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Section 3. Glasses and disordered systems

LOW-TEMPERATURE GLASS DYNAMICS PROBED BY OPTICAL DEPHASING MEASUREMENTS

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Optical dephasing measurements in glasses are affected by dynamical processes which occur on a very broad range of time scales. The relaxation rate distribution of a glass can be measured by using a combination of experiments which operate on different characteristic timescales. A four-time correlation function treatment of the observables is used to extract the fluctuation rate distributions at short and long times from photon echo and time-dependent holeburning measurements at low temperatures (1.0 to 5.0 K). The temperature dependence of the optical dephasing is characteristic of the 'two level system' (TLS) structural dynamics of a glass. Evidence confirming that glasses have fixed potential surfaces at low temperature (the basis for the TLS model) is provided by temperature cycled holeburning measurements. Dephasing at higher temperatures (~ 10 K) is shown to be a property of the glass, not from a local motion of the chromophore as previously believed.

1. Introduction

Optical dephasing measurements provide a powerful method for studying the dynamics of glasses at low temperatures. At low temperature the disorder in glasses introduces time-dependent processes which have no counterparts in crystalline systems. These processes are responsible for anomalies in specific heat [1], thermal conductivity [2], and dielectric response [3] which have been observed in glasses.

Phenomena associated with the glassy state of matter have been explained with a variety of models, the most widely used is the two level system (TLS) description proposed independently by Phillips [4] and Anderson [5]. A TLS is composed of two local potential minima separated by a barrier. Structural changes are modeled as tunneling between these wells. To account for the wide variety of local structures, the distribution of TLS parameters, such as energy differences between the two wells, are taken to be very broad. The broad distributions of parameters associated with the TLS give rise to a broad distribution of rates of dynamical processes.

The spectral lineshape (frequency domain) or the dephasing rate (time domain) of an ensemble of optical centers (chromophores) in a medium is related to the dynamical processes of the medium. The large number of solvent configurations surrounding the optical centers in a glass results in inhomogeneous broadening which obscures the intrinsic lineshape. An absorption spectrum of chromophores in an organic glass is hundreds of wavenumbers wide whereas the intrinsic linewidths of interest are hundredths of a wavenumber.

Optical line narrowing experiments have been extensively used to remove inhomogeneous broadening. Line narrowing experiments such as photon echoes [6], accumulated grating echoes [7], fluorescence line narrowing [8], and non-photochemical holeburning [9] have been applied to glassy systems. Each of these techniques has associated with it a characteristic time scale, and the observables will be influenced by glass dynamics which occur during the characteristic time scale [10]. Combining the results of different dephasing techniques with the recently developed theoretical formalism provides a powerful means for extracting quantitative information on rate distributions and other dynamical properties.

In this paper we use the results of two pulse photon echoes and time-dependent holeburning experiments to determine TLS fluctuation rate distributions of organic glasses at low temperatures (1.0 to 5.0 K). We also discuss a temperature cycled holeburning experiment which confirms the TLS model. This is in contrast to other experimental measurements, such as heat capacities, which can be explained by the TLS model or by models based on defect and particle diffusion. Temperature dependent echo data (5.0 to 12.0 K) are used to show that additional dephasing processes which become important at the higher temperatures are not local motions of the chromophore, but are rather dynamics of the glassy medium.

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2. Theory

At a finite temperature, the mechanical fluctuations of a solid will modulate the transition energies of molecules embedded within it. Optical dephasing measurements rely on preparing the chromophore–glass system in a coherent superposition of ground and excited states and monitoring the loss of the coherence as the chromphores interact with the time evolving environment. Optical absorption formalisms have usually been used to describe these experiments in which the lineshape is the Fourier transform of a two-time dipole moment correlation function. This is insufficient in that the absorption lineshape of chromophores in a glass is dominated by inhomogeneous broadening. In addition, the two-time correlation function description is incapable of accounting for the characteristic time scales associated with the various experiments. An appropriate treatment of the problem was developed by Berg et al. [10] and extended by Bai and Fayer [11]. They showed that a four-time correlation function is the quantity of interest and that all dephasing experiments currently in use can be treated in terms of the four-time correlation function of the stimulated echo. The stimulated echo correlation function C is

$$C(\tau, T_w, \tau) = \langle \mu^*(T_w + 2\tau)\mu(T_w + \tau)\mu(\tau)\mu^*(0)\rangle = \left\langle \exp\left[-i\int_0^{\tau} \Delta(t)\, dt + i\int_{T_w+\tau}^{T_w+2\tau} \Delta(t)\, dt \right] \right\rangle, \quad (1)$$

where τ, T_w, and τ are the intervals between the four times in the correlation function, $\Delta(t)$ is the time dependent perturbation of the transition frequency, and μ is the transition dipole moment operator. For example, holeburning experiments are described in terms of the Fourier transform of eq. (1).

A photon echo is the limit of a stimulated echo in which the second and third pulses are time coincident, i.e., T_w is zero in eq. (1). It is the only optical line narrowing experiment for which this is the case. The photon echo removes inhomogeneous broadening while extracting the dephasing rate arising from dynamical processes on its characteristic time scale, ps to ns. The dephasing measured by the photon echo is usually referred to as homogeneous dephasing because the slow dynamical processes (ms, s, etc.) are seen as static and therefore do not contribute to the optical dephasing rate. Therefore, the photon echo will yield the slowest dephasing rate (narrowest linewidth) of any of the line narrowing experiments.

Other dephasing experiments are sensitive to slower dynamical processes. These processes are generally referred to as spectral diffusion. An experiment will be sensitive to spectral diffusion as slow as the characteristic time scale of the experiment, which is T_w. In a nonphotochemical holeburning experiment (permanent holeburning), for short burning and reading times, T_w is the time between burning and reading the hole. This is typically 100 s. Therefore dynamics on a ms or s time scale, which did not influence the photon echo experiment, will contribute to the linewidth measured by holeburning.

3. Experimental results and discussion

The systems used to perform echoes and holeburning as well as details of sample preparation have been extensively described [10] Samples are organic dyes in low concentration in glasses such as ethanol, d-ethanol, glycerol, and PMMA. In some samples, holeburning during echo decay measurements is a serious effect which must be properly corrected for [10]. Great care is taken to test for all sources of artifacts, such as power broadening, sample heating, optical density effects [12] concentration, and wavelength dependences. In holeburning experiments, only shallow ($< 2\%$) holes were used [10,13,15]. Again, care was taken to test for possible artifacts. The cooling rate of the ethanol samples was high enough to insure the formation of the true glassy state [10].

3.1. Photon echo results

Fig. 1 shows a semilog plot of echo decays measured in the cresyl violet/d-ethanol and resorufin/glycerol systems. The decays are exponential for 5 or more factors of e. To observe an exponential decay in a photon echo experiment two conditions must be met. (1) The coupling between the TLS and the chromophores must be via a dipole–dipole interaction. (2) The TLS fluctuation rate distribution, $P(R)$, i. e. the probability of the glass having a dynamical process with a rate R, must go as $1/R$ for the rates which have inverses that fall within the experimental time scale [16] The exponential decays presented in fig. 1 are typical of all systems studied and indicate that the $1/R$ distribution holds for rates from $\simeq 1/1\ \mathrm{ps}^{-1}$ to $\simeq \frac{1}{4}\ \mathrm{ns}^{-1}$.

Temperature dependences of echo decays show a power law behavior at low T where the pure dephasing time $T_2^* \propto T^{\alpha}$ between 1 K and 5 K. At higher temperatures, the dephasing is faster due to contributions from an exponentially activated process [6,10,13]. Exponential temperature dependences have been observed in crystalline systems and demonstrated to arise from a localized motion of the chromophore [17]. Recent experiments demonstrate that the situation is different in glasses [18]. Fig. 2(a) shows a temperature dependent photon echo study of rhodamine B (RB) and octadecylrhodamine B (ODRB) in PMMA. ODRB has an eigh-

teen carbon alkyl chain in place of the acid proton on RB and consequently has very different mass and moments of inertia. Note that the two temperature dependences are identical. Fig. 2(b) shows further that echo decays taken at the same temperature on the different samples are superimposable [18]. Since local motions are translations and rotations which depend on the mass and moments of inertia, respectively, the activated process is not a motion of the chromophore. The activated process itself is exponential indicating that the mode responsible must have a narrow distribution of energies. A host optical phonon can produce such an effect, and we suggest that this is the dominant dephasing mechanism at high T.

3.2. Holeburning results

Glasses have a very broad distribution of structural relaxation rates, ranging from very fast to very slow [broad $P(R)$]. Holeburning is sensitive to fast and slow rates because hole widths are broadened by processes as slow as T_w. Therefore the linewidth measured by holeburning is expected and found to be wider than the Fourier transform of the photon echo decay (photon echo measured linewidth). Fig. 3 shows a hole spectrum of resorufin/ethanol at 1.5 K with a plot of the linewidth obtained from the transform of the echo decay. Note that the hole linewidth is six times broader than the echo determined linewidth. Similar differences are

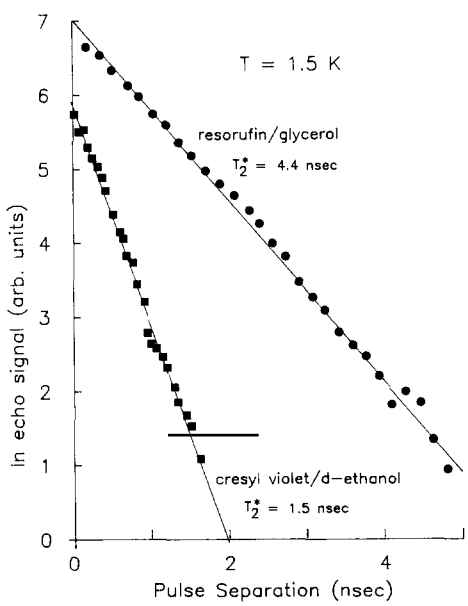

Fig. 1. Semilog plots of photon echo decays in resorufin/glycerol and cresyl violet/ethanol at 1.5 K. Decays are single-exponential over several lifetimes demonstrating that the fluctuation rate distribution, $P(R)$, goes as $1/R$ from approximately $1/1\ \mathrm{ps}^{-1}$ to $\frac{1}{4}\ \mathrm{ns}^{-1}$.

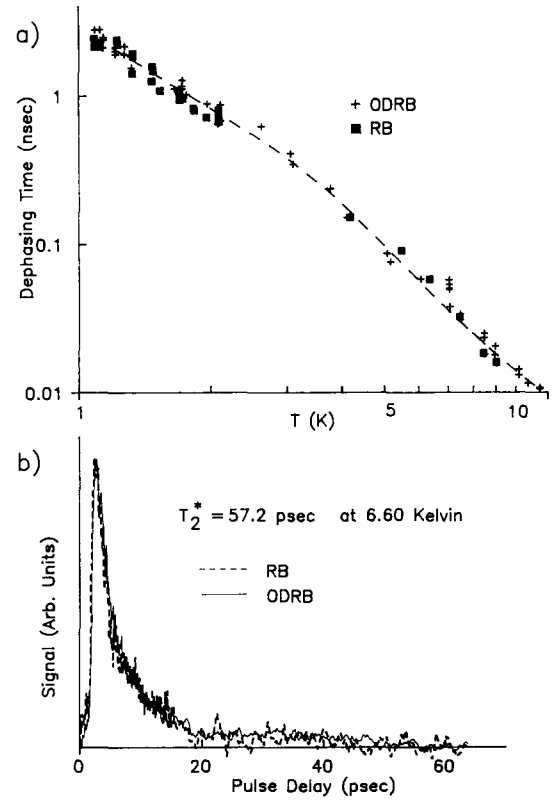

Fig. 2. (a) Photon echo temperature study of RB (■) and ODRB (+) in PMMA. The dephasing times are identical at all temperatures. (b) Superimposable echo decays from RB (------) and ODRB (———) in PMMA at 6.6 K. The identical dephasing times shown in (a) and (b), despite the large variations in mass and moments of inertia between the two guest molecules, demonstrate that a guest motion is not the dephasing mechanism at high T.

seen in other dyes and glasses in this and other laboratories [6,10,13,14]. The Lorentzian shape of all of the holes in the various systems again requires a dipole–dipole coupling mechanism, but does not place restrictions on the rate distribution, $P(R)$.

It is shown in ref. [11] that the holeburning observable is the equivalent of a frequency domain stimulated echo. Furthermore, it is possible to find $P(R)$ from the T_w dependence of the hole width.

$$\Delta\nu_H(T_w) \propto -\int dR\, P(R)[1-\exp(-RT_w)] + T_w \text{ independent contributions of fast fluctuations.} \quad (2)$$

The $1-\exp(-RT_w)$ term is called a gate function. It arises as a natural consequence of the dynamics in glassy systems. The observable is a convolution of $P(R)$ with the gate function.

Fig. 4 shows the results of a study on the cresyl violet/ethanol system [15] in which the hole width was

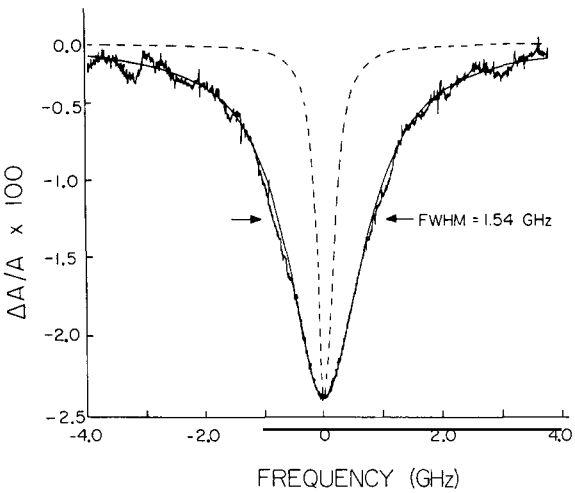

Fig. 3. Hole spectrum and Lorentzian fit burned in the resorufin/ethanol at 1.5 K. The dashed line is the hole width obtained from the Fourier transform of the echo decay at 1.5 K and is six times narrower than the measured hole. The difference is due to slow relaxations (spectral diffusion) that broaden the hole width but do not influence the echo decay.

measured as a function of the time after burning. As T_w is increased, processes with slower rates contribute to the hole width, broadening the hole. The solid line through the data is obtained by fitting eq. (2) to the data with various forms of the rate distribution, $P(R)$.

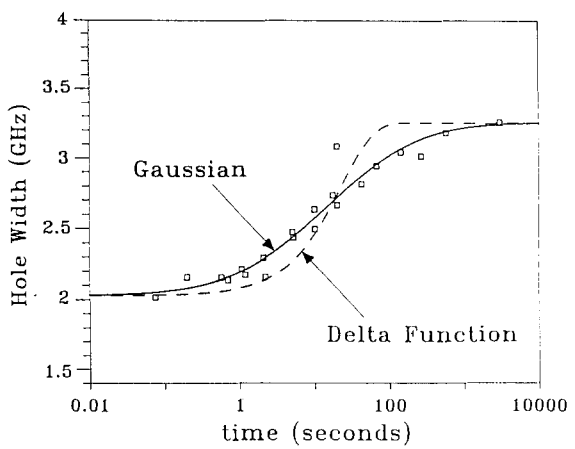

Fig. 4. Semi-log plot of of various holes versus log waiting time for a sample of cresyl violet in ethanol at 1.30 K. The hole width changes most dramatically in the range centered around 20 s while flattening out at both short and long times. This indicates that there exists a distribution of fluctuation rates centered around $\sim\frac{1}{20}$ 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 (dashed line,) while accounting for the magnitude of the change, overestimates the steepness of the increase.

The best fit is obtained with a log normal distribution (a Gaussian on a log scale) for $P(R)$.

$$P(R)\,\mathrm{d}R \propto \exp\left[-(\ln(R/R_0))^2/\sigma^2\right]\,\mathrm{d}(\ln R) \qquad (3)$$

with $R_0 = 0.02$ s^{-1} and $\sigma = 3.8$. Thus there is a peak in the rate distribution at 0.02 s^{-1}. This same peak is found with resorufin in ethanol but it is not observed in glycerol systems. Thus, the peak in $P(R)$ is a property of the ethanol glass.

On a ps to several ns time scale, photon echo experiments reveal that $P(R)$ goes as $1/R$ in ethanol glass at very low temperatures. The holeburning yields $P(R)$ on the 0.1 s to 10000 s time scale. We are extending the holeburning measurements to 10 μs and using stimulated echoes and accumulated echoes to bridge the gap between photon echoes and holeburning. In this manner it is possible to measure $P(R)$ over sixteen decades of time.

Our detailed understanding of what $P(R)$ means microscopically is based on the TLS model. Many other models have been used to understand the properties of low temperature glasses. These are usually based on defect or particle diffusion. Unlike the TLS model, alternative models take the glass potential surface to be evolving in time [19]. In contrast, the TLS model is an approximate description of a fixed glass potential surface on which there is limited motion that does not change the shape of the surface.

A temperature cycled holeburning experiment has been used as a test of these fundamentally contrasting microscopic descriptions [20]. If a hole is burned and read as a function of T_w at a fixed temperature, one obtains a result like that in fig. 4. In the temperature cycling experiment, a hole is burned and read at an initial low temperature, the temperature is raised and the hole width is measured, and finally the temperature is returned to its original value, and the hole width is measured. If the potential surface is not static, the hole would be irreversibly broadened. In contrast, if the potential surface is fixed, high energy TLS will be activated at the higher temperature, causing additional broadening, but when the temperature is again lowered, the hole will narrow. The high energy TLS will relax back to their low energy configurations at the lower temperature. This will reverse the high temperature contribution to the spectral diffusion. After the temperature cycle, the hole will have the width which corresponds to the elapsed time, T_w, with no extra width introduced by the temperature cycle.

Fig. 5 shows the result of a hole cycling study on cresyl violet/ethanol where the hole was burned at 1.3 K, taken to 2.1 K, and returned to 1.3 K. From the data it can be seen that the hole reverted to the long-waiting time hole width of a 1.3 K hole [15,20]. Using the time dependent hole data, it was possible to calculate the

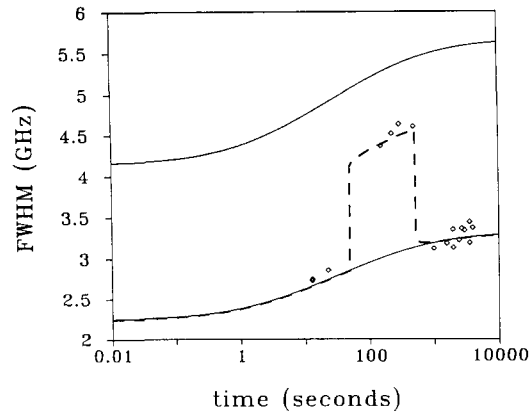

Fig. 5. Temperature cycled holeburning data from the cresyl violet/ethanol system. The lower and upper solid lines are the time dependent hole widths at 1.3 and 2.1 K, respectively. The hole width increases during the temperature increase from 1.3 K to 2.1 K but returns to the original long waiting time value after the temperature is returned to 1.3 K. The dashed line is a calculation of the temperature cycle without adjustable parameters.

temperature cycle data without adjustable parameters [20] by applying the theory of ref. [11] to the TLS temperature cycle problem. This experiment confirms the fixed potential view of low temperature glasses and demonstrates the accuracy of the TLS model.

4. Conclusions

Optical dephasing experiments are important tools for studying complex systems, but their interpretation requires careful consideration of the time scale on which any particular technique is sensitive to dynamics. A proper approach to the study of glass dynamics requires exploiting this sensitivity to obtain dynamical information. The methods and theory briefly outlined here can be applied to many types of complex systems. For example, experiments on complex crystals have been quantitatively analyzed using the Bai and Fayer theory [11]. Expanded applications of these methods to glasses, complex crystals, proteins, and other systems will greatly expand our knowledge of the dynamics and interactions for a wide variety of materials.

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