Thermal history and temperature-dependent photon echo and hole burning linewidths in low temperature glycerol glasses

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Temperature-dependent two-pulse photon echo and hole burning linewidths are reported for the system resorufin in glycerol glass from 1 to 25 K. At low temperature a factor of ≈ 4 difference between the linewidths measured by the two techniques is observed owing to the broad fluctuation rate distribution of glass dynamics. Using cooling rates of 600 K/min and 0.2 K/min, it is shown that the linewidth of both spectroscopies is markedly dependent on how the sample was prepared. In terms of the two level system model of glass dynamics, the cooling rate dependence has direct implications on the structure of the glass at low temperature.

1. Introduction

By examining the temperature dependence of the hole burning and photon echo linewidths of a dye molecule in glycerol glasses prepared with different cooling rates, it is demonstrated that the low temperature glass is not completely amorphous but is structured in a way which depends on its thermal history. The word glass does not have as specific a definition as the term crystal does. When thinking of a crystal, one imagines a solid composed of atoms and/or molecules packed in a highly ordered array. The differences between different crystal structures are almost always clearly defined and unambiguous [1]. However, a glass is not nearly so well characterized. It is not a completely random arrangement of atoms and molecules. This is a very strict definition requiring complete absence of order. Many glasses do have structure. The structure is that which the super cooled liquid had as it passed through the glass transition temperature [2,3].

This lack of total randomness has been demonstrated experimentally. Heat capacity measurements

have shown a significant change in the specific heat of glycerol glasses when the glass is prepared with different cooling rates [4]. The glass transition temperature is known to depend on, among other things, how quickly the glass forming liquid is cooled [2]. The faster the cooling is, the higher T_G is. Thus the respective structure of two samples cooled at different rates will reflect the structure of the liquid at two different temperatures. If the glass were truly amorphous, no change should be seen.

Molecular modeling of glycerol glass has also shown temperature-dependent structure of liquid glycerol. The structure of the liquid in terms of atomic pair correlation functions shows a weak but significant dependence on temperature [5]. In retrospect, these results are not surprising. The very existence of any glass depends on the cooling rate. That is, if a glass forming liquid is cooled too slowly, it will crystallize. In addition, alternate phases of a glass have been observed when the cooling rate is varied [6,7]. This is a more dramatic example of how the structure of a glass depends on the cooling rate.

The studies mentioned above have focused on how the cooling rate affects the moderately low temperature properties of glasses. It is reasonable to assume that the very low temperature properties will be similarly affected. Low temperature dynamics are characterized by a broad distribution of low energy modes

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usually modeled as a distribution of double well potentials in the glass structural potential energy surface. These are the two level systems (TLS) first introduced by Anderson et al. [8] and Phillips [9]. These TLS are used to model a great variety of low temperature glass properties [8-14]. By varying the cooling rate in forming the glass, it is possible that one changes the properties of the two level systems. For example, different cooling rates may yield different distributions of barrier heights or energy differences between the TLS potential wells. This will show up as changes in the low temperature properties of the glass.

Johari, in a review of heat capacity data, has reported just such an effect [15]. The relatively high temperature heat capacity of Se glass is known to depend on its cooling rate [16]. This is understood in terms of secondary relaxation of the glass. When the glass is held at a relatively high temperature yet still below T_G, the structure of the glass relaxes effectively reducing the number of configurational modes which contribute to C_p [15]. However, this type of annealing also has a dramatic effect on the heat capacity in the TLS regime. Slow cooling reduces the heat capacity of the glass below 1 K by over 50% [17]. These and other data suggest that the modes responsible for near T_G heat capacity and the TLS are intimately related [15].

Recently, glycerol glass has been investigated optically using photon echo and hole burning spectroscopies [18]. A difference between the results of the two experiments was initially explained in terms of a timescale argument. Since glasses exhibit fluctuations over a very broad range of timescales, an inherently "slow" experiment like hole burning will be sensitive to more dynamic processes (more TLS) than a two pulse photon echo [18,19]. However, later hole burning measurements cast doubt on the validity of these results [20]. This study produced narrower hole widths.

The results presented here will show that the temperature dependence of the linewidth is substantially affected by the cooling rate. This is shown to be a factor in both the hole burning and the photon echo experiments demonstrating that the treatment of the sample at almost 200 K ($T_G \approx 190$) affects the dynamics below 5 K across all timescales. Hole burning and photon echo experiments on glycerol samples

which do not have the same thermal history cannot be directly compared. This resolves the apparent discrepancy in the literature [20].

2. Experimental

The sample studied was a 2×10^{-4} M solution of resorufin in dry glycerol. The dry glycerol was prepared from a fresh bottle (Mallinckrodt) which contained < 0.5% water. It was opened under dry argon and mixed with ≈ 5 g activated alumina while heating and stirring. After filtration, 100 ml was stored over molecular sieves for ≈ 30 days before a small portion was decanted to prepare the dye solution. The sample was never exposed to air, and was sealed in a 1 mm spectroscopic cuvette.

In preparation for the experiments, the sample was cooled in one of two ways. For quick cooling of the sample, the cuvette was plunged directly into liquid helium. It took ≈ 10 s for the sample to pass through the glass transition temperature (≈ 190 K) and approximately 100 s to reach liquid helium temperature. For slow cooling of the sample, the cuvette was first placed in a warm cryostat. The sample chamber was then evacuated, and the liquid nitrogen compartment was filled. In this way the sample was cooled very slowly over the course of a day. It took ≈ 8 h for the sample to pass through the glass transition temperature. For both cooling methods, the sample thermal history was continuously recorded by a resistance thermometer in direct contact with the sample. The cooling curves for both processes are shown in fig. 1. The precipitous drops around 20 h in fig. 1b mark where the sample chamber was filled with liquid helium.

The experiments were carried out in a variable temperature gas flow cryostat. Temperatures were measured with a germanium resistance thermometer attached directly to the sample. Holes were burned and detected with a Coherent CR599-21 scanning single mode dye laser (≈ 2 MHz bandwidth). The sweep width of the dye laser was kept relatively large so that a substantial part of the wings of the holes could be scanned. At high temperatures (> 18 K), where the hole widths become quite large, the scanning operation of the dye laser was modified to allow up to 90 GHz scans. All spectra were recorded in
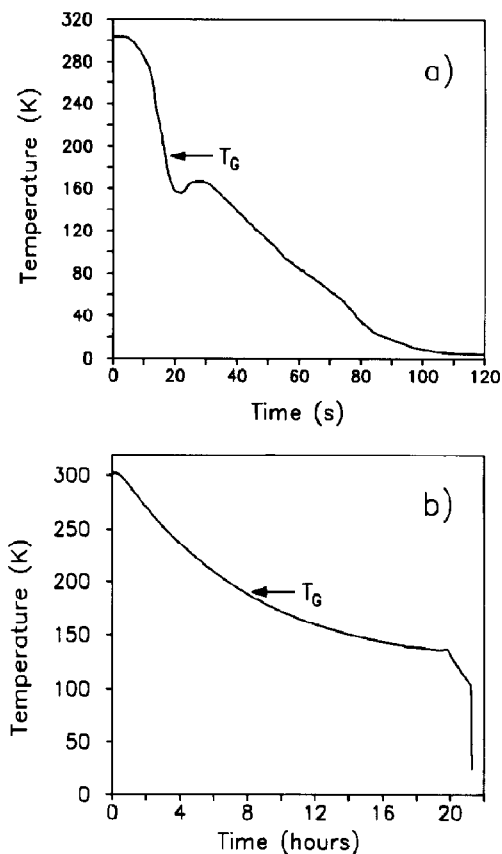
Fig. 1. Temperature of the sample versus time for both quick cooling (a) and slow cooling (b) of the glass. The drops around 20 h in (b) mark where liquid helium was added to the sample chamber.

Table 1
Typical burn times and burn fluences used to create spectral holes for resorufin in glycerol glass

Temperature (K)	Burn time (s)	Fluence ($\mu K/cm^2$)
1.7	1.5	9
2.1	2.5	15
12	20	120
23	12	600

transmission on the red side of the 0–0 absorption at 590 nm. The optical density at this wavelength was ≈ 0.8.

The laser intensity used to burn the holes was typically 6 $\mu W/cm^2$ although higher intensities were used above 10 K. See table 1 for a brief list of burn intensities. The laser spot diameter was 1 mm. Holes

were also burned with very long exposures of the weak probe beam (≈ 100 nW/cm^2) to check for saturation effects. No difference in the hole width was observed. It has been reported that the hole width for resorufin in glycerol is very dependent on the burning fluence [20,21]. This was also observed in these measurements especially at very low temperatures. To account for this the hole linewidth is usually extrapolated to zero burning fluence [20]. The extrapolation method is somewhat dubious since the dependence of hole width on depth for this system is unclear. In previous experiments "smooth curves" were drawn through the data [21]. In lieu of an analytical expression, a linear extrapolation seems to be the most innocuous. Therefore, the hole widths of the data below 4 K reflect the hole width extrapolated linearly to zero burning fluence. The slope of the extrapolated line was significant. For example, at 1.3 K the extrapolated linewidth was $\approx 15\%$ narrower than the linewidth of a 1% hole. Above 4 K, little to no fluence dependence was observed therefore the hole width reported is that of the shallowest holes burned – $\approx 1\%$.

The photon echo apparatus has been described previously [22]. An amplified sync-pumped dye laser generates approximately 2 μJ, 4 ps pulses at a repetition rate of 700 Hz. The spot size used was 150 μm. The pulses were attenuated considerably (to ≈ 100 nJ) to test the echo decays for dependence on the energy of the pulses [18,23]. The data reported are independent of intensity. The loss of signal due to hole burning while the echo decay was being recorded was accounted for using the burning curve method described previously [18]. New data were collected only on the slowly cooled sample. Data collected on a quickly cooled sample were taken previously [18] and are reported in section 3 for purposes of comparison. The cooling was performed in the identical manner for both echo and hole burning experiments. Measurements of cooling rates showed that they were reproducible for all the data used.

3. Results and discussion

Fig. 2 shows two holes burned in the system resorufin in glycerol glass. The hole in fig. 2a is in a slowly cooled sample as is described in section 2. The

Fig. 3. Plot of hole linewidth versus temperature for resorufin in both slowly (■) and quickly (△) cooled glycerol. The difference in the linewidth is quite substantial at low temperatures and reduces somewhat as the temperature is raised. The solid lines are fits to eq. (1) (see text).
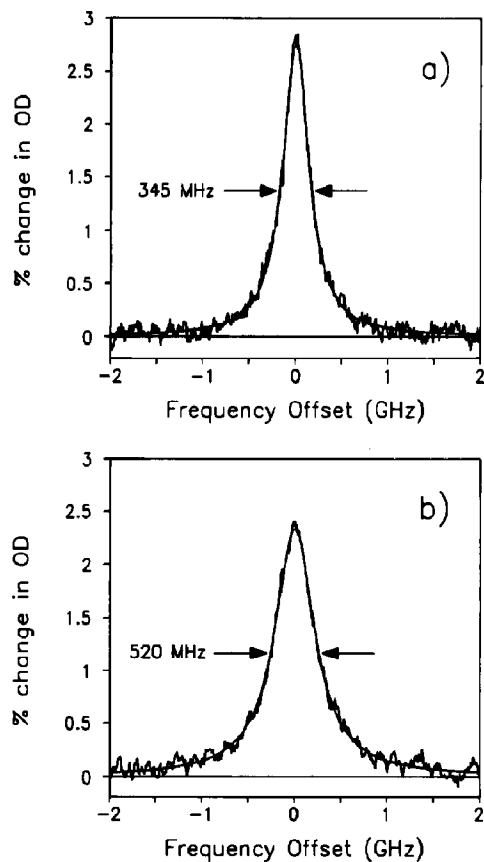

Fig. 2. Two holes burned in the system resorufin in glycerol glass at 1.6 K. (a) Slowly cooled sample. (b) Quickly cooled sample. Notice the substantial narrowing of the line when the sample is cooled slowly.

Fig. 4. Plot of linewidth versus temperature for resorufin in slowly cooled glycerol (■) and photon echo linewidth versus temperature for resorufin in both slowly cooled (○) and quickly cooled (△) glycerol. The quickly cooled data are taken from ref. [18]. The solid lines are fits to eq. (1) (see text). The difference between cooling slowly and quickly noted in the hole linewidths is also seen in the echo results. This indicates that slowly cooling the sample affects the glass dynamics across all timescales.

hole in fig. 2b is in a quickly cooled sample. As can be seen, the hole width depends substantially on how the glass was prepared. Fig. 3 is a plot of the full temperature dependence of the hole linewidth ($\Gamma = \frac{1}{2}$ hole width) with the lifetime contribution (Γ_0) removed. The lifetime was measured previously and determined to contribute 45 MHz to the linewidth ($T_1 = 3.5$ ns) [18]. As can be seen in the figure, the difference between the hole widths is approximately 40% of the quickly cooled value at the lowest temperature and decreases as the temperature is increased. The solid lines are fits to a power law plus an exponential term which will be described below.

The fact that the linewidth is so drastically dependent on the thermal history of the glass is consistent with the heat capacity data mentioned in section 1. In light of the Se glass experiments reported by
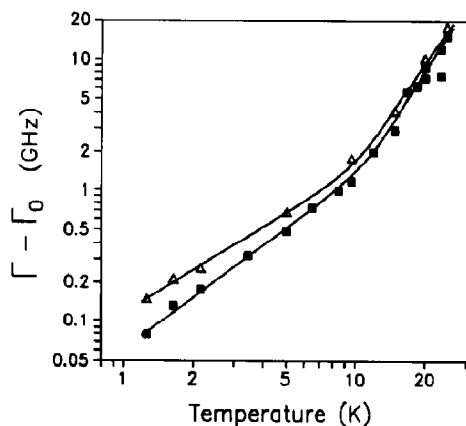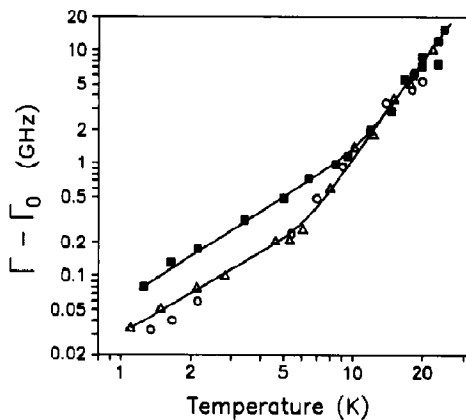
Johari [15], the observation of history-dependent heat capacity in the high temperature regime of glycerol [4] strongly suggests one would also notice thermal-history-dependent effects at low temperature. The data reported in fig. 3 are certainly consistent with this.

Fig. 4 is a plot of the temperature dependence of the hole linewidth ($\Gamma = \frac{1}{2}$ hole width) and of the line-

width calculated from the echo experiment. The echo signal decays as $\exp(-4\tau/T_2)$, where τ is the time separating the two pulses. For the photon echo $\Gamma = 1/\pi T_2$. The hole burning results are only those of the slowly cooled sample (see fig. 3 for comparison of two cooling rates). The echo results are those of both samples. The solid lines are again fits to a power law plus an exponential which will be described shortly. The substantial difference between hole burning and photon echo results reported earlier [18] is still evident in the data presented here. At low temperatures, the ratio between echo linewidth and hole linewidth is almost a factor of 4. This difference begins to diminish above 5 K, and the two experiments give virtually identical linewidths above 10 K.

The difference can be explained in terms of the broad timescale of glass dynamics. As has been shown previously [18,19], the hole burning and photon echo experiments are inherently sensitive to dynamics with different rates. Hole burning spectroscopy has been shown to be sensitive to dynamics with rates in the range $1/T_W < R < 1/T_{PE}$, where T_{PE} is the photon echo dephasing time and T_W is the waiting time between burning and reading the hole [18,19]. Photon echo experiments, on the other hand, are sensitive only to rates on the order of $1/\tau$, where τ is the pulse separation [18,19]. Therefore, in a glass, which can exhibit dynamics across many orders of magnitude in time, hole burning will be sensitive to many more decades of rates. In most systems studied so far this is responsible for a factor of 6–8 difference in the linewidth measured by the two spectroscopies (for hole burning experiments on a 100 s timescale) [18,24]. The fact that the difference is only a factor of 4 in glycerol is an indication that the glycerol glass is relatively void of TLS dynamics. Indeed, it has been demonstrated that there exist essentially no dynamics in the range 0.1 to 5000 s [14]. The factor of 4 difference reported here is clearly in accord with these earlier results.

The second point of interest in the data of fig. 4 is that the line narrowing due to slow cooling is visible in the low temperature echo data as well as in the hole burning data. The difference in the echo data is not as great – $\approx 25\%$ relative difference in the linewidth (as opposed to 40% for the hole burning data) at the lowest temperatures, and decreases rapidly, disappearing at 5 K. This implies that at low tem-

perature slowly cooling the sample affects the dynamics across all timescales – picoseconds to hundreds of seconds. The fact that the change is not as great in the photon echo data could be due to experimental uncertainty. When the echo decay nears the lifetime limit, as in this case, the relative uncertainty in the echo linewidth grows. However, the scatter of the data indicates an uncertainty of only $\pm 10\%$ so the difference may be real.

In terms of the two level system model, the experimental results can have several implications. Since the glass dynamics, measured by the linewidths, is reduced by cooling the sample slowly, it is possible that the number density of the TLS in the sample is reduced. The properties of the TLS may be altered by slow cooling so that they are no longer as active in the timescales and temperatures studied here. This can occur in one of two ways. First, the barrier heights between the states of some of the TLS may have changed. If a TLS barrier becomes too large or too small, its relaxation rate will slip out of the time window where it contributes to the observed linewidths [18,19]. The second possibility is that the distribution of energy separations of the two states of the TLS is shifted to higher energies so that fewer TLS are active at a given temperature. The fact that the reduction in linewidths occurs over all timescales suggests that a shift in the density of states is more likely.

It is not possible to distinguish between the possibilities with the results of a study such as are presented here. Recently it has been demonstrated that a time-resolved hole burning experiment may map out the dynamics of a dye/glass system over eight orders of magnitude in time [14,25]. Experiments such as stimulated echoes and accumulated grating echoes have also been suggested as useful techniques [19]. Using these methods, the fluctuation rate distribution for the two forms of glassy glycerol can be determined, and it should be possible to discern over what range of rates the fluctuation rate distribution is modified by varying the thermal history.

As was mentioned previously, the solid curves in figs. 3 and 4 are fits to a power law plus an exponential. Explicitly this function is

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

Table 2
Parameters which yield the best fit to the data in figs. 3 and 4 using eq. (1)

Sample	Exp. method	a (MHz)	α	b (GHz)	ΔE (cm^{-1})
slow cooled	HB	30 ± 2	1.3 ± 0.1	100 ± 70	50 ± 15
quick cooled	HB	60 ± 5	1.1 ± 0.1	75 ± 50	45 ± 15
quick cooled	PE	15 ± 1	1.2 ± 0.1	55 ± 40	35 ± 15

where Γ_0 is the lifetime contribution to the hole width. This function was introduced by Jackson and Silbey [26] to describe the influence of narrow band mode of a glass, i.e. a pseudo-local mode or optical phonon, on the hole burning linewidth of a doped chromophore. It has been used recently to describe the high temperature (> 5–10 K) optical dephasing of chromophores in organic glasses [18,24,27–29]. Studies in PMMA have indicated that the mode is not a pseudo-local mode of the chromophore, but is an inherent property of the glass [27,28]. The best fit parameters for the hole burning and photon echo temperature dependences are listed in table 2. Note the large uncertainties in the value of the mode energy, ΔE. The number of free parameters is apparently too large and the scatter of the data, especially at high temperatures, is too large to make a precise fit to eq. (1) for this data. The fact that the data may be fit to eq. (1) does, however, show that the process responsible for high temperature dephasing is consistent with that observed in other systems [18,24,27–29].

Fig. 5 is a graph of the hole burning data taken on slowly cooled glycerol plotted along side previously reported data taken on a similar sample [20]. These data were initially presented in contrast to the hole burning data of ref. [18]. However, the data taken on slowly cooled glycerol and the data of ref. [20] agree very well across nearly the entire temperature range. There is a slight difference at intermediate temperatures. However, since it is unclear how quickly the sample was cooled in ref. [20], some differences may be attributable to different cooling rates. Since the data are quite close, it is safe to say that the sample was most likely cooled with a similar cooling rate as that reported in fig. 1b. There is a more significant difference at the highest temperatures. However, the error in measuring hole widths for such wide holes can be quite substantial, especially if one
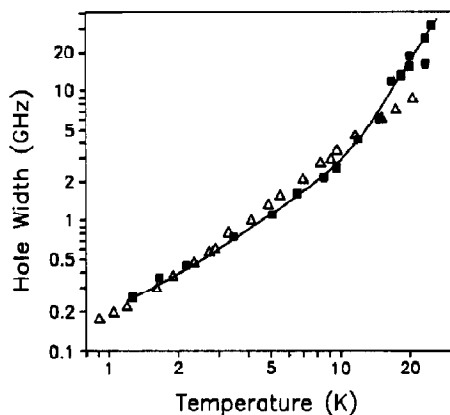

Fig. 5. Plot of the hole width versus temperature of resorufin in slowly cooled glycerol (■) and the data from ref. [20] (△) taken on a similar sample with an unspecified cooling rate. The data agree well across nearly the entire temperature range indicating the cooling rates were most likely similar.

is limited to a sweep of ≈ 1 cm^{-1} which is a common limitation for many scanning single mode dye lasers used to record spectral holes [20]. Since the highest temperature hole width data reported here were taken with a 90 GHz sweep, these data are probably more accurate.

Because of the inherent nonequilibrium nature of glasses, their physical properties are very sensitive to the thermal history of the system. The results reported here, in addition to reaffirming the conclusions of earlier studies of glass dynamics [18], show that the microscopic structure of the dye/glycerol glass system is dependent on the way in which it was prepared. Using techniques such as these in conjunction with waiting time-dependent observables, such as have been recently reported [14], it is now possible to examine the dynamic structure of glasses, and by inference, the physical structure, in great detail.

Acknowledgement

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