

High temperature optical dephasing mechanism for dye molecules in PMMA glass

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Picosecond photon echo experiments on rhodamine B and octadecyl rhodamine B in a PMMA matrix between 1.0 and 12.5 K are compared. The two dyes have identical first electronic excited state transitions but different masses and moments of inertia. Echo decay times are identical and individual decays at the same temperature from the two systems are superimposable. The high-temperature echo data can be fit to an activated process with an energy of 15 cm^{-1} . We conclude that in this glassy matrix, high-temperature dephasing is caused by a mode of the host and not a mode of the guest as has been suggested for glasses and is common in crystals.

1. Introduction

Amorphous materials at low temperature have markedly different physical and thermal properties from crystals [1]. Extensive thermodynamic measurements have found excess specific heats and other anomalous thermal and dielectric properties in low-temperature glassy matrices [2]. It has also been shown that many properties, such as the specific heat, depend on time [3]. A wide variety of optical experiments have been performed on chromophores embedded in glasses [4–14]. The large body of evidence indicates that glasses undergo continual structural evolution. Because glasses are of considerable importance in many areas of physics, chemistry, and materials science [4,5] it is important to quantitatively understand the nature of their dynamic processes.

The electronic transition energy of an optical center is affected by fluctuations of its surroundings which causes optical dephasing. Measurements of optical dephasing can provide detailed information on glass dynamics [6–14]. In practice, this requires the extraction of a linewidth from a wide, inhomogeneously broadened absorption band. A number of

line narrowing (dephasing) techniques have been developed and employed to study intrinsic linewidths and hence, dynamical processes in crystalline and amorphous materials [6–14]. Among these are two-pulse photon echoes (PE) [15] and spectral hole burning (HB) [8,16,17]. It has been shown that in complex systems, i.e. for materials such as spin-active crystals [18] and glasses [9,11,13,14,19–22], the time required to make the measurement directly affects the measured linewidth. The PE is sensitive to fluctuations on the timescale of the separation of the pair of pulses used to generate the signal, typically 1 ps to 10 ns. Recent work has focused on using techniques operating on different time scales to understand the microscopic nature of dephasing [6,9,11,19–24] as well as to extract dynamical information such as relaxation rate distributions in glasses at very low temperatures. In this Letter, however, we present experimental results which address the mechanism of optical dephasing at higher temperatures.

Temperature-dependent dephasing measurements on many glassy systems have shown that below $\approx 4 \text{ K}$, the dephasing time T_2^* goes as $aT^{-(1+\alpha)}$, where $0.2 < \alpha < 0.7$ [10,11,13,19,20,24–26]. This is the time regime where tunnelling two-level systems (TLS) control the dynamics [27,28]. The TLS model and its connection with dephasing measure-

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ments has been explored in several recent review articles [7,8,13,24,26]. At higher temperatures, a marked deviation from the power law is observed. Dephasing data on a number of systems above ≈ 5 K are fit well to a model of an activated process [11,19,20,29]. Activated dephasing has been seen in mixed molecular crystals and is attributed to pseudolocal modes, motions of the guest in the host matrix [30–32]. Jackson and Silbey have suggested [33] that activated dephasing should also occur in glasses. In this paper, we report results of PE experiments on a polymer glass which demonstrates that a pseudolocal mode is not responsible for the high-temperature dephasing. Two dyes with identical first electronic excited states but very different masses and moments of inertia are doped into polymethylmethacrylate (PMMA). Temperature-dependent echo measurements on these two systems show identical dephasing times and superimposable echo decays. This is in sharp contrast with crystalline systems in which even a small change in the mass/moment of inertia of the guest gives a significant change in activation energy. We conclude that a mode of the glass, such as a localized optical phonon, is responsible for the high-temperature dephasing in this glass and perhaps others as well. This is consistent with the original Jackson–Silbey suggestion that either a guest or host mode could result in an activated process.

2. Experimental procedures

PE experiments were performed with a tunable amplified sync pumped dye laser with pulsewidth of 3.5 ps, a bandwidth of 10 cm^{-1} , and a repetition rate of 700 Hz [11,13]. Dye doped polymer samples were solvent cast. Rhodamine B (RB) or octadecyl rhodamine B (ODRB) were dissolved with PMMA in methylene chloride. Clear films of thickness 0.2–0.6 mm and optical density (OD) ≈ 1 were obtained by holding the samples at $\approx 60^\circ\text{C}$ under vacuum to remove the solvent. Samples were mounted on a copper block and placed in either an immersion dewar or a variable-temperature helium gas flow cryostat. Temperatures below 2.17 K were maintained by controlling the vapor pressure of the superfluid liquid helium in which the sample was immersed. Above 2.17 K, the temperature was regulated by controlling

the temperature of helium gas in contact with the sample and measured by a calibrated germanium resistance thermometer mounted directly on the sample. Temperature regulation in all cases was better than 0.05 K. The two different samples, RB/PMMA and ODRB/PMMA, were mounted side-by-side and could be probed by laterally displacing the dewar ≈ 5 mm. This ensured that beam alignment and all other experimental parameters were kept constant. Samples were excited at 572–574 nm with pulse energies of $\approx 100 \text{ nJ/pulse}$. Power studies demonstrated that there were no effects of power or sample heating on the measured dephasing times.

In contrast to previously studied systems [11,19,20], no hole burning was observed in these samples with the pulse energies used. It was, therefore, unnecessary to make corrections for sample hole burning. The pulse separation, τ , was increased until the signal level was constant, yielding the baseline due to scattered light. Usually, ten scans were averaged. Decays were exponential over four or more factors of e . Spots in the sample were varied and no significant differences could be found in the decay times indicating no temperature- or sample-dependent artifacts. Identical results were obtained with samples prepared from different batches. Decays above 10 K were determined by fitting the observed decay to an exponential convolved with the instrument response. The latter was determined by taking a decay at room temperature.

Fluorescence lifetimes (T_1) were measured with a time-correlated single-photon counting setup. Very low OD (< 0.1 at the absorption maximum) samples were used to eliminate effects due to reabsorption. Reproducibility was better than 5%.

3. Results and discussion

Fig. 1 shows on a log–log plot the pure dephasing times T_2^* (fluorescence contribution removed) of RB and ODRB in PMMA as a function of temperature. The data can be fit to a form proposed by Jackson and Silbey [33]

$$\frac{1}{\pi T_2^*} = aT^\alpha + \frac{b}{1 - \exp(-\Delta E/kT)} \exp(-\Delta E/kT). \quad (1)$$

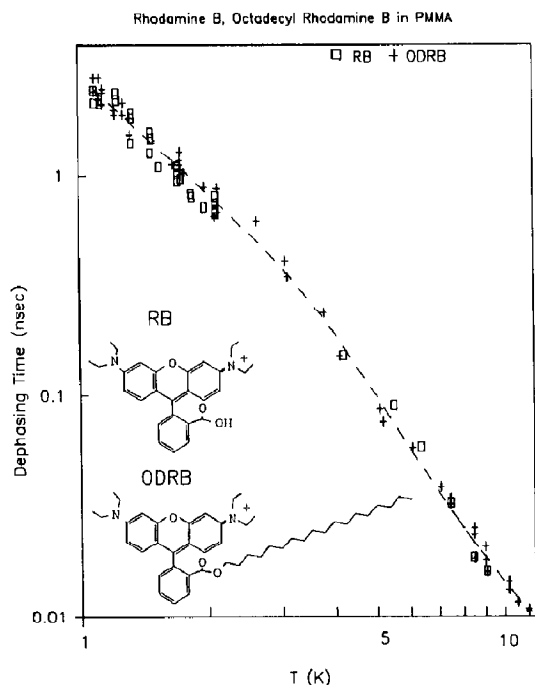


Fig. 1. Log-log plot of the homogeneous dephasing time in rhodamine B (RB) and octadecyl rhodamine B (ODRB). The temperature dependences are identical even though the two chromophores have very different masses and moments of inertia.

The power-law behavior at low temperature reflects the density states of the glassy TLS [7,14,26,34,35]. This behavior has been seen by various dephasing methods such as hole burning, fluorescence line narrowing, and accumulated echoes on several molecular and network glasses [6,7,10,11,14,19,20,24-26,29]. At higher temperatures, the exponential term begins to dominate. The temperature-dependent prefactor to the activated process is simply the thermal occupation number for photons of energy ΔE . In studies of crystalline systems, only exponentially activated dephasing is seen, there is no power-law dependence at low temperatures [30,32]. The activation energy in crystalline systems is very sensitive to the mass/moments of inertia of the guest.

The dye-glass coupling strength must be considered when comparing different systems probed by any dephasing technique [11,19,2022] since any observed differences at a given temperature can be a result of differences in coupling strength. The two dyes in this study, RB and ODRB, have identical first

electronic excited state transitions. ODRB is an 18-carbon alkyl ester of RB. The addition of the alkyl chain (see fig. 1) to the σ framework does not influence the π electron system responsible for the S_0 - S_1 transition under study.

The masses and moments of inertia of the two molecules are vastly different, therefore ODRB and RB should exhibit different activation energies if the pseudolocal mode analogy with crystalline systems is valid. Pseudolocal modes are a combination of librations and translations of the chromophore [32]. The mass of ODRB is almost twice that of RB and the alkyl chain changes all of the moments of inertia. Fig. 1, however, shows that both systems exhibit identical dephasing times over all temperatures studied. Wiersma et al. [30] and Olson et al. [32] have found that partial deuteration or methylation of relatively large chromophores can cause changes of over 20% in the pseudolocal mode energy.

Fig. 2 compares the decay from each system at 6.60 K. At small pulse separations, there is a fast component to the decay which arises from excitation of higher-lying vibrations and the acoustic phonon sideband. The slower component is due to S_0 - S_1 zero-phonon-line dephasing. Two-component decays have been seen in the incoherent accumulated echo studies of Saikan and co-workers on similar polymers [36], in which the electron-phonon coupling is known to be strong. A temperature-dependent study of the intensity of the fast component versus that of the zero-phonon line could, in principle, yield the Debye-Waller factor for this system. The intensity of the fast component increased with increasing temperature which is in qualitative agreement with expected behavior. The power dependences of the fast and slow components were, however, different. The phonon contribution varied as the cube of the excitation intensity (small flip angle limit) whereas the zero-phonon line varied roughly linearly with the intensity (large flip angle limit). This makes for a practical difficulty in extracting the Debye-Waller factor. The sample must be excited well to the red of the absorption maximum to avoid contributions from molecular vibrations and at sufficiently low power that both contributions to the decay are in the small flip angle limit. Since the issue was tangential to the focus of this work, it was not pursued. Our previous echo studies on dyes in organic glasses [11,13,19,20]

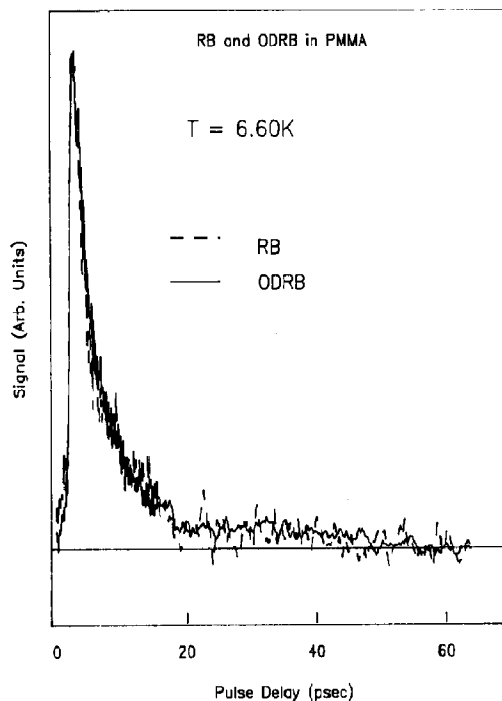


Fig. 2. Comparison of two echo decays, RB/PMMA and ODRB/PMMA at 6.60 K. The decays are superimposable. Taken together with the data of fig. 1, this means that the mode responsible for dephasing at high T in PMMA is a property of the polymer matrix and not some localized motion of the chromophore as is the case in crystalline systems.

showed a fast component due to molecular vibrations only when excited near the absorption maximum. Detuning to the red eliminated the vibrational contribution. We attribute the absence of a fast contribution to weaker electron-phonon coupling in these materials.

The key point of this work is that individual decays as well as the full temperature dependence of both RB and ODRB in PMMA are identical. Figs. 1 and 2 eliminate the possibility that guest pseudolocal modes are responsible for the higher-temperature dephasing in these systems.

The temperature dependence of the dephasing at high temperatures in these and several other systems [11,13,19,20] can be fit to a single activation energy. Fig. 3 is an Arrhenius plot of the high-temperature dephasing times with the low-temperature, power-law contribution removed. The straight line indicates an activated process with an energy of 15 ± 2

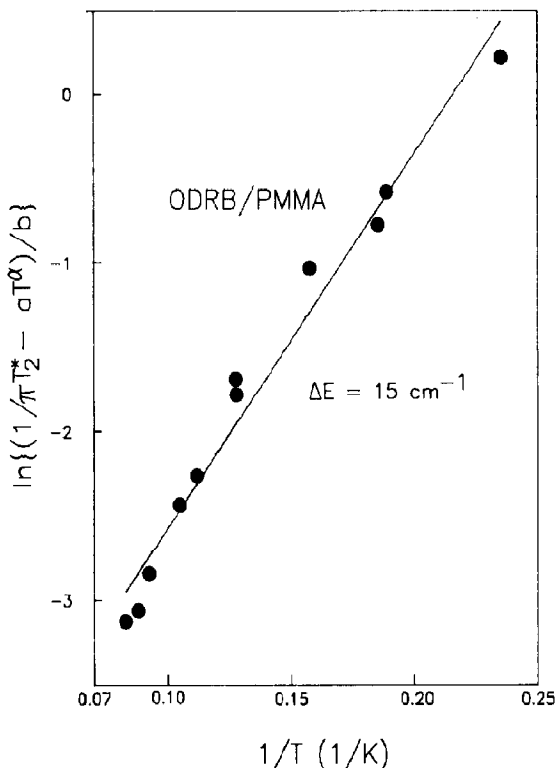


Fig. 3. Arrhenius plot of the high-temperature dephasing times in ODRB/PMMA after removal of the contribution of tunnelling TLS. The straight line indicates the mode has an energy of 15 ± 2 cm^{-1} . Quadratic coupling to a host optical phonon is suggested as the dominant dephasing mechanism.

cm^{-1} . The main uncertainty in activation energy is due to the uncertainty in the power law, which must be subtracted from the high-temperature data. Recently, Greenfield et al. [37] have obtained echo decays on the HITCI/PMMA system. HITCI, a near-IR dye which was studied with a free electron laser, is completely different from RB/ODRB. The PMMA sample was prepared identically to those studied here. The results show an activation energy of 15 cm^{-1} [37].

The range of possible activation energies is broad and depends on the system. Table 1 contains fit parameters for some of the other systems studied to date. The resorufin/glycerol system has an unusually high activation energy of $\approx 35 \text{ cm}^{-1}$ [11]. Small organic solvents such as ethanol have lower activation energies, typically 20 cm^{-1} . The energies obtained in glasses are also very similar to the pseudolocal mode

Table 1

Dye	Glass	T_1 (ns)	a (ns ⁻¹ K ^{α})	α	b (ns ⁻¹)	ΔE (cm ⁻¹)
RB	PMMA	4.8	0.11	1.7	150	15
ODRB	PMMA	4.7	0.11	1.7	150	15
RB	ethanol- <i>d</i>	3.2	0.14	1.5	330	24
resorufin [20]	ethanol- <i>d</i>	4.2	0.26	1.3	230	21
resorufin [11]	glycerol	3.5	0.10	1.2	330	37

energies that have been measured in mixed crystals [30,32].

Several groups have addressed the problem of temperature-dependent dephasing and guest-host coupling mechanisms in crystals [38-43]. These studies have shown that quadratic coupling to acoustic phonons gives a T^2 dependence. Hsu and Skinner treated optical dephasing induced by pseudolocal modes and optical phonons with a non-perturbative theoretical technique [42]. Lee and Fayer obtained similar results using optical Redfield theory [43]. Both treatments showed that narrow-band optical phonons produce dephasing which is approximately exponentially activated. Lee and Fayer considered several forms of the density of phonon states and showed that, while the temperature dependences of optical dephasing are not strictly exponential (straight line on an Arrhenius plot) over the range of temperatures considered in experiments, they could not be distinguished from exponentially activated processes. The results in fig. 3 are, therefore, consistent with quadratic coupling to an optical phonon. In a disordered material, an optical phonon could become a localized host mode yet still possess a narrow distribution of energies. Such a localized host mode is consistent with the experimental photon echo results which show that a mode of the guest molecule is not a candidate as the high-temperature dephasing mechanism of RB and ODRB in PMMA.

We note that the energy of host modes can vary substantially from system to system. The high-temperature dephasing will be dominated by the mode which lies lowest in energy, since it will activate first. For some materials, this could be a pseudolocal mode of the chromophore.

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