OPTICAL DEPHASING OF CHROMOPHORES IN AN ORGANIC GLASS: PICOSECOND PHOTON ECHO AND HOLE BURNING EXPERIMENTS

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The homogeneous optical dephasing time T_2 for the organic glass system resorufin in ethanol is measured by picosecond two-pulse photon echoes from 1.5 to 11.4 K. A non-power law temperature dependence of T_2 is measured. Non-photochemical hole burning (NPHB) linewidths are four times broader than the homogeneous linewidth, demonstrating that additional factors contribute to NPHB.

1. Introduction

The low-temperature properties of glasses are distinctly different from those of crystals as has been demonstrated by thermal and acoustic measurements [1]. Models based on the existence of two-level systems (TLS) have been successful in at least qualitative explanation of many of these properties [1]. Still, the physical nature and exact properties of the TLS are largely unknown. Two-pulse photon echo studies of the electronic dephasing of chromophores doped into crystals have proven to be sensitive probes of microscopic dynamics [2]. Similar measurements on glasses will be valuable in unraveling the unique properties of the glassy state.

A large number of studies have measured temperature dependent linewidths in glasses [3]. All of these results can be fit to a T^α temperature dependence with $1 < \alpha < 2$. A great deal of theoretical work has attempted to explain this result [3–8]. In most studies in organic glasses, the linewidth from persistent non-photochemical hole burning (NPHB) has been reported. Non-photochemical hole burning is a phenomenon unique to certain glasses and crystals in which a quasi-permanent hole can be burned in the inhomogeneously broadened spectrum of photochemically stable chromophores. However, the relationship of the NPHB linewidth to the homogeneous dephasing time is unclear. For example, the mechanism for NPHB and its role in determining the hole-width are not understood. Furthermore for unknown reasons, the holewidths are sensitive to laser powers and burn times [9]. In general, it has been assumed, but never verified, that very shallow holes give the homogeneous linewidth. This condition could imply the sampling of a special subset of the chromophores with the fastest burning rates. Spectral diffusion on timescales between the excited state lifetime and the minute timescale on which typical NPHB experiments are performed could also lead to holes broader than the homogeneous width [10].

Two-pulse photon echoes measure homogeneous dephasing times without these uncertainties. The theory of photon echoes from dilute chromophores is well understood and tested [2]. Also, the entire ensemble of absorbing molecules is sampled in the photon echo experiment. Finally, the echo signal is generated on the timescale of the dephasing and therefore will not probe ground-state spectral diffusion processes. It is important to use two-pulse photon echoes to unambiguously determine the dephasing time in glasses for several reasons. First, it is crucial to know if the fractional temperature dependences reported so far are actually correct and of fundamental significance as has been implied [11]. Furthermore, photon echoes can be extended to glasses which do not hole burn to determine whether the dynamics of dephasing and NPHB are related. Finally, comparison of photon echo decays to NPHB

linewidths will help in understanding the origin of NPHB. To date the only two-pulse photon echo experiment in a glass has been in an inorganic system for which NPHB results are unavailable [12].

In this Letter, an initial report on the first two-pulse photon echo measurements·on an organic glass is given. The echo is found to decay exponentially; a significant result since the dephasing rate might be expected to vary among different sites in the glass [13,14]. The temperature dependence is not found to be well described by a fractional power law as in previous reports; however, a combination of a linear temperature dependence and an exponentially activated process is consistent with the data. Finally, the echo results show a homogeneous linewidth substantially narrower than that found in NPHB [11] demonstrating that NPHB experiments need to be carefully re-examined. A more detailed account of these experiments will appear elsewhere [15].

2. Experimental

The sample consisted of a 2.4×10^{-4} mol/ℓ solution of resorufin (Aldrich) in ethanol in a 1 mm spectroscopic cuvette. The sample was cooled rapidly (≈ 1 K/s) through the glass transition to avoid the formation of other phases [16]. Reproducible results were obtained for many different samples and cooling rates, indicating that the details of the glass preparation are not important.

Photon echoes were generated with an amplified picosecond laser which produces single, tunable, 1.5 μJ pulses at 700 Hz. Both the laser system and the experimental apparatus have been described elsewhere [17]. A time resolution of 4 ps was determined by measuring the self-diffraction decay from the room-temperature dye solution, which has a very fast dephasing time. Excitation was at 582 nm, well to the red of the absorption maximum at 578 nm. This ensures that only transitions to the vibrationally unexcited S_1 state were made. Results were unchanged by shifting the excitation frequency 35 cm^{-1} to the red and the blue, confirming that there was no participation from low-frequency vibrations and that the system's dynamics do not vary at different positions in the inhomogeneous line [13].
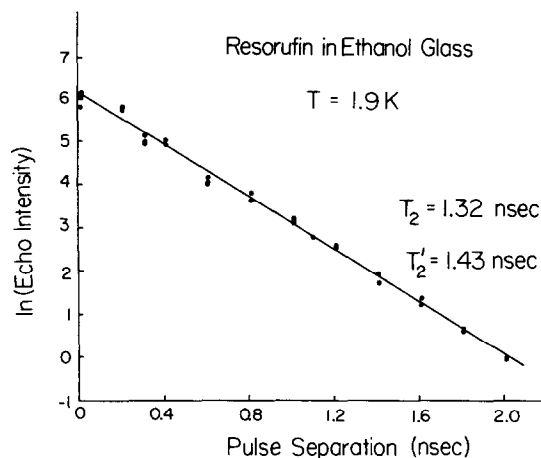
The echo decay could not be recorded by scanning

Fig.1. Decay of the photon echo signal from resorufin in ethanol glass at 1.9 K as a function of the pulse separation, τ. Each point is the signal recorded immediately after unblocking the laser at a new spot in the sample. 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.

an optical delay line to vary the pulse separation, τ, since hole burning caused the signal to drop rapidly after the laser was unblocked. Instead, the signal was recorded immediately after unblocking the laser while the delay line was set for a particular τ. The laser was then blocked, the sample moved to an unburned area, and the signal recorded for a new pulse separation. By plotting the signal level immediately after unblocking the laser as a function of the pulse separation, the echo decay function was found (fig. 1). The echo decay is independent of the time delay between unblocking the laser and the echo measurement provided a constant delay is used throughout the determination of the decay [15]. For each delay line setting, τ, several measurements of the echo intensity are recorded (fig.1). The reproducibility of the measurements is quite good. The fact that reproducible results and well defined decays were found using dozens of different spots in the sample indicates that macroscopically the sample was highly homogeneous.

Temperature-dependent NPHB experiments on this system have been previously reported [11]. The experiment was repeated at 1.56 K to confirm that variations in sample preparation did not affect the results. A Coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to

burn and detect the holes. The holes were detected by transmission with normalization for fluctuations in the laser power. A range of hole depths, including holes smaller than 1% deep, were measured. Burn powers of 0.25–15 μW/cm^2 and burn times of 0.1–20 s were used. The hole was detected using powers from 0.04–0.25 μW/cm^2. In the limit of shallow holes, the width became independent of depth. Our results are in basic agreement with the previous report [11].

3. Results and discussion

An example of a photon echo decay at 1.9 K is shown in fig. 1. The decay is a single exponential over 6.4 factors of e; the decays at all other temperatures were also highly exponential. This is a significant result since even at a single wavelength, a wide range of microscopic environments are excited [18,19]. If these different environments have a range of dephasing times, a non-exponential decay would be expected. Many theories of glass dephasing [4–6] have ignored this effect by averaging the linewidth over the ensemble of sites and not averaging the lineshape [7].

A possible explanation for an exponential decay is that the chromophore interacts with a very large number of TLS. Each chromophore will then sample a representative set of all possible TLS, so each chromophore will have virtually the same dephasing rate. In inorganic glasses, the TLS are relatively dilute [20], so either the molecular glass has a much higher density of TLS, or the interaction between the chromophore and the TLS is very long range. A second possibility has been proposed by Huber et al. [14]. They have presented a model in which an exponential decay is produced by averaging over a particular distribution of non-exponential decays. This result is only found when the interaction between the chromophore and the TLS is dipole–dipole. Whatever the correct explanation, the observation of an exponential decay places a severe restriction on theoretical models.

The temperature dependence of the dephasing was measured from 1.5 to 11.4 K and corrected for the population decay time of the resorufin [11] to obtain the pure dephasing times (figs. 2 and 3). Unlike many previous dephasing studies, the temperature depen-
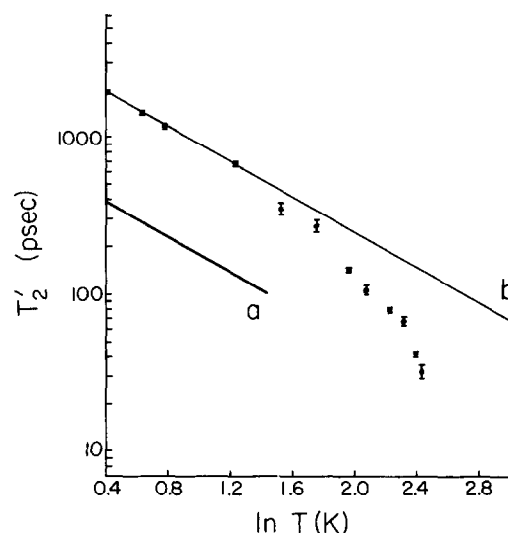

Fig. 2. Temperature dependence of the homogeneous pure dephasing time of resorufin in ethanol glass determined by photon echoes. Error bars represent the estimated standard deviation [21]. The data are not well described by a single-power law. (a) Dephasing times implied by NPHB measurements ($T_2' \propto T^{-1.3}$) (ref. [11]). (b) $T_2' \propto T^{-1.3}$ temperature dependence fit to low-temperature points.

dence is not well described by a single-power law (fig. 2). The systematic deviations from the best power-law fit ($T_2' \propto T^{-1.93}$) greatly exceed the errors in the measurements. In a number of mixed molecular crystals, it has been shown that optical dephasing of the chromophore is due to phonon excitation of librational modes of the chromophore [22]. This gives rise to an Arrhenius temperature dependence [2,23]. Jackson and Silbey proposed that a chromophore in a glass is also dephased by librational modes as well as by the TLS characteristic of the glass [8]. Based on previous theories, they assumed that the TLS contribution has a linear temperature dependence, so the net dephasing rate is

$$1/T_2' = aT + b \exp(-\Delta E/T) \qquad (1)$$

where T_2' is the pure homogeneous dephasing time and ΔE the librational frequency. $1/b$ is related to the librational lifetime. This model has been used to fit data from a vapor-deposited amorphous film [24]. However, deviations from a power-law fit were not seen in that experiment. When the present data are displayed on an Arrhenius plot (fig. 3a), the high-temperature points are nearly linear, suggesting a
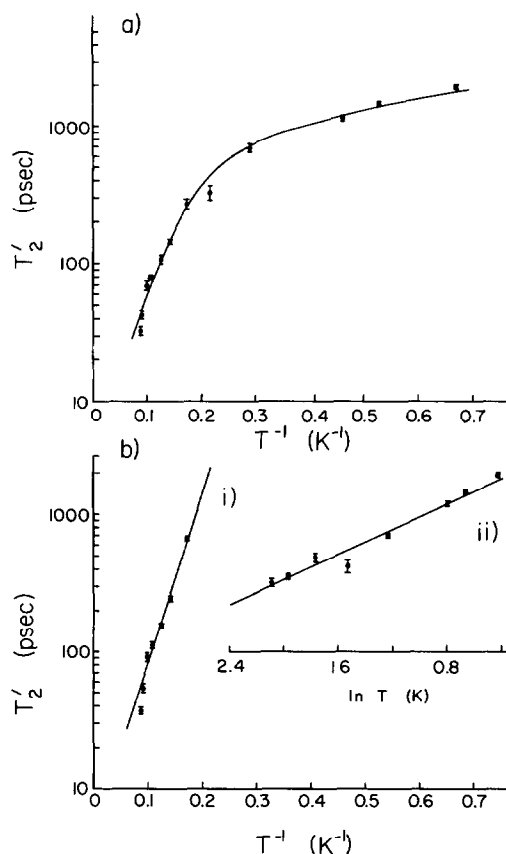
Fig. 3. (a) Arrhenius plot of the homogeneous pure dephasing time of resorufin in ethanol glass. The curve is the best fit to eq. (1). (b) Dephasing data decomposed into: (i) the librational contribution, $T_2' = 4.8$ ps $\exp(19.4\,\mathrm{cm}^{-1}/kT)$, and (ii) the intrinsic glass contribution, $T_2' = 2625$ ps K T^{-1}. Note the different temperature axis for (ii).

contribution from an exponentially activated process. Eq. (1) (curve in fig. 3) fits the data very well with the parameters $a = 3.8 \times 10^{-4}$ ps^{-1}, $b = 0.21$ ps^{-1}, and $\Delta E = 19.4$ cm^{-1}. These values are typical of the values found for librations of similarly sized chromophores in molecular crystals [2,22] and suggest that the activated process is due to librations. In fig. 3b, the individual contributions from the libration and from the TLS dynamics are displayed. The curves were obtained by subtracting the librational component from the low-temperature data (ii) and the TLS component from the high-temperature data (i). It should be noted that a glass dynamic contribution with a fractional power-law dependence as steep as $T^{1.5}$ is also consistent with the data, if a higher librational frequency is assumed [15].
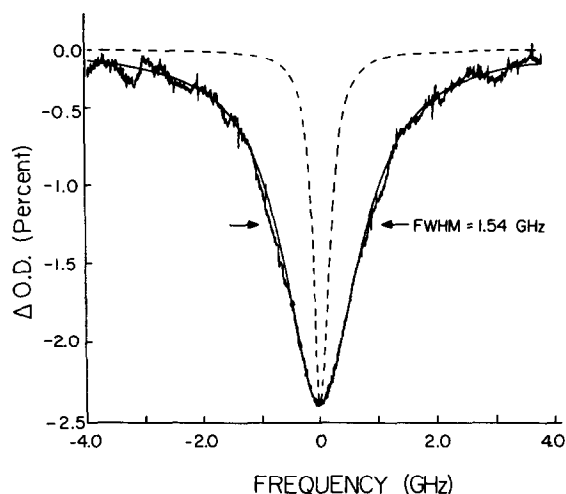

Fig. 4. Non-photochemical hole burned at 582 nm in the spectrum of resorufin in ethanol glass at 1.5 K. The hole is in the range of hole depths in which the fwhm is independent of hole depth. For a hole broadened only by homogeneous dephasing processes, fwhm $= 2/(\pi T_2)$. Solid line: Lorentzian fit to the hole (fwhm $= 1.54$ GHz). Dashed line: homogeneous hole (fwhm $= 326$ MHz) deduced from photon echoes.

The temperature-dependent dephasing times derived from NPHB are also shown in fig. 2 [11]. The times given by NPHB are approximately a factor of four shorter than the photon echo times in the temperature range in which both measurements were performed. The same NPHB linewidths have been measured by us (fig. 4) and by Thijssen et al. [11], indicating that there has not been a systematic error in the linewidth measurements, but rather that the NPHB technique intrinsically does not measure the homogeneous linewidth.

One possible reason for the difference between the photon echo experiment and NPHB is the time between excitation of the molecules and the reading of the signal. In the photon echo, the signal is generated within a time comparable to the dephasing itself, i.e. less than a nanosecond. In NPHB, several minutes typically elapse between burning the hole and reading it. During this time spectral diffusion of molecules in their ground state can broaden the hole. It has already been demonstrated that spectral holes in glasses evolve on a range of timescales between minutes and weeks [10], so it is plausible that they can also evolve on shorter timescales. Another possibility is that the hole is broadened by the dynamics of

the burning process itself.

Comparisons have recently been made between accumulated photon echo experiments and NPHB in polymeric [6] and inorganic [25] glasses. In the accumulated echo the signal is built up on the lifetime of the bottleneck state, typically tens of microseconds to milliseconds. Therefore long-timescale dynamics can play a role in accumulated echoes. The exact effect of ground-state spectral diffusion on these experiments is complicated and has not been explored. Furthermore, there is uncertainty in the reproducibility of the NPHB results [6,11] and in how the effect of NPHB during the echo experiments was dealt with. Thus, it is not possible to discuss these related experiments in light of our results.

4. Concluding remarks

The first two-pulse photon echo measurements in an organic glass have been reported and several important conclusions have been reached. First, the highly exponential decays observed provide a stringent condition on theories for the effect of glass dynamics on electronic dephasing. In particular, a correct average of the decay function, not the decay constant, is necessary to address this observation. Second, the temperature dependence of the dephasing rate does not conform to the power law frequently observed experimentally and predicted theoretically. It is suggested that dephasing is due to chromophore librations as well as intrinsic glass dynamics. Experiments over an insufficiently wide temperature region cannot distinguish between these two processes, leading to an effective power law which is not characteristic of either process. Once the possible contribution of librational dephasing is recognized, the data are consistent with simple models of glass dynamics assuming a constant or slowly varying distribution of TLS energies. Low-temperature thermodynamic measurements on molecular glasses are needed to determine if this assumption is correct.

Finally, the discrepancy between the photon echo measurements and the NPHB linewidths demonstrates that NPHB will not necessarily measure homogeneous dephasing times. Furthermore, even in systems which undergo photochemical hole burning, environmental effects similar to those causing NPHB

may affect the burning process. Therefore, these experiments must also be interpreted with caution. On the other hand, NPHB experiments clearly are probing important dynamics characteristic of the glassy state. It was suggested that ground-state spectral diffusion occurring faster than a few minutes could be an important contribution to these dynamics. Further experiments combining photon echo measurements with NPHB will help to elucidate many features of glass dynamics including the origin of NPHB, the source of NPHB line broadening, and the mechanism of electronic dephasing.

References

[1] W.A. Phillips, ed., Amorphous solids. Low-temperature properties (Springer, Berlin, 1981).
[2] W.H. Hesselink and D.A. Wiersma, in: Modern problems in condensed matter, Vol.4, eds. V.M. Agranovich and A.A. Maradudin (North-Holland, Amsterdam, 1983) p.249.
[3] J.M. Hayes, R. Jankowiak and G.J. Small, in: Persistent spectral hole burning: science and applications, ed. W.E. Moerner (Springer, Berlin), to be published.
[4] S.K. Lyo, Phys. Rev. Letters 48 (1982) 688.
[5] P. Reineker and H. Morawitz, Phys. Rev. B29 (1984) 4546.
[6] L.W. Molenkamp and D.A. Wiersma, J. Chem. Phys. 83 (1985) 1.
[7] D.L. Huber, M.M. Broer and B. Golding, Phys. Rev. B33 (1986) 7297.
[8] B. Jackson and R. Silbey, Chem. Phys. Letters 99 (1983) 331.
[9] H.P. Thijssen and S. Völker, Chem. Phys. Letters 120 (1985) 496.
[10] W. Breinl, J. Friedrich and D. Haarer, J. Chem. Phys. 81 (1984) 3915.
[11] H.P.H. Thijssen, R. van den Berg and S. Völker, Chem. Phys. Letters 120 (1985) 503.
[12] J. Hegarty, M.M. Broer, B. Golding, J.R. Simpson and J.B. MacChesney, Phys. Rev. Letters 51 (1983) 2033; M.M. Broer and B. Golding, J. Opt. Soc. Am. B3 (1986) 523.

[13] Ph. Avouris, A. Campion and M.A. El-Sayed, J. Chem. Phys. 67 (1977) 3397.

[14] D.L. Huber, M.M. Broer and B. Golding, Phys. Rev. Letters 52 (1984) 2281.

[15] C.A. Walsh, M. Berg, L.R. Narasimhan and M.D. Fayer, J. Chem. Phys., in preparation.

[16] O. Haida, H. Suga and S. Seki, J. Chem. Therm. 9 (1977) 1113.

[17] R.J. Gulotty, C.A. Walsh, F.G. Patterson, W.L. Wilson and M.D. Fayer, Chem. Phys. Letters 125 (1986) 507.

[18] H.J. Griesser and U.P. Wild, J. Chem, Phys. 73 (1980) 4715.

[19] H.W.H. Lee, C.A. Walsh and M.D. Fayer, J. Chem. Phys. 82 (1985) 3948.

[20] R.B. Stephens, Phys. Rev. B8 (1973) 2896.

[21] D.P. Shoemaker, C.W. Garland and J.I. Steinfeld, Experiments in physical chemistry, 3rd Ed. (McGraw-Hill, New York,1974) ch.2.

[22] F.G. Patterson, W.L. Wilson, H.W.H. Lee and M.D. Fayer, Chem. Phys. Letters 110 (1984) 7.

[23] H.W.H. Lee and M.D. Fayer, J. Chem. Phys. 84 (1986) 5463.

[24] R. Jankowiak, H. Bässler and R. Silbey, Chem. Phys. Letters 125 (1986) 139.

[25] R.M. Shelby, Opt. Letters 8 (1983) 88.