hole scanned at three different waiting times. The solid lines represent the best Lorentzian fits to the data. As has been observed previously [7,9,19], all holes are Lorentzian, regardless of depth or waiting time. Fig. 3 shows the results of a waiting-time-dependent hole width study. One notes that the hole widths change very little with T_w at short times and at long times but exhibit a sharper increase in the range centered around 20 s. Qualitatively, this implies that there must be some nonzero distribution of fluctuation rates around $\approx 1/20$ s^{-1} which

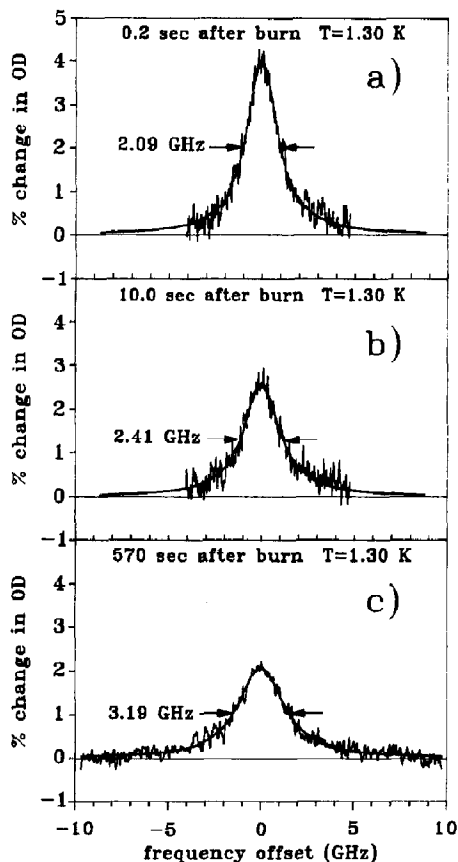


Fig. 2. Three holes burned in a 2×10^{-4} M cresyl violet in ethanol glass at 1.30 K and with various waiting times before detection. The three holes a, b, and c were detected after waiting 0.2, 10.0, and 570 s respectively. The solid lines are the best Lorentzian fits to the data. The holes were burned at 620.5 nm for 10 ms with a fluence of 48 $\mu\text{J}/\text{cm}^2$.

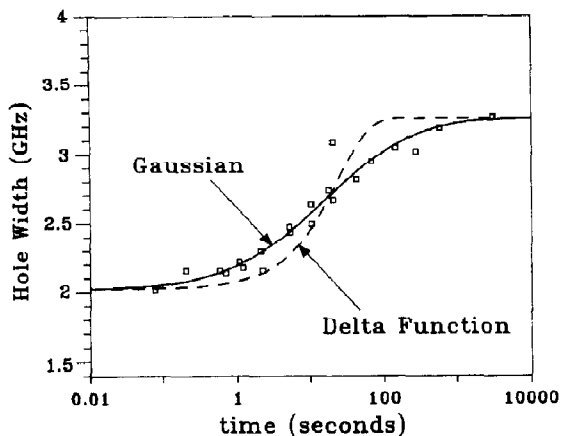


Fig. 3. Semi-log plot of fwhm of various holes versus log waiting time for a sample of cresyl violet in ethanol at 1.30 K. The hole width changes most dramatically in the range centered around 20 s while flattening out at both short and long times. This indicates there exists a distribution of fluctuation rates centered around $\approx 1/20 \text{ s}^{-1}$. The solid line through the data is the best fit to a distribution of rates which is a Gaussian function on the log scale. See text for values of the parameters. The delta function distribution, while accounting for the magnitude of the change, overestimates the steepness of the increase.

falls to zero at both shorter and longer times.

To fit the data with a rate distribution, a trial function is required. Once a functional form is selected, it is convolved with the function $1 - \exp(-RT_w)$ according to eq. (5). Adjusting the appropriate parameters yields the best fit. There is some uncertainty in choosing the form of the trial function. Convolution with the function $1 - \exp(-RT_w)$ tends to smooth out sharp features of a function. Thus we have chosen a simple distribution which gives a good fit to the data. The fit is displayed as the solid line in fig. 3. The best fit is obtained using a distribution of fluctuation rates which is Gaussian on a ln scale, i.e.

$$P(R) dR \propto \exp\left\{-\left[\ln(R/R_0)\right]^2/2\sigma^2\right\} d(\ln R), \quad (7)$$

where $R_0 = 0.043 \text{ s}^{-1}$ and $\sigma = 1.98$. A delta function (distribution is only a single rate) cannot be made to fit the data (see fig. 3), indicating the underlying distribution must have a significant width. A rectangular distribution with essentially the same center position and area as the Gaussian can also be made to fit the data fairly well. The fit is not as good, however, and such a distribution is unphysical. The

Gaussian distribution is a simple, two-parameter function which gives an excellent fit to the data.

Fig. 4 shows the final form of the fluctuation rate distribution function obtained from a combination of T_w -dependent hole burning experiments and PE experiments. The narrowest hole linewidth detected is still a factor of 5 broader than the linewidth obtained from the PE experiments. Therefore, there is significant broadening between 10 ns and 10 ms. The fact that the PE decays are exponential [9] demonstrates that the distribution goes as $P(R) \propto 1/R$ on the PE time scale of $\approx 1 \text{ ps}$ to 10 ns [16]. The $1/R$ distribution when plotted on a log scale is a horizontal line. This is shown in the large R part of fig. 4. The shape of the fluctuation rate distribution between 10 ns and 10 ms is still unclear; however, the magnitude of the broadening between these times specifies the area under the curve in this region. If the distribution continues past 10 ns as $1/R$, the area constraint dictates a cut off at $\approx 10 \text{ ms}^{-1}$. This is

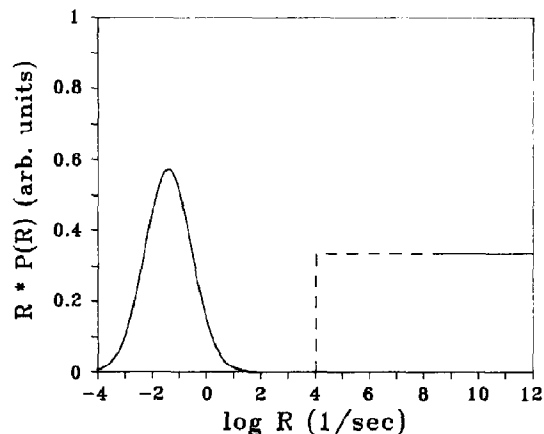


Fig. 4. Plot of the Gaussian fluctuation distribution used to fit the data in fig. 3. When $P(R)$ is weighted to the final hole width, $\Delta\nu_H(\infty)$, the area under this part of the curve is 1.3 GHz. The echo measurement at this temperature is sensitive to rates centered around $\log R \approx 10$ [9]. The exponential form of the PE decay implies that the distribution of rates is $P(R) \propto 1/R$ (horizontal line) on the echo time scale, 1 ps to 10 ns (solid line). The shape of the distribution from $1/10 \text{ ms}^{-1}$ to $1/10 \text{ ns}^{-1}$ has not been determined; however, the area under the curve in this region is known from a comparison of hole burning and photon echo data (dashed line). Note that it is the area under the dashed line and not its shape which has been determined (see text). The area under the curve from the echo time scale to the cutoff is 2.0 GHz.

represented by the dashed line in fig. 4. The dashed line is included not to suggest some information of the shape of the distribution, but to reflect knowledge of the area under the fluctuation rate curve in this region. Any function which maintains the same area under the curve will also account for the broadening. In light of the slow rate ($R < 1/10 \text{ ms}^{-1}$) results reported here, it is conceivable that the distribution is more structured at fast times than is shown in fig. 4. Waiting-time-dependent experiments carried out in this region will pin down the further details of the fluctuation rate distribution.

The results reported here represent an important advance in the development of probes of dynamics in complex condensed matter systems. In a typical lineshape study of optical dephasing in a simple crystal, the fluctuation rate distribution is known (for example, a Debye density of acoustic phonon states), and the question involves the strength of coupling to the phonons [2]. In complex systems, such as glasses, complex crystals, or proteins, the fluctuation rate distribution is unknown. Here we have shown that combining time-scale-dependent optical dephasing measurements with recent theoretical results, it is now possible to examine the rates of dynamic processes in complex condensed matter systems.

Acknowledgement

This work was supported by the National Science Foundation Division of Materials Research (DMR87-18959). Additional support was provided by the Office of Naval Research (N00014-89-J-1119 and N00014-86-K-0825). KAL would like to thank AT&T Bell Laboratories for a Graduate Fellowship.

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