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Spectral diffusion of molecular electronic transitions in amorphous solids: Weak and strong two-level-system phonon coupling

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The two-level-system (TLS) model of glasses is used with nonphenomenological TLS distribution functions [R. Jankowiak *et al.*, J. Phys. Chem. **90**, 3896 (1986)] to account for the time-dependent spectral-diffusion data for cresyl violet and zinc porphin in ethanol glasses at low temperatures [K. A. Littau and M. D. Fayer, Chem. Phys. Lett. **176**, 551 (1991); H. C. Meijers and D. A. Wiersma, Phys. Rev. Lett. **68**, 381 (1992)]. The two distributions of faster and slower TLS relaxation rates required to fit the data are characterized for both weak and strong TLS-phonon coupling. Comparison of the values obtained for the TLS parameters with those determined earlier for specific heat, thermal conductivity, pure dephasing, and spontaneous filling of nonphotochemical holes establishes that the faster and slower distributions are associated with intrinsic and extrinsic TLS. The pronounced effects of strong coupling on the TLS relaxation-rate distributions are discussed.

I. INTRODUCTION

That the widths of the zero-phonon lines (ZPL) of impurity molecules and R^{3+} ions imbedded in amorphous hosts are anomalous in their magnitude and temperature dependence for $T \lesssim 10$ K has been known since the late 1970's (for recent reviews see Refs. 1–7). Initially, persistent nonphotochemical hole burning[2,3] (NPHB)[2,3] was used to probe the T dependence of the ZPL profile in organic systems.[8] Earlier,[9] a mechanism for NPHB had been proposed that is based on phonon-assisted tunneling of a static distribution of two-level systems (TLS) intimately associated with the impurity. These TLS's are now referred to as extrinsic, $\mathrm{TLS_{ext}}$. Shortly thereafter, it was proposed that[8] the anomalously large optical linewidths of impurity molecules, with their near linear dependence on temperature, were a manifestation of the interaction between the impurity and a different, faster relaxing type of TLS, now recognized to be intrinsic to the glass host, $\mathrm{TLS_{int}}$. The same conclusion was independently reached for R^{3+} ions in inorganic glasses.[10–12] Theories of *pure* dephasing from impurity $\mathrm{TLS_{int}}$ coupling, in which the off-diagonal[8,12,13] or diagonal[10,11,14–18] modulation terms of the impurity TLS interaction Hamiltonian were considered, rapidly emerged. Until 1986,[19–21] theories were guided by the phenomenological TLS distribution function of Anderson, Halperin, and Varma[22] and Phillips;[23] namely, $P(\Delta,\lambda)=\text{const}$ for $\lambda_{\min} \le \lambda \le \lambda_{\max}$ and $\Delta_{\min} \le \Delta \le \Delta_{\max}$ and zero otherwise. Here λ and Δ are the TLS tunnel and asymmetry parameters. The tunnel state splitting is $E=(\Delta^2+W^2)^{1/2}$ where the tunneling frequency $W=\omega_0 \exp(-\lambda)$ and ω_0 is the average harmonic frequency of the two wells of the TLS. The above distribution function leads to a density of states $\rho(E) \sim \text{const}$. Utilization of phenomenological distribution functions in dephasing theories for averaging over the TLS interacting with the impurity necessitates assumptions[12,15,16] beyond that of an absence of correlation between Δ and λ. The dephasing theories have also taken the TLS-phonon interaction to be weak.

Thermal-cycling-hole-burning experiments had proven early on that[24,25] broadening of the zero-phonon hole (ZPH) occurs by spectral diffusion induced by slow thermally assisted, irreversible glass relaxation processes with the impurity in its *ground* state. However, it has only been recently[5,26–30] that the question of the contribution of spectral diffusion to persistent nonphotochemical, photochemical, and transient population bottleneck ZPH's produced under normal protocol has been actively pursued. By normal it is meant that the burn and read temperatures (T_B, T_R) are the same. In the thermal-cycle experiment the hole is burned and read at T_B, the sample temperature raised to $T > T_B$, then lowered to T_B and the hole read again. The resulting partial thermal annealing of the hole is accompanied by broadening.[25,31] Given the result from thermal cycling, that the longitudinal relaxation time (τ_1) of the typical probe molecule is short, a few ns, and the time dependence of the specific heat,[32–34] it would be reasonable to expect a contribution to the ZPH width from spectral diffusion when the waiting and reading times (t_W, t_R) are long. In a series of beautiful two-pulse photon echo and NPHB experiments with resorufin and cresyl violet in alcohol (ethanol, glycerol) glasses Fayer and co-workers[5,26,28,29,35] determined that the homogeneous width of the ZPL determined by photon echo is substantially narrower $(\sim \times 6)$ than that determined by NPHB for $T \lesssim 8$ K. They ascribed the difference to spectral diffusion. Although later NPHB experiments on the same systems by Völker and co-workers[4,36,37] led to some controversy concerning the magnitude and temperature dependence of the spectral diffusion reported by Fayer and co-workers, very recent two-pulse photon echo and fast $(\gtrsim 10\ \mu\text{s})$ hole-burning experiments by Littau and Fayer[28] and Littau *et al.*[29,35] on cresyl violet in ethanol glass, stimulated photon echo experiments by Meijers and Wiersma[38] on zinc porphin in ethanol glass, and fast population bottleneck hole-burning experiments on bacteriochlorophyll-*a* in triethylamine and ethanol glasses by Wannemacher *et al.*[39] have further established that spectral diffusion does *occur* in organic systems on a time scale ranging from several nanoseconds to minutes (see also Refs. 28 and 40). In addition, the *single*-molecule experiments of Basché and Moerner[41] on perylene in amorphous poly(ethylene) have revealed intriguing optical transition frequency excursions of *single* molecules on a long-time scale.

In this paper we investigate the time-dependent spectral diffusion data of Littau and Fayer[28] and Meijers and Wiersma[38] within the framework of weak and strong TLS-phonon coupling. To this end, the nonphenomenological TLS distribution functions of Jankowiak, Small, and Athreya[19] (JSA) are utilized. The time-dependent hole-burning data of Littau and Fayer[28] extend from ~10 μs to 1000 s and indicate there are two (faster and slower relaxing) TLS distributions that contribute to the spectral diffusion. The same would appear to be true from the stimulated photon echo data of Meijers and Wiersma. We had shown earlier that[42] the log-normal distribution for the slower relaxation rates used by Littau and Fayer[28] follows from the JSA distribution function for λ, vide infra. Furthermore, it was noted, in passing, that the parameter values required to fit the data are similar to those used to describe spontaneous filling of nonphotochemical holes.[43] NPHB and spontaneous hole filling are associated with the $\mathrm{TLS}_{\mathrm{ext}}$. With the temporally extended data sets one is better able to assess this connection, to determine whether a log-normal distribution for the faster relaxing TLS is also appropriate and, if so, whether the parameter values for this distribution correspond to those for the $\mathrm{TLS}_{\mathrm{int}}$ connected with pure dephasing and other observables. Of particular interest to us was the effect of strong TLS phonon coupling on spectral diffusion.

II. RESULTS AND DISCUSSION

A description of spectral diffusion requires distribution functions for the TLS relaxation rates. For weak TLS phonon coupling the rate for the kth TLS is

$$R^{k}_{\mathrm{WC}}=AW_k^2E_k\coth(E_k/2kT)\ , \tag{1}$$

where A depends on the square of the TLS deformation potentials. Very recently Kassner and Silbey[44] (see also Refs. 45 and 46) have reemphasized that the common assumption of weak coupling is questionable on the basis of existing experimental data.[47] Using methods from polaron theory, they treated the problem of phonons dressed with TLS and concluded that, to a good approximation, the relaxation rate for strong coupling is

$$R^{k}_{\mathrm{SC}}=\exp[-G(\Delta_k/E_k)^2]R^{k}_{\mathrm{WC}} \tag{2}$$

for temperatures below several K. Here G is a function of the TLS deformation potentials from which they estimate $G\sim 175$ for organic glasses. One anticipates from Eq. (2) that the main effect of strong coupling will be to produce a distribution of relaxation rates, $P(R)_{\mathrm{SC}}$, that is significantly different from $P(R)_{\mathrm{WC}}$ for the slower relaxation rates, i.e., $P(R)_{\mathrm{SC}}$ should have an extended tail for such rates. We note that the unitary transformation employed by Kassner and Silbey only includes the diagonal part of the TLS-phonon interaction.

Given Eqs. (1) and (2) one needs suitable distribution functions for the TLS parameters W and Δ. Phenomenological functions such as those discussed earlier and others reviewed in Ref. 16, which do not have a firm physical basis, are of little use because, as already mentioned, they necessitate additional and difficult to justify assumptions for ensemble averaging. We use, therefore, the distribution functions of JSA (Ref. 19) which are based on the physically reasonable assumptions that the functions for Δ and λ are normal Gaussians with mean values Δ_0 and λ_0 and variances σ_Δ^2 and σ_λ^2. With the additional assumption that Δ and λ are uncorrelated, distribution functions for W^2 and Δ^2 obtain easily.[19] These distribution functions have been used to explain the T dependencies of pure dephasing[20,21] and thermal conductivity,[48] the time dependence of specific heat,[49] the dispersive kinetics of NPHB and spontaneous hole filling,[50,51] and to calculate $\rho(E)$ for $\mathrm{TLS}_{\mathrm{int}}$.[52] Nevertheless, they have not been widely adopted and so we take this opportunity to emphasize again that they provide for a systematic description of a wide variety of physical properties of glasses at low temperatures in terms of the standard tunnel model.

The distribution function for W^2 leads to a log-normal distribution for $P(R)_{\mathrm{WC}}$,[42]

$$P(R)_{\mathrm{WC}}R_{\mathrm{WC}}=(\sigma\sqrt{2\pi})^{-1}\exp-[\{\ln(R/R_0)\}^2/2\sigma^2]\ , \tag{3}$$

where $\sigma=2\sigma_\lambda$, $R_0=\Omega_0\exp(-2\lambda_0)$, with λ_0 the mean value of λ, and $\Omega_0\approx\omega_0$. Littau and Fayer[28] found that their spectral diffusion data for $t\gtrsim 1$ ms were well explained in terms of the above distribution function.

To obtain the distribution function for strong coupling, $P(R)_{\mathrm{SC}}$, it is convenient to write

$$R_{\mathrm{SC}}=\exp[-C\Delta^2+\ln R_{\mathrm{WC}}]\equiv\exp(y)\ , \tag{4}$$

where $C=G/E^2$. We define $f(y)$ as the distribution function for y ($y=\ln R_{\mathrm{SC}}$) and note that plotting $f(y)$ vs y is equivalent to plotting $P(R)_{\mathrm{SC}}R_{\mathrm{SC}}$ vs $\ln R_{\mathrm{SC}}$. Therefore, we need only determine $f(y)$ which is the convolution of the distribution functions for $\ln R_{\mathrm{WC}}$ and $C\Delta^2$, g, and h, respectively. Therefore, we can write

$$f(y)=\int_0^\infty dt\, g(y+t)h(t)\ . \tag{5}$$

Since the distribution function for Δ is a Gaussian with variance σ_Δ^2, it follows that (for $\Delta_0\approx 0$)

$$h(t)=(\sqrt{2\pi C}\,\sigma_\Delta)^{-1}t^{-1/2}\exp[-t/2\sigma_\Delta^2C]\ . \tag{6}$$

The distribution function for $\ln R_{\mathrm{WC}}\sim N(\mu,\sigma^2)$ can be written as

$$g(y+t)=(\sqrt{2\pi}\sigma)^{-1}\exp\{-[(y+t)-\mu]^2/2\sigma^2\}\ . \tag{7}$$

With Eqs. (3)–(6) and some straightforward algebra one finds that

$$f(y)=\alpha_1 \exp(\alpha_2)\exp[\beta(y)] \times \int_0^\infty \frac{dt}{\sqrt{t}} \exp\{-[t+\gamma(y)]^2/8\sigma_\lambda^2\} \quad (8)$$

with $\alpha_1=(4\pi\sigma_\lambda\sigma_\Delta\sqrt{C})^{-1}$, $\alpha_2=\sigma_\lambda^2/2\sigma_\Delta^4C^2$, $\beta(y)=(y-\mu)/2\sigma_\Delta^2C$, $\gamma(y)=y-\mu+2\sigma_\lambda^2/\sigma_\Delta^2C$, $C=G/E^2$, and $\mu=\ln R_0$. The variance σ^2 is defined following Eq. (3). For the calculations which follow, E was set equal to kT of the experiment but we note that, for the large-G values considered, $f(y)$, Eq. (8), is insensitive to significant variations from kT.

Following the work of Hu and Walker,[53] Bai and Fayer[26] used the four-point correlation function formalism of Mukamel[54] and Mukamel and Loring[55] to derive, for the spectral diffusion contribution to the optical linewidth,

$$\Gamma_{SD} \propto \int P(R)[1-\exp(-Rt_W)]dR , \quad (9)$$

where $P(R)$ is the distribution function for the TLS relaxation rate [for weak (WC) or strong (SC) TLS-phonon coupling] and t_W is the waiting time. Equation (9) is obtained after spatially averaging over independent TLS. It is applicable for the case of strong TLS-phonon coupling when the off-diagonal terms of this interaction are neglected as in Ref. 44. Since Eq. (2) stems from this work we do not consider here the possible complications from TLS-TLS interactions induced by the off-diagonal terms. The reader is referred to Refs. 44, 45, and 56 (and references therein) for detailed discussions of phonon-induced TLS-TLS interactions. In the stimulated echo experiment the three pulses are applied at times 0, τ and $\tau+t_W$, i.e., $t_W=0$ corresponds to the two-pulse photon echo which yields the homogeneous width of the optical transition (as operationally defined by Fayer and coworkers). For $t_W=0$, Γ_{SD} is zero. Hole burning is the Fourier transform of the stimulated echo and so the waiting time can be viewed in time-dependent hole burning as the time of burning and reading of the hole. In the highest resolution (~ 10 μs) time-dependent hole-burning experiments reported a population bottleneck via the lowest triplet state has been employed,[28] as in the three-pulse stimulated echo experiments.[38,40] Equation (9) is obtained following spatial averaging over the TLS interacting with the chromophore. The interaction, if dipole-dipole, leads to a Lorentzian hole shape, as is generally observed. As written, Eq. (9) is applicable to a given temperature. Elsewhere we will examine the T dependence of spectral diffusion.[57]

With Eqs. (8) and (9) and noting again that $y=\ln R_{SC}$, one obtains

$$\Gamma_{SD}(t_W)_{SC} \propto \int_{-y_{\min}}^{y_{\max}} P(y)[1-\exp\{-\exp(y)t_W\}]dy \quad (10)$$

for strong TLS phonon coupling. The expression used to calculate $\Gamma_{SD}(t_W)_{WC}$ follows directly from Eqs. (3) and (9). Integrations were performed numerically. Finally, we emphasize that the shape of the distribution $P(R_{SC})R_{SC}$ plotted vs $\log_{10}R_{SC}$ is weakly dependent on G as long as $G \gtrsim 30$. The combined dependence of the distribution of relaxation rates on G and temperature will be discussed elsewhere.[57]

A. Spectral diffusion of cresyl violet in ethanol-*d* glass at 1.2 K

The data of Littau and Fayer are shown as the crosses in Fig. 1(A). The crosses correspond to selected points from their best fit to the data when the excited-state lifetime contribution, $\Gamma_0=28$ MHz,[58] and the pure dephasing contribution (determined by two-pulse photon echo measurements[59]) have been subtracted from the observed holewidths, Γ_{hole}. Following the approach of Littau and Fayer we have fit the data, within the weak TLS-phonon coupling approximation, with two relaxation rate distributions for spectral diffusion as defined by Eq. (9). The fit is shown as the dashed curve in Fig. 1(A). The two log-normal distributions are shown as the long-dashed and dash-dotted curves in Fig. 1(B). Their resultant is the short-dashed curve. To be consistent with our earlier work with the JSA distribution functions, we have used a value of $\Omega_0=7.6\times10^{12}$ s^{-1} (40 cm^{-1}) in the relaxation rate expression $R=\Omega_0\exp(-2\lambda)\propto W^2$. The left-most

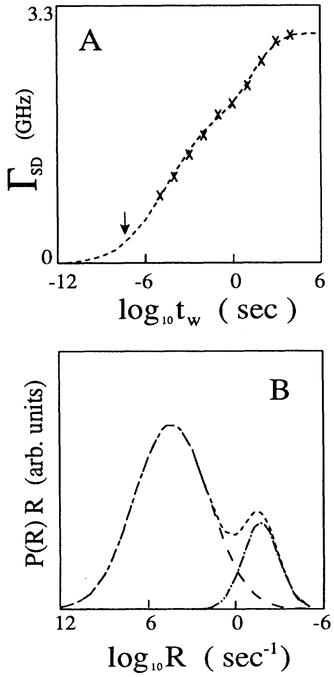

FIG. 1. (A) Spectral diffusion contribution (Γ_{SD}) vs log time (t_W) for cresyl violet in ethanol-*d* glass at $T=1.2$ K. Crosses correspond to the data of Littau and Fayer (Ref. 28), when the contribution from pure dephasing was subtracted. The dashed line is the fit obtained with the two distribution functions shown in (B). The arrow locates the excited-state lifetime (τ). Γ_{SD} (for $\log_{10}t_W=\log_{10}\tau$) = 120 MHz (see text for details). (B) Plot of the relaxation rate distributions $P(R)$ (weak TLS phonon coupling) for TLS$_{\text{int}}$ ($\lambda_0=9.8$, $\sigma_\lambda=2.9$; the left-most distribution) and TLS$_{\text{ext}}$($\lambda_0=16.8$, $\sigma_\lambda=1.4$), used to fit the data in (A). The short-dashed line is the resultant of the two log-normal distributions.

log-normal distribution is then characterized by $\lambda_0=9.8$ and $\sigma_\lambda=2.9$ and is responsible for the near linear dependence of Γ_{SD} on $\log_{10}t_W$ for $-7, \lesssim \log_{10}t_W \lesssim -3$. The right-most distribution is defined by $\lambda_0=16.8$ and $\sigma_\lambda=1.4$. The fit in the region of the data points is comparable to that of Littau and Fayer who invoke a $P(R)$ distribution of $1/R$ (Refs. 28 and 29) for $\log_{10}R \gtrsim 0.6$ and a log-normal distribution for the slower rates with the result that there is essentially a forbidden gap in the region around $\log_{10}R=0.6$. This gap, which is far less pronounced in the resultant Fig. 1(B), is responsible for the inflection point of Γ_{SD} near $\log_{10}t_W=0$.

The arrow in Fig. 1(A) locates the excited-state lifetime of cresyl violet, at which time the calculated spectral diffusion is $\Gamma_{SD}=120$ MHz. The tail of the calculated curve to the left of the arrow in Fig. 1(A) indicates that spectral diffusion might be observable for 100 ps $\lesssim t_W \lesssim$ excited-state lifetime. Interestingly, Narasimhan *et al.*[60] have recently obtained three-pulse stimulated photon echo data for rhodamine 101 in the PMMA polymer at 1.35 K that show a ~100-MHz contribution from spectral diffusion to the linewidth at $t_W=3.4$ ns (excited-state lifetime). Also of interest is that our results show that the $P(R) \propto 1/R$ approximation is poor for short t_W's. This may be of consequence to the question of nonexponentiality of three-pulse stimulated echo decays at short ($\lesssim$ lifetime) t_W's.[60] From our studies of the dispersive kinetics of nonphotochemical hole growth,[50,51] it is clear that the often invoked $1/R$ distribution (which stems from the TLS distribution function of Anderson *et al.* and Phillips, vide supra) is accurate only in the intermediate-time regime. It is more physically reasonable to use two log-normal distribution functions to fit the data of Fig. 1(A) especially if their $\lambda_0, \sigma_\lambda$ values can be related to those of other physical properties, cf. discussion at the end of this section.

Next we examine the consequences of strong TLS-phonon coupling on spectral diffusion (the effect on pure dephasing is beyond the scope of this paper). Now the distribution function for the asymmetry parameter comes into play, cf. Eqs. (2) and (10). As discussed by Kassner and Silbey[44] and Kassner,[45] the experimental evidence for strong coupling for $\mathrm{TLS_{int}}$ is quite convincing. Later on we associate the fast and slower distributions of relaxation rates with the $\mathrm{TLS_{int}}$ and $\mathrm{TLS_{ext}}$, respectively. Figure 2(A), the curve c is a fit to the data with the a and b curves, respectively, the contributions from the faster and slower relaxing distributions which are shown in Fig. 2(B). The distribution function parameters $(\tilde{\sigma}_\Delta, \sigma_\lambda, \lambda_0)$ are (0.20, 2.3, 7.3) and (0.02, 0.82, 16.2), respectively, where $\tilde{\sigma}_\Delta=\sigma_\Delta/\Omega_0$ and $\Omega_0=40\ \mathrm{cm}^{-1}$. A value of 175 (Ref. [44]) for G, the TLS phonon coupling parameter, was used. Comparing the distributions of Figs. 1 and 2 one observes (note different scales) that strong coupling leads to pronounced tailing to slower relaxation rates and that it is mainly the tailing of the $\mathrm{TLS_{int}}$ distribution that leads to the prediction that spectral diffusion should continue to times much longer than $\sim 10^4$ s. Figures 1 and 2 demonstrate that a comparably good fit to the data could be obtained with strong and weak coupling for the distributions of faster and slower relaxation rates, respectively. Our preliminary calculations indicate that it may be possible to distinguish between strong and weak coupling on the basis of the T dependence of the time evolution of spectral diffusion. (The broader distribution of relaxation rates produced by strong coupling suggests that the T dependence for strong coupling should be weaker than for weak coupling.) Two further points are that strong coupling significantly reduces the values of λ_0, e.g., from 9.8 to 7.3 for the distribution of faster relaxation rates, and reduces the probability for the fastest relaxation rates $[\gtrsim(\mathrm{lifetime})^{-1}]$. Our previous studies of specific heat[49] and thermal conductivity[48] have led to the finding that $\lambda_0 \approx 7$ and $\sigma_\lambda \approx 3$ are appropriate values for $\mathrm{TLS_{int}}$. Because the strong-coupling distribution function for the TLS relaxation rate is novel, we present in Fig. 3 some results that illustrate its dependence on $\tilde{\sigma}_\Delta$ and σ_λ.

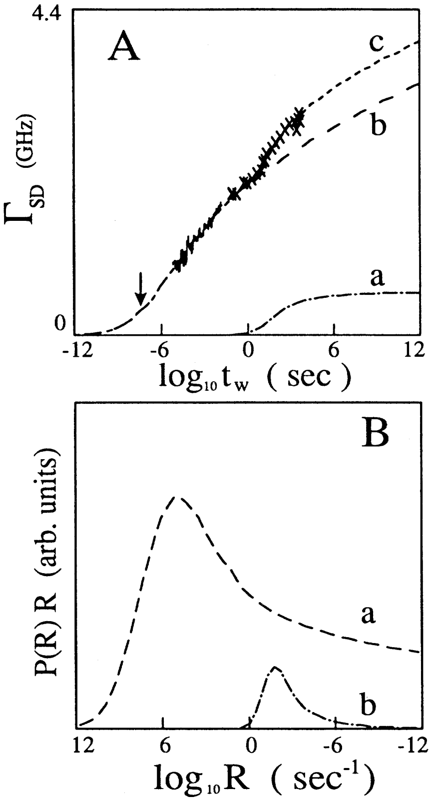

FIG. 2. (A) Fit (curve c) to the experimental data of Γ_{SD} (GHz) [of Littau and Fayer (Ref. 28)] within the strong TLS phonon coupling approximation with the faster ($\mathrm{TLS_{int}}$; curve b) and slower ($\mathrm{TLS_{ext}}$; curve a) distributions of relaxation rate. The arrow locates the excited-state lifetime. (B) $P(R)R$ vs $\log_{10}R$ for strong TLS phonon coupling. The distribution function parameters $(\tilde{\sigma}_\Delta, \sigma_\lambda, \lambda_0)$ are (0.2, 2.3, 7.3) and (0.02, 0.82, 16.2) for $\mathrm{TLS_{int}}$ (curve a) and $\mathrm{TLS_{ext}}$ (curve b), respectively. $G=175$, $\Delta_0=0$, and $\Omega_0=7.6\times10^{12}\ \mathrm{s}^{-1}$.

B. Spectral diffusion of zinc-porphin in ethanol-*d* glass at 1.5 K

The three-pulse stimulated photon echo data of Meijers and Wiersma[38] are shown in Fig. 4(A) as the contribution

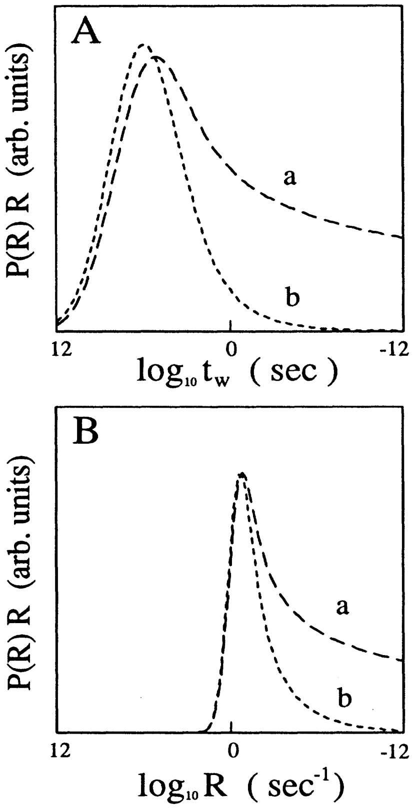

FIG. 3. Probability distribution function of relaxation rate (for strong TLS phonon coupling) plotted as $P(R)R$ vs $\log_{10}R$ for different σ_λ and $\tilde{\sigma}_\Delta$ values. In (A), distribution functions were obtained for $\Delta_0=0$, $\lambda_0=7$ $\sigma_\lambda=2.5$, and two $\tilde{\sigma}_\Delta=0.02$ and 0.2, curves *b* and *a*, respectively. The distributions in (B) were obtained for $\Delta_0=0$, $\lambda_0=15$, $\sigma_\lambda=0.8$, and $\tilde{\sigma}_\Delta=0.02$ and 0.2, curves *b* and *a*, respectively. The TLS phonon coupling parameter [$G=175$ (Ref. 44)] and $\Omega_0=7.6\times 10^{12}\ \mathrm{s}^{-1}$ were used for all calculations.

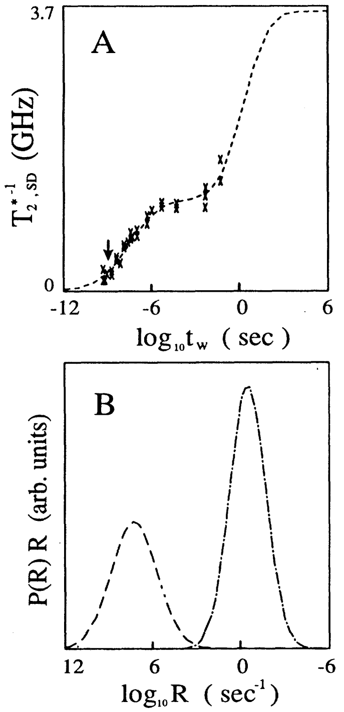

FIG. 4. (A) Plot of $T^{*-1}_{2,\mathrm{SD}}$ (lifetime and pure dephasing contributions were subtracted) as measured in a stimulated photon echo experiment vs the logarithm of the waiting time t_W. Experimental data (crosses) are from Meijers and Wiersma (Ref. 38). The short-dashed line is a resultant fit to the data using relaxation rate distribution functions [Eq. (3)] for $\mathrm{TLS}_{\mathrm{int}}$ and $\mathrm{TLS}_{\mathrm{ext}}$ in the weak TLS phonon approximation, with parameters listed in (B). The arrow locates the excited-state lifetime. (B) $P(R)R$ plotted vs $\log_{10}R$. For the left ($\mathrm{TLS}_{\mathrm{int}}$) and right $\mathrm{TLS}_{\mathrm{ext}}$) distributions ($\lambda_0,\sigma_\lambda$) equals (6.8, 1.8) and (15.4, 1.4), respectively. $\Omega_0=7.6\times 10^{12}\ \mathrm{s}^{-1}$.

from spectral diffusion ($T^{*-1}_{2,\mathrm{SD}}$ to the inverse of the effective T_2^*, which is the observable. That is, both the lifetime (2.1 ns) and pure dephasing contributions have been subtracted from the data. The inverse of the pure dephasing time at 1.5 K is ~500 MHz.[38] Meijers and Wiersma have taken the "apparent" plateau between $\sim 10^{-5}$ and 10^{-2} s as real [but see Fig. 5 where two data points (circled ×) are rejected]. Following their suggestion we have fit the data in the weak TLS-phonon coupling limit with the two log-normal distributions shown in Fig. 4(B). For the left and right distributions, respectively, (λ_0,σ_λ) equals (6.8, 1.8) and (15.4, 1.4).

In Fig. 5(A), the dashed curve is the strong TLS-phonon coupling fit with a single distribution of faster relaxation rates to the actual data, guided by a rejection of the two points (circled ×), obtained with $(\tilde{\sigma}_\Delta,\sigma_\lambda,\lambda_0) = (0.12, 1.11, 4.44)$. The very extended tailing of $P(R)R$, Fig. 5(B), results in a near linear dependence of $(T_2^*)^{-1}$ on $\log_{10}t_W$ between $\sim 10^{-3}$ and 10^8. The solid arrow in Fig. 5(A) [also Fig. 4(A)] locates the excited-state lifetime of zinc-porphin. Comparison of the theoretical fits to $T^{*-1}_{2,\mathrm{SD}}$ indicate that strong coupling reduces the spectral diffusion at very short waiting times ($t_W \lesssim 1$ ns).

C. Characterization of the two-level systems

We have shown that the spectral diffusion data for two organic systems can be understood (within the confines of the current model of spectral diffusion) in terms of the JSA-TLS distribution functions under the assumption of either weak or strong TLS-phonon coupling. For weak coupling, log-normal functions for the distributions of the faster and slower relaxing TLS account well for the data. This is significant because the JSA distribution functions have a physical basis. Thus, it is not necessary to utilize the phenomenological $P(R) \propto 1/R$ distribution function which cannot be expected to be sufficiently accurate at the extremes of the distribution. It has been emphasized that the JSA functions provide a vehicle for systematic testing of the standard tunneling model against data from a wide variety of measurements including specific heat,[49] thermal conductivity,[48] the gap in the $\mathrm{TLS}_{\mathrm{int}}$ density of states at very low temperatures,[52] the pure dephasing of

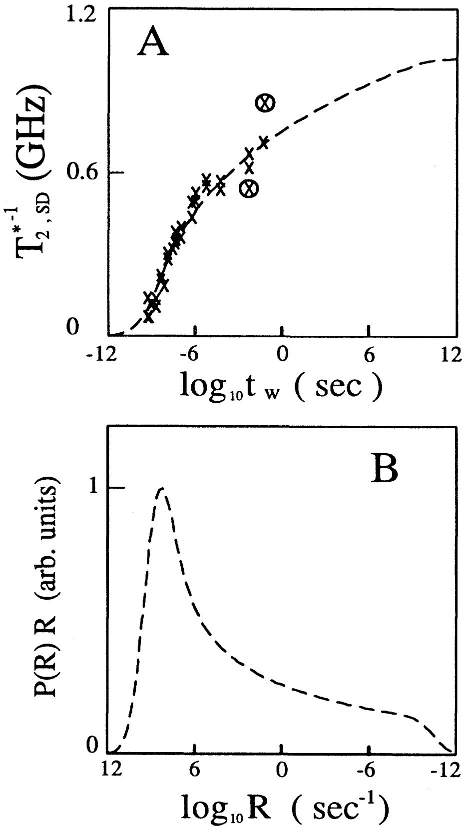

FIG. 5. (A) $T^{*-1}_{2,\mathrm{SD}}$ plotted vs $\log_{10}t_W$. Experimental data (crosses), as in Fig. 4(A). The dashed line is the strong TLS phonon coupling fit with a single distribution of faster relaxation rates (see text). (B) $P(R)$ (for TLS_{int}) obtained from the fit in (A) with $(\tilde{\sigma}_\Delta,\sigma_\lambda,\lambda_0)=(0.12,1.11,4.44)$ for strong TLS phonon coupling.

impurity transitions,[48,61] NPHB growth kinetics,[50,51] and spontaneous hole filling.[51] Spectral diffusion can now be added to the list. The question is then whether the JSA distribution function parameter values determined here for spectral diffusion correlate with those of other physical properties. We consider first the distribution of slower relaxation rates, which for cresyl violet in ethanol-*d* at 1.2 K and zinc-porphin in ethanol-*d* at 1.5 K, are characterized by $(\lambda_0,\sigma_\lambda)=(16.8,1.4)$ and (15.4,1.4), respectively. The large and relatively small values of λ_0 and σ_λ, respectively, correlate well with those determined for spontaneous (in the dark) filling of nonphotochemical holes in three similar systems at comparable temperatures.[43,51] For example, $(\lambda_0,\sigma_\lambda)=(17.6,1.3)$ for cresyl violet in a polyvinyl alcohol [PVOH film at 1.6 K (Ref. 51) and $(\lambda_0,\sigma_\lambda)=18,1.5$] for oxazine 720 in glycerol at 1.6 K.[50] From Refs. 50 and 51 it is clear that, for the efficient NPHB systems, cresyl violet in ethanol and PVOH, and oxazine 720 in glycerol and PVOH, that the above λ_0 values are far too high to be correlated with nonphotochemical hole growth (where $\lambda_0\sim 9-10$) which involves phonon-assisted tunneling of the $\mathrm{TLS}_{\mathrm{ext}}$ triggered by electronic excitation of the chromophore (for recent discussions of the NPHB mechanism see Refs. 51 and 62). Spontaneous hole filling is most reasonably ascribed to $\mathrm{TLS}_{\mathrm{ext}}$ relaxation processes which occur with the chromophore in its *ground* state. It is important to note that the $\mathrm{TLS}_{\mathrm{ext}}$ coordinate(s) responsible for NPHB and hole filling is associated with a relatively strong interaction between the chromophore and the inner shell of hydrogen binding solvent molecules and, for the above systems, that it involves considerable amplitude of motion of the hydroxyl proton of the host. The latter follows from the fact that deuteration of the hydroxyl proton leads to a reduction of the average quantum yield for NPHB of well over an order of magnitude.[51] In sharp contrast, the pure dephasing is unaffected by deuteration[5] which strongly suggests that the $\mathrm{TLS}_{\mathrm{int}}$ coordinate(s) are due to spatially extended hydrogen bonding networks of the host molecules occupying mainly the outer shell. This provides support for the diagonal modulation theory of Lyo[15,17] in which pure dephasing is due to weak interactions of the chromophore with a sea of $\mathrm{TLS}_{\mathrm{int}}$.

In our earlier mentioned work on several physical properties, whose T dependencies are dictated by *intrinsic* TLS, λ_0 and σ_λ values in the range $\sim 6-7$ and ~ 3, respectively, were utilized for the $\mathrm{TLS}_{\mathrm{int}}$. As one example, it proved possible to understand, for several inorganic glasses, why the temperature dependence ($T<1$ K) of the thermal conductivity deviates from $T^{2-\mu}$ when the $\mathrm{TLS}_{\mathrm{int}}$ density of states is $\rho(E)=\rho_0E^\mu$ (and the power law for specific heat is $T^{1+\mu}$).[48,49,52] The $T^{2-\mu}$ prediction of the standard tunneling model is a consequence of approximate averaging; e.g., the assumption that $\langle W^2\rangle_E/E^2$ is independent of E. We note that the values of $(\lambda_0,\sigma_\lambda,\tilde{\sigma}_\Delta)$ found to be suitable in Ref. 48 lead to $\mu\sim 0.2-0.3$ over about two decades of temperature $\lesssim 1$ K. Above ≈ 1 K the density of states begins to decrease. We note that the weak TLS-phonon coupling approximation was used in Ref. 48.

We consider next our findings for the spectral diffusion of cresyl violet in ethanol-*d* from the distribution of faster relaxing TLS. For weak and strong coupling $(\lambda_0,\sigma_\lambda)=(9.8,2.9)$ and (7.3,2.3), respectively, with $\tilde{\sigma}_\Delta=0.20$ for strong coupling. These σ_λ values are consistent with those determined earlier for $\mathrm{TLS}_{\mathrm{int}}$ (the fact that they are considerably larger than those for $\mathrm{TLS}_{\mathrm{ext}}$ is qualitatively understandable given the stronger interaction between the chromophore and inner shell). For strong coupling, especially, the λ_0 value is similar to those determined earlier for $\mathrm{TLS}_{\mathrm{int}}$. We consider it reasonable, therefore, to assign the faster relaxing TLS as mainly $\mathrm{TLS}_{\mathrm{int}}$. We draw the same conclusion for zinc-porphin in ethanol-*d*. Comparison of the data for this system with the above system is difficult because two different phases of amorphous ethanol were used, ethanol I and II, respectively. Phase II is the plastic phase and is more ordered than phase I.[63] That the σ_λ value for phase II is smaller than that for phase I is consistent with this. However, we do not have an explanation for why phase II has the lower λ_0 value (6.8 vs 9.8 for weak coupling).

Finally we point out that the applicability of the basic equation used, Eq. (9), for spectral diffusion is limited to waiting times $t_W > 10\tau$,[5] where τ can be viewed as the total dephasing time T_2. For the systems studied then this means $t_W \gtrsim 10$ ns. Thus, our spectral diffusion results for shorter waiting times should only be considered as indicative.

III. CONCLUSIONS

In this paper we have shown that the TLS distribution functions of JSA (Ref. 19) can be used to determine the distribution function of TLS relaxation rates for both weak and strong TLS phonon coupling. For both experimental data sets investigated, weak and strong coupling are equally capable of accounting for the spectral diffusion. Previous work has provided quite compelling evidence for the coupling being strong for $\mathrm{TLS}_{\mathrm{int}}$.[44–47,64] We suggest that detailed studies of the temperature dependencies of spectral diffusion and pure dephasing may be important for ascertaining whether or not the coupling is indeed strong.

Our results show that strong coupling has pronounced effects on the distribution of relaxation rates; namely, significant tailing to slower relaxation rates, a shift of the maximum to a faster rate value, and a reduction in the probability of very fast rates. For the cresyl violet in ethanol-*d* system, strong coupling for the $\mathrm{TLS}_{\mathrm{int}}$ leads to a reduction in the contribution from the distribution of slower relaxation rates to spectral diffusion at long times.

Finally, a comparison of the values of the distribution function parameters, determined on the basis of the spectral diffusion data, with those determined earlier for thermal conductivity, specific heat, pure dephasing, and spontaneous nonphotochemical hole filling indicate that the faster and slower distribution of rates can be associated with $\mathrm{TLS}_{\mathrm{int}}$ and $\mathrm{TLS}_{\mathrm{ext}}$, respectively.

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