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Thermal recovery of spectral holes of dye molecules in polymer films. Site distribution in two-level systems

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Abstract

We have measured the temperature-annealing and the temperature-cycling hole-burning spectra of 5-(and 6-)carboxy-X-rhodamine-N-hydroxy-succinimidyl ester doped in polyvinyl alcohol films. The difference of the reduction of zero-phonon hole between annealing and cycling spectra can be described by the linear electron–phonon coupling, which provides the information of site distribution of asymmetric energy.

1. Introduction

The configurational relaxation of glasses is normally described by a two-level system (TLS) [1,2]. Since an amorphous glass has a wide variety of local configurations, a distribution of a TLS characterized by the asymmetric energy (ϵ) and the barrier height (V) determines the transitions among local structures. These two parameters are defined in a TLS diagram as shown in Fig. 1. The molecule can interconvert between the two wells by hopping over the barrier or tunneling through it [1,2]. The measurements of the distribution of barrier heights and asymmetric energy are important for better understanding the glass properties.

Spectral hole-burning (SHB) method has been extensively applied to investigate the configurational relaxation of low-temperature glasses [3–8]. Hayes and Small [9] first applied the TLS to describe the hole formation and then determine the rate of site interconversion in organic glasses. Furthermore, they used the TLS to interpret the hole filling in temperature-annealing spectra and found that the tunneling mechanism is dominant for $T \leqslant 10$ K, and the thermally activated process is dominant for $T \geqslant 10$ K [10]. Recently, Friedrich and co-workers have introduced a temperature cycling method to investigate the distribution of barrier heights in various chromophore–glass systems [11–14]. They found that the barrier heights V follow a distribution of $P(V) \sim V^{-1/2}$ based on the tunneling model [1]. Elschner and Bässler [15] have employed a Gaussian distribution for the barrier heights to describe the thermally induced hole filling. Unfortunately, it is not able to determine the distribution among various functions for describing glass dynamics at this moment. To our knowledge no attempt has been made to study the site distribution by probing the distribution of asymmetric energy.

In this work, we propose an experimental method to measure the site distribution in glasses. We have measured the temperature-annealing and the tem-

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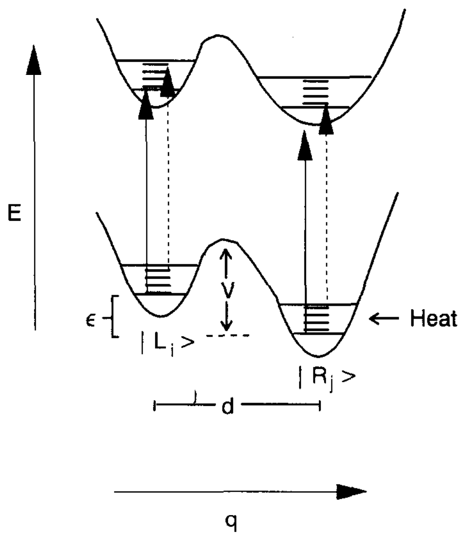

Fig. 1. A schematic representation of the double-well potential characteristic of two-level systems. V: barrier height, ε: asymmetric energy, d: difference between two minima, q: coordinates. The solid and dashed lines correspond to the transition at low and high temperatures, respectively.

perature-cycling hole-burning spectra for 5-(and 6-)carboxy-X-rhodamine-N-hydroxy-succinimidyl ester (RhSE) doped in polyvinyl alcohol (PVOH) films. The difference of the hole reduction of zero-phonon hole (ZPH) as a function of temperature can be utilized to extract information about the electron–phonon coupling parameters. In addition, the difference between them resulting from the linear electron–phonon coupling may provide the information of site distribution of asymmetric energy.

2. Experimental

We have obtained absorption spectra by dispersing the output of a xenon arc lamp (Oriel 68742) through a 1 m Jobin–Yvon THR 1000 spectrometer and then splitting the output into two beams. One beam was used to produce a reference signal and another beam was focused onto the sample to produce a sample signal. Both signals were recombined and monitored by the same photomultiplier tube whose output was sent to two lock-in amplifiers (Stanford SR530) referenced to the chopping frequencies. The outputs of the lock-in amplifiers were sent to personal computers and they were used to calculate the logarithmic ratio which provided a signal directly proportional to the sample absorbance. The hole-burning spectrum was burned by using an Ar^+ laser pumping a dye laser with a width of ≈ 1 cm^{-1} at $\lambda_B \approx 5812$ Å. We intended to produce a broader ZPH for eliminating the linewidth effect in the integrated hole area. However, the ZPH can be seriously interfered by the phonon side band hole while using high laser power and long burning time. Thus, both factors are carefully controlled during the experiments. The typical burning time is 5 min and the photon flux is $\leqslant 40$ mW/cm^2. The spot size of the burning beam was ≈ 1 mm and that of the reading beam was ≈ 200 μm. Extreme care was taken to ensure that the cross section of the probe beam at the sample should be inside the area of the burn laser.

The dye molecule (RhSE) was introduced into the polymer solution which was made by dissolving the polyvinyl alcohol (PVOH) in purified deionized water [16]. The syrupy solution was poured onto a quartz plate. The samples were placed into a desiccator and were allowed to dry into films. Sample thicknesses were 65 ± 10 μm. The absorption spectra were taken at room temperature (Hitachi U-3200 spectrophotometer), at which the lowest absorption band is located at ≈ 574 nm [16]. The optical densities (OD) of various samples at 574 nm are 0.4 ± 0.1. The samples were mounted on a brass plate with several drilled holes of ≈ 1 mm diameter, which were put into a Janis dewer and were cooled by passing cold helium gas over it. The temperature was measured by a calibrated silicon diode temperature sensor (Lake Shore Cryotronics Model). Because of the low thermal conductivity of polymer sample, all spectra were taken after the temperature stabilized for $\geqslant 30$ min to ensure the same temperature of the sample as the mount. The deviation of the temperature is ± 0.5 K at low temperature.

3. Results

Fig. 2a shows the absorption spectra before and after hole burning of RhSE doped in PVOH films at $T_b = 6$ K. The structure of the RhSE dye molecule is also presented in Fig. 2a. The width of zero-phonon hole is ≈ 6 cm^{-1} and the lineshape is close to Gaus-

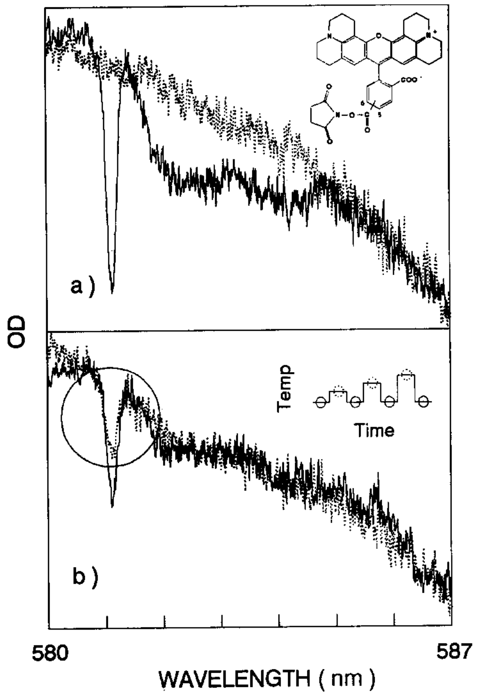

Fig. 2. The absorption spectra before hole burning at 6 K (dashed line in (a)), after hole burning (solid line in (a)), annealing at 25 K (dashed line in (b)), and cycling back from 25 to 6 K (solid line in (b)). The structure of RhSE is shown in (a). The cycle annealing procedure is shown in (b). The HB spectrum is measured by burning a hole at a low temperature, T_b. Then, the temperature of the system is raised to some value T_a, where the annealing spectrum is measured. The system is cycled back to the burning temperature, $T_c = T_b$, where the cycling spectrum is measured.

sian. Fig. 2a also shows an asymmetric phonon side band hole with tailing on the low-energy side. In addition, an unusual broad hole located at ≈ 3 nm to the red of the ZPH is observed in Fig. 2a. Fig. 2b presents the annealing ($T_b \rightarrow T_a$) and the cycling ($T_b \rightarrow T_a \rightarrow T_c$) spectra, where $T_a > T_b$ and $T_c = T_b$. The hole area is reduced by 60% in the annealing spectrum taken at $T_a = 25$ K. However, part of the holes is recovered when the system is cycled back to the burning temperature at $T_c = 6$ K. It is important to investigate the difference between these two processes.

The lineshape of ZPH circled in Fig. 2b shows a significant difference between annealing and cycling spectra. The shape of the blue side is quite steeper in the cycling spectrum than in the annealing spectrum. For clarity, Fig. 3 presents the lineshape of ZPH of annealing and cycling spectra at 15 and 25 K. Both lineshapes at 15 K are close to Gaussian, but the lineshape of the annealing spectrum at 25 K is close to Lorentzian and that of the cycling spectrum is again close to Gaussian. The fitting parameters of linewidths of these spectra are identical, 1.1 Å for the Lorentzian lineshape and 0.75 Å for the Gaussian lineshape. The width of ZPH in the cycling spectra is independent of temperature until 35 K. The width in the annealing spectra shows no significant difference until 25 K. In addition, we have measured the hole area of ZPH as a function of waiting time in order to examine the spontaneous filling. Our results show that the ZPHs are nearly identical within experimental error after three hours waiting time in the annealing and cycling spectra at 6 and 20 K, respectively [16].

Fig. 4a shows the plots of the integrated hole area versus temperature in the annealing and cycling spectra. It is noted that the main deviation of the integrated hole area is due to the interference of anti-hole and phonon side band hole as shown in Fig. 2. For clarity only two error bars are displayed in Fig. 4a. Nevertheless, the hole area is clearly reduced when the temperature is increased for both cases. The ZPH disappears at ≈ 40 K in the annealing spectra and at ≈ 55 K in the cycling spectra as shown in Fig. 4a. In addition, the difference of the integrated hole area between annealing and cycling spectra as a function of annealing temperature is plotted in Fig. 4b.

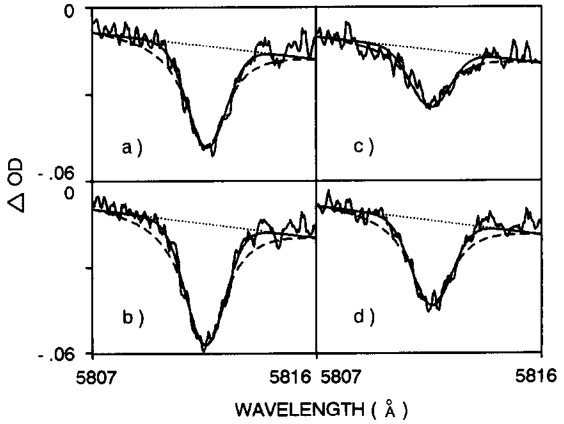

Fig. 3. Temperature dependence annealing and cycling hole spectra. (a) Annealing at 15 K, (b) cycling at 15→6 K, (c) annealing at 25 K, (d) cycling at 25→6 K. Fits to Gaussian and Lorentzian shapes are shown (solid line versus dashed line).

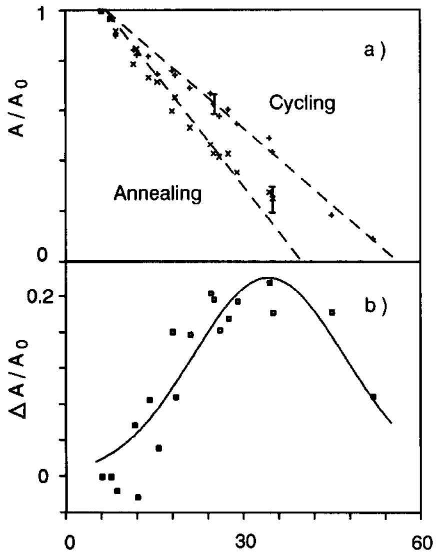

Fig. 4. (a) The relative hole area A/A_0 as a function of annealing (×) and cycling (+) temperatures. The dashed lines are for visual guides. (b) The difference between annealing and cycling hole area as a function of temperature. The solid line is a fit of Eq. (6) to the experimental data by using $T_p = 35$ K and $\sigma_G/\alpha = 9$ cm^{-1}.

4. Discussion

In general, the initial distribution function in a glass can be viewed as stationary in the sense that the population interconversions among different sites are in equilibrium. After an optical excitation, the initial distribution is perturbed and some types of guest–host interaction processes deplete the population ΔN_j at original state to produce a hole in the absorption spectrum [9,10]. However, this perturbed system tends to restore the initial distribution because of population gradient [17]. This is confirmed by the identical absorption spectra taken before hole burning and after the thermally induced hole filling at $\geqslant 100$ K. Therefore, we consider the hole filling due to the population ΔN_j returned from the product state back to the original state.

Two processes are involved in the reduction of hole area, which are spontaneous filling and thermally activated processes. The former results from the phonon-assisted tunneling and the latter is attributed to the hopping from the product state to the original state [10–14]. Spontaneous filling can be examined as a function of waiting time and thermally activated processes can be studied as a function of temperature. Since the line width of the cycling spectra is independent of temperature until 35 K as shown in Fig. 3 and the hole area shows no significant change for three hours, the spontaneous filling is unlikely to be the dominant hole-filling effect in this work.

Concerning the effect of linewidth to the hole area, the Gaussian lineshape of ZPH can be described by $\sum_i N(\omega_i) g(\omega_i)$, where $N(\omega_i)$ is the population at transition ω_i and $g(\omega_i)$ is a lineshape function. For simplicity, we assume that $g(\omega_i)$ is independent of ω_i for a small frequency region, i.e. $\sum_i N(\omega_i) g(\omega_i) \approx g(\omega) \sum_i N(\omega_i)$. Since the temperature dependence of $g(\omega_i)$ is identical at the same temperature during cycling spectra, the change of the integrated hole area can be utilized to probe the distribution of barrier height [11,12]. Furthermore, if the hole width is much broader than the temperature-dependent homogeneous linewidth, the asymmetric energy may be measured from the reduction of hole area in the annealing spectra.

At this moment, we are not able to measure the homogeneous line width since the width of our laser is ≈ 1 cm^{-1}. However, Völker and co-workers [18,19] have measured the linewidth of ZPH for free base porphin in PVOH. The linewidth is ≈ 0.06 cm^{-1} at 5 K and ≈ 0.3 cm^{-1} at 20 K. In addition, they found that power broadening the linewidth is normally presented in the HB spectra. In order to observe the reliable homogeneous linewidth, one should control not only the burning power and the burning time but also the detection method [20,21]. The width of ≈ 6 cm^{-1} is probably attributed to the power broadening. However, we are interested in the change of hole area after hole burning. The nearly identical linewidth of ZPH in the cycling spectra as shown in Fig. 3 implies that the effect of power broadening can be neglected in this work.

Molenkamp and Wiersma [22] found that the linewidths measured by SHB for pentacene doped in PMMA were much broader than those obtained from photon echo. Fayer and co-workers [7,23] have carefully investigated the difference between hole linewidth and echo linewidth for cresyl violet and resorufin doped in ethanol glasses. The significantly broader linewidths measured by SHB than by photon echo were attributed to the spectral diffusion processes. Although the detailed mechanism of spectral diffusion is not clear, the hole area due to the linewidth effect can be neglected because of the much broader linewidth of ≈ 6 cm^{-1} produced in this work.

Since the annealing and the cycling spectra are measured at different temperatures, the difference of hole reduction between them may simply be due to the temperature effect. It is known that the integrated intensity of the ZPH is temperature-dependent because of linear electron–phonon coupling, which can be described by the Debye–Waller factor $\alpha(T)$ [4,24–26],

$$\alpha(T) = \exp[-2S(T)] \,. \qquad (1)$$

The factor 2 in Eq. (1) is due to the two-photon processes involved in the hole-burning spectra at the same temperature. $S(T)$ is the coupling constant (or the Huang–Rhys factor), which is given by [27,28]

$$S(T) = \sum_j P_j/\hbar\omega_j \coth(\hbar\omega_j/2kT)$$
$$= \sum_j S_j \coth(\hbar\omega_j/2kT) \,, \qquad (2)$$

where $P_j = \frac{1}{2} m\omega_j^2 q_j^2$ is the half Stokes energy shift for the jth mode and q_j is the shift of the equilibrium position of the oscillator. Since it is difficult to determine all the modes involved in the summation of the equation, an average frequency, ω_p, is introduced for reducing Eq. (2) to

$$S(T) = \sum_j S_j \coth(\hbar\omega_p/2kT)$$
$$= S_0 \coth(\hbar\omega_p/2kT) = S_0[2\bar{n}(T)+1] \,, \qquad (3)$$

where S_0 is the coupling constant at $T = 0$ K and $\bar{n}(T)$ are the thermal occupation numbers at mean phonon frequency of ω_p, $\bar{n}(T) = [\exp(\hbar\omega_p/k_B T) - 1]^{-1}$. When the temperature increases, the Debye–Waller factor $\alpha(T)$ decreases. In the annealing spectra, the hole is burned at a low temperature, but is probed at higher temperatures, the Debye–Waller factor $\alpha(T)$ follows

$$\alpha(T) = \exp\{-S_0[2\bar{n}(T)+2]\} \,. \qquad (4)$$

It is known that the reduction of the hole area in the cycling spectra is attributed to the depleted population crossing the barrier from the product state to the original state via thermally induced hole filling [11–15]. This reduction of the hole area is also involved in the annealing spectra. If the difference of hole areas between the annealing and the cycling spectra results from the linear electron–phonon coupling [4,24–26], the ratio of these two intensities $I_{ZPH}(T_a)/I_{ZPH}(T_c)$ as a function of temperature should follow

$$I_{ZPH}(T_a)/I_{ZPH}(T_c) = \alpha(T_a)/\alpha(T_c)$$
$$= \exp[-2S_0\bar{n}(T_a)] \,, \qquad (5)$$

while $T_c \to 0$. The solid curves in Fig. 5 are the fits of Eq. (5) to the experimental data. The use of parameters $S_0 \approx 0.7$ and $\omega_p \approx 30$ cm^{-1} can fit our experimental results. The agreement between the fits and our experimental data indicates that the difference of hole area between annealing and cycling spectra is attributed to the linear electron–phonon coupling.

Since an amorphous glass has a wide variety of local configuration, a distribution of TLS characterized by the asymmetric energy ϵ_j determines the optical transition. After photobleaching a specific site of the absorbers at laser frequency, a hole is produced in the absorption spectra. In the temperature-annealing spectra, two processes can reduce the hole area. The population of ΔN_j in the product state with barrier height $V_j < kT_a$ can cross the barrier and return back to the initial state. This is a temperature-irreversible process. In addition, the thermally activated populations of $\Delta N_{e\text{-}p}$ via the linear electron–phonon coupling in the product state with an asymmetric energy of $\epsilon_a \leqslant kT_a$ can also absorb the photon as the dashed line shown in Fig. 1. This is a temperature-reversible process. The hole area observed in the annealing spectra corresponds to the populations of

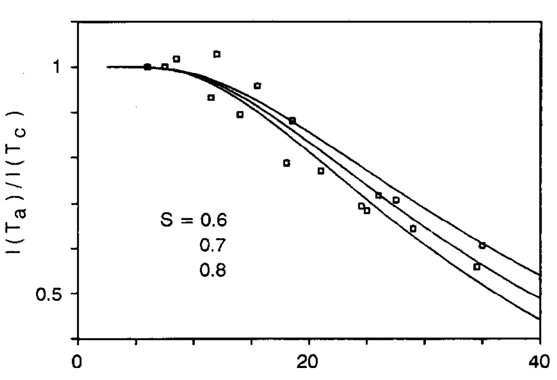

Fig. 5. The plots of the ratio of $I_{ZPH}(T_a)/I_{ZPH}(T_c)$ as a function of temperature. The solid lines are the fit of Eq. (5) to the experimental data by using $\omega_p = 30$ cm^{-1}.

$\Delta N - \Delta N_j - \Delta N_{\text{e-p}}$. In the temperature-cycling spectra, those populations of ΔN_j returned back to the initial state are temperature-irreversible [11–15], but the populations of $\Delta N_{\text{e-p}}$ are retrapped since $\epsilon_a > kT_b$. Therefore, the hole area determined by $\Delta N_{\text{e-p}}$ is recovered after a temperature-cycling as presented in Fig. 2b. Since the magnitude of the Stokes energy shift produced by the linear electron–phonon coupling is a function of temperature, it can be utilized to monitor the distribution of asymmetric energy. We further assume that the ≈ 6 cm^{-1} of the hole width is much broader than the temperature-dependent homogeneous linewidth in this work. Thus, we believe that the difference of hole area between annealing and cycling spectra as shown in Fig. 4b can provide the distribution of $\Delta N_{\text{e-p}}$ as a function of asymmetric energy ϵ_a. To our knowledge, this is the first direct measurement of the site distribution in glasses by using SHB method.

Therefore, we further examine the distribution function of asymmetric energy. A Gaussian form is used for this purpose, which is given as

$$G(T) \propto \exp\{-[E(T) - E(T_m)]^2 / 2\sigma_\epsilon^2\}, \qquad (6)$$

where $E(T) = \alpha kT$ and α is a parameter. $E(T_m)$ and σ_ϵ correspond to the mean-value of the activation energy and the half width, respectively. Without considering the linewidth effect, the solid curve in Fig. 4b is a fit of Eq. (6) by using $E(T_m) = 35$ K and $\sigma_\epsilon / \alpha = 9$ cm^{-1}. Considering that this is an approximation model the agreement between experiment and theory appears reasonable. With reference to the Gaussian function employed in the study of barrier heights [15], it is suggested that the Gaussian distribution is more appropriate for describing the glass properties. Further detailed examination among the different distribution functions is in progress.

Finally, the Lorentzian shape in Fig. 3c may be due to thermal broadening effect. It is noted that the Lorentzian shape may not correspond to the true homogeneous linewidth [4,19]. In addition, the 6 cm^{-1} linewidth at 25 K seems too large in relative to the ≈ 0.3 cm^{-1} linewidth at 20 K for free-base porphin in PVOH [18,19]. Further study on the annealing HB spectra at high temperature is in progress.

In summary, we have demonstrated that the difference of the hole area between annealing and cycling spectra can be described by the linear electron–phonon coupling. Furthermore, we proposed that the difference of them can provide a distribution of asymmetric energy, which can be described by a Gaussian distribution function. We believe that the SHB method is a useful method to measure the site distributions in the TLS for better understanding the configuration relaxation of glasses.

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