

Spectral Diffusion in Organic Glasses: Time Dependence of Spectral Holes

J. M. A. Koedijk,[†] R. Wannemacher,^{†,‡} R. J. Silbey,[§] and S. Völker^{*,†}*Huygens and Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands, and
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139**Received: May 21, 1996; In Final Form: September 19, 1996[®]*

Time-resolved spectral hole-burning experiments have been performed to probe the dynamics of the $S_1 \leftarrow S_0$ 0–0 transition of bacteriochlorophyll-*a* at low concentration (1×10^{-5} M) in four different glasses (2-methyltetrahydrofuran, protonated and deuterated ethanol, diethyl ether, and triethylamine) as a function of delay time t_d (from 10^{-6} to 10^3 s) and temperature T (1.2–4.2 K). It is shown that spectral diffusion, the broadening of the optical linewidth followed here over nine orders of magnitude in time, increases with temperature as $T^{1.3 \pm 0.1}$ and strongly depends on the glass structure. The functional dependence, however, is not influenced by the specific glass. The variation of the “effective” homogeneous linewidth (Γ'_{hom}) with T and t_d is described by a function $\Gamma'_{\text{hom}}(T, t_d)$ derived by modifying the standard model of two-level systems (TLS). This revised TLS model, in which the distribution functions of the TLS tunneling parameters are different from those in the standard model, takes into account the common origin of the dependence of Γ'_{hom} on t_d and T . It is shown that other hole-burning and photon-echo data reported in the literature can also be fitted by the same function $\Gamma'_{\text{hom}}(T, t_d)$. In ethanol glass, the number of TLSs and the amount of spectral diffusion appear to be independent of the probe molecule.

1. Introduction

Glasses are assumed to consist of a large number of two-level systems (TLSs), double-well potentials representing distinct structural configurations of the glass.^{1,2} The transition from one potential well to another then describes a change in the glass structure. TLSs are assumed to have a broad distribution of tunneling parameters and energy splittings, which leads to a broad distribution of fluctuation rates.^{3–5} As a consequence, not only the thermal properties of glasses^{6,7} but also the linewidth of an optical transition of a probe molecule in a glass at low temperature are predicted to depend on the experimental time scale,^{8–10} an effect not observed in crystalline materials. The broadening of the “effective” homogeneous line with the experimental delay time is due to spectral diffusion (SD)^{2,3,11} caused by frequency fluctuations of the optical transition due to relaxation of TLSs in the surrounding glass; the rates of this SD may vary over many orders of magnitude.

The first delay-time-dependent optical linewidths were observed by Haarer et al.¹² in hole-burning experiments. They reported a logarithmic increase of the holewidth with time between burning and probing the hole that varied from minutes to days for an organic glassy system. The groups of Wiersma¹³ and Fayer¹⁴ later observed that the values of Γ'_{hom} obtained by two-pulse photon echoes measured in a time of picoseconds differed from those obtained by hole-burning in a time of minutes. These differences were interpreted in terms of spectral diffusion. Hole-burning experiments, on the other hand, showed that extreme care has to be taken when comparing results obtained by different experiments.^{15,16} The value of Γ'_{hom} not only may vary with the time scale of the experiment but may also strongly depend on the way the sample is cooled.¹⁵

Moreover, very low laser powers have to be used to avoid heating of the sample owing to poor thermal conductivity of the glass.¹⁶

Subsequent time-resolved hole-burning experiments between milliseconds and minutes on doped ethanol^{17a,b} and down into the microsecond regime on ethanol,^{17c,d,18} 2-methyltetrahydrofuran (MTHF),¹⁸ and diethylether¹⁸ yielded holes that broadened with time, confirming the occurrence of spectral diffusion in these glasses. By contrast, in doped polyethylene (PE)¹⁹ and triethylamine (TEA)^{18,20} no broadening of the holes was observed with delay time, from which it was concluded that there is no measurable spectral diffusion in PE or TEA in this time range.

On the other hand, single-molecule spectroscopy experiments on crystalline²¹ as well as on glassy systems^{22–24} have revealed jumps of the transition frequency of a single molecule occurring between microseconds and hours; these were interpreted in terms of flipping TLSs.^{23,25} Results of three-pulse stimulated photon-echo experiments on organic glasses²⁶ and proteins²⁷ performed over waiting times from picoseconds to a few tens of milliseconds (the triplet-state lifetime of the probe molecules) have further been used to extract the TLS distribution functions of fluctuation rates.

The temperature dependence of the “effective” homogeneous linewidth Γ'_{hom} in glasses generally follows a power law varying between linear and quadratic in T at low temperature ($T \leq 20$ K).^{28–34} This is in contrast to a T^7 power law found for certain ionic crystals³⁵ and an exponential dependence observed for molecular mixed crystals.^{36,37} Organic glasses and polymers have a universal behavior, with $\Gamma'_{\text{hom}} \propto T^{1.3 \pm 0.1}$, independent of the nature of the glass and the probe molecule.^{13b,14b–e,15,16,18–20,38–41} A $T^{1.3}$ power law, also observed for the specific heat,^{33,42,43} has been explained by assuming a dipole–dipole coupling between the probe molecule and the TLSs, with a density of states of the TLSs varying as $\rho(E) \propto E^{0.3}$, where E is the energy splitting of the eigenstates of the TLSs.^{8–10,33,44} In the original standard TLS model,^{1,2} $\rho(E)$ was

* To whom correspondence should be addressed.

[†] University of Leiden.[§] Massachusetts Institute of Technology.[‡] Present address: Institut für Physik, Technische Universität Chemnitz-Zwickau, 09107 Chemnitz, Germany.[®] Abstract published in *Advance ACS Abstracts*, November 15, 1996.

assumed to be constant leading to a linear T dependence of the specific heat and $\Gamma_{\text{hom}}'^{3-5}$

In contrast to the universal $T^{1.3}$ temperature dependence, different delay-time (t_d) dependences of Γ_{hom}' have been reported for different organic glassy systems. These have been interpreted in terms of differences in the distribution functions of the fluctuation rates of the TLSs. For instance, the Haarer group measured holewidths that varied logarithmically with time up to delay times of hours,¹² leading to a $1/R$ (hyperbolic) distribution of rates and, on the other hand, holes that broadened as a power law with time for long delay times (weeks).⁴⁵ This behavior was attributed in ref 45 to strongly interacting TLSs. The Wiersma group²⁶ interpreted their three-pulse photon-echo data on glasses with two hyperbolic distributions of rates separated by a gap, whereas the Fayer group¹⁷ assumed a combination of a hyperbolic distribution and a log-normal distribution of rates to explain their hole-burning data. These rate distributions do not, in general, lead to a $T^{1.3}$ dependence of Γ_{hom}' (but see ref 41 for a discussion of the use of the log-normal form). Note that the standard TLS model yields $\Gamma_{\text{hom}}' \propto T \log(t_d)^{3-5,46}$

After reviewing our previous studies of the temperature dependence of spectral diffusion,¹⁸ we report in this paper on the delay-time dependence of the “effective” homogeneous linewidth Γ_{hom}' of the $S_1 \leftarrow S_0$ 0–0 transition of bacteriochlorophyll-*a* embedded in a series of organic glasses: 2-methyltetrahydrofuran, protonated and deuterated ethanol, diethyl ether, and triethylamine. The goal was to examine, from an experimental point of view, the general validity of the theoretical models for optical dephasing. To this end, we have carried out time-resolved hole-burning experiments over 9 orders of magnitude in time, from 10^{-6} to 10^3 s, at temperatures varying between 1.2 and 4.2 K. The results confirm that the degree of spectral diffusion (SD) is strongly dependent on the glass,¹⁸ but for all glasses the variation with temperature of the additional SD contribution to Γ_{hom}' follows a $T^{1.3 \pm 0.1}$ dependence like the “pure” dephasing contribution to Γ_{hom}' . The time (t_d) dependence of Γ_{hom}' is very nearly proportional to the logarithm of t_d for all samples studied, the slope $\Delta\Gamma_{\text{hom}}'/\Delta \log(t_d)$ increasing with temperature as $T^{1.3 \pm 0.1}$. The temperature as well as the delay-time dependence of Γ_{hom}' observed in our experiments can be understood by introducing a slight modification in the probability distributions of the tunneling parameters of the TLSs in the standard model.⁴⁷ This modified model for optical dephasing⁴⁶ also is capable of fitting the time-dependent data of Γ_{hom}' reported in the literature,^{17c,d,26,27a} without the need to introduce gaps or log-normal functions in the TLS distributions of relaxation rates.

2. Experimental Section

Samples of bacteriochlorophyll-*a* (BChl-*a*) in the glasses 2-methyltetrahydrofuran (MTHF), protonated and deuterated ethanol (EtOH, EtOD), diethyl ether, and triethylamine (TEA) were prepared as described elsewhere.^{18,48} The concentration of all samples was about $c \approx 1 \times 10^{-5}$ M. The solutions were quickly cooled down to liquid-helium temperatures in a well-defined way¹⁸ in order to obtain transparent glasses. A ⁴He-bath cryostat was used in which the temperature could be varied between 1.2 and 4.2 K. The temperature was determined by means of a calibrated carbon resistor and, simultaneously, by the vapor pressure of the helium, with an accuracy of ± 0.005 K.

For the hole-burning experiments we used the setup sketched in Figure 1a with a temperature- and current-controlled single-mode GaAlAs diode laser (power ≈ 5 mW, linewidth ≈ 50 MHz). This setup is a modified version of that used in ref 18

(see below). The laser beam was gated by two acousto-optic modulators in order to produce burn and probe pulses with lengths t_b and t_p , respectively. The delay t_d between them was varied over 9 orders of magnitude in time (see also Figure 1b). The laser frequency was scanned over the profile of the hole by applying a voltage ramp to the external modulation input of the current control (2 MHz bandwidth) of the diode laser. Holes were monitored in transmission through the sample.

Since we were interested in scanning not only transient holes that decay with the triplet-state lifetime but also permanent holes at variable and well-defined delays, we modified our previous setup¹⁸ in the following way. First, a probe pulse was applied at a given laser bias current to obtain a reference scan, then a burn pulse produced a hole in the absorption profile, and finally the profile of the hole was scanned by a second probe pulse after an adjustable delay t_d . The pulse sequence is illustrated in Figure 1b.

While the reference scan before burning was stored in one input channel of the digital oscilloscope, the probe scan after burning was stored in the other channel, as shown in Figure 1a. To switch between the channels and to ground the inactive channel, Reed relays were used, whose switching time of about 10 ns was sufficiently fast compared to the repetition frequency of about 10 Hz used in the experiment. After each probe–burn–probe cycle, the laser bias current was slightly changed to set the laser frequency to a new value outside of the profile of the previously burnt hole, and a new cycle was started. The procedure was repeated a number of times within a current range determined by the requirement that the laser works in a single longitudinal mode and with an intensity that does not vary by more than a factor of about 2 over the whole range.

Depending on the width of the holes, which at 1.2 K varied between about 1 and 5 GHz for the different glasses and burning fluences used, it was possible in this way to burn about 12 holes at frequency positions at which no previous hole had been burnt. Our laser covered a frequency range of about 60 GHz in a few seconds. The scans before and after burning were averaged separately on the two channels of the digital oscilloscope and subtracted afterward from each other to yield the average hole profile. Permanent holes were averaged between 10 and 100 times, whereas transient holes were averaged more than 1000 times.

Figure 1c shows the frequency excursion of the diode laser for three current ramp durations as a function of time during the probe pulse. The values were determined with a Fabry-Perot etalon (dots). We see that the curves do not instantaneously follow the linear current ramp, probably because of thermal time constants of the diode laser. Further, we see that each scan is sufficiently linear around the central frequency such that the hole profiles are not distorted if detected within this region. The scan rates, which are more than 10^4 times higher than for a commercial single-mode dye laser, vary from 2–3 GHz/ μ s to about 15 GHz/ μ s. Notice also in Figure 1c that the shorter the current ramp duration, the smaller the frequency range over which the diode laser can be scanned; for example, a scan range of about 40 GHz can be covered if the ramp duration is $\sim 30 \mu$ s, whereas a range of only about 4 GHz can be covered for a ramp of 1 μ s. Simultaneously, the scan efficiency defined in GHz/mA decreases from about 1.7 to 1.2 GHz/mA.

The delay time t_d , defined as the time between the centers of the burn- and probe pulses, was varied over 9 decades, between 10^{-6} and 2×10^3 s. The widths of the burn and probe pulses were usually chosen to be of the same order as t_d , with the

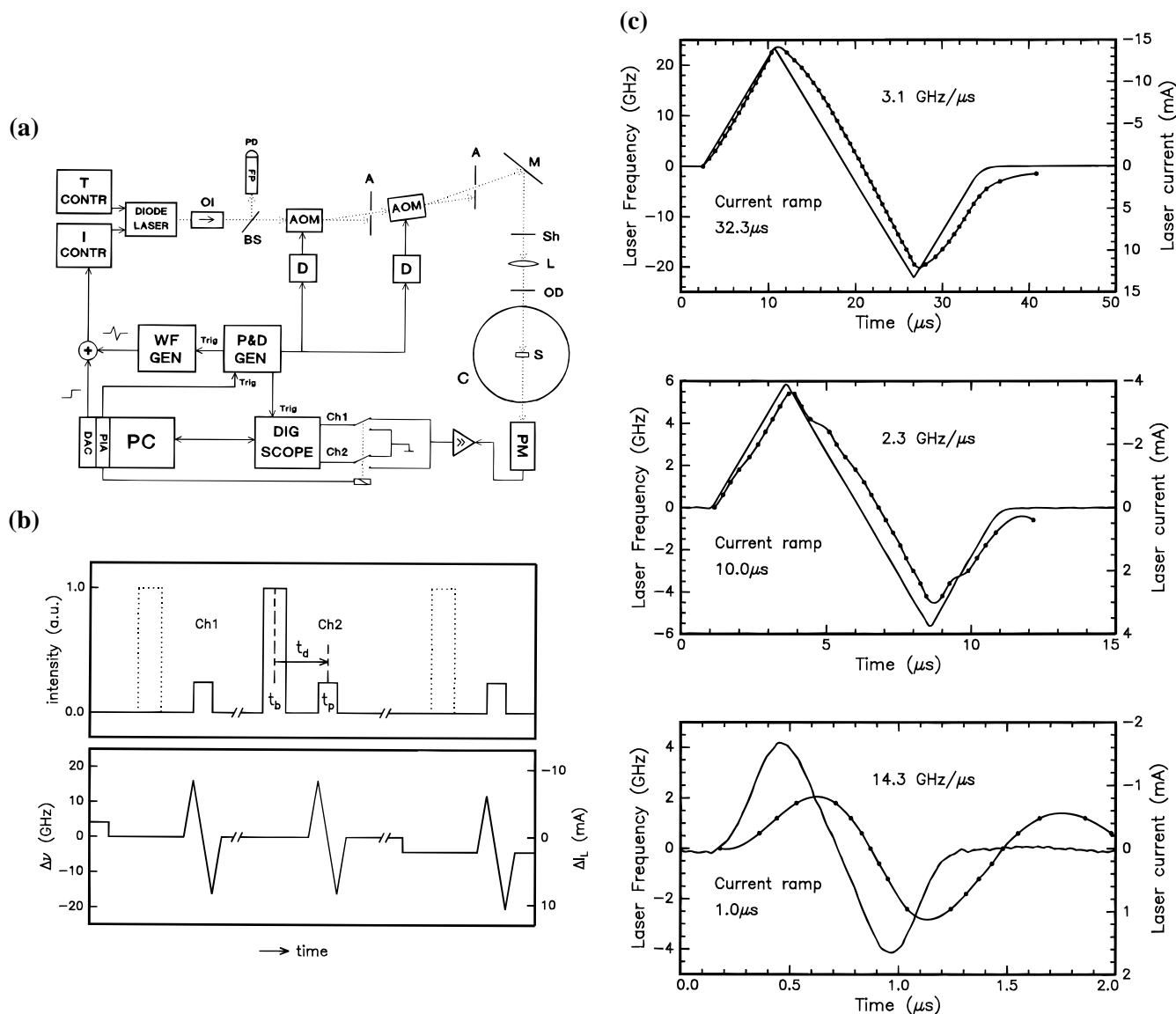


Figure 1. (a) Experimental setup for time-resolved hole-burning with a diode laser: T-CONTR, temperature control; I-CONTR, current control of the diode laser; OI, optical isolator; FP, Fabry-Perot spectrum analyzer; AOM/D, acousto-optic modulators and drivers; Sh, shutter; S, sample; C, cryostat; WF GEN, waveform generator; P&D GEN, pulse and delay generator; PM, photomultiplier; DIG SCOPE, 150 MHz digital oscilloscope. A couple of relays switch the signal before and after burning to channel 1 and 2 of the oscilloscope. (b) Timing of the laser pulses (top) and current ramp and current steps (bottom): t_b , burn time; t_d , delay time; t_p , probe time; $\Delta\nu$, change in laser frequency; ΔI_L , change in laser current. "0" corresponds to the initial bias current of the diode laser on the current control. (c) Frequency excursion of the diode laser as a function of time during the probe pulse determined with a Fabry-Perot etalon (dots). For comments, see text.

exception of the longer delays (10^2 – 10^3 s), for which pulses of about 2–10 s were used in order to avoid distortions of the scan due to slow amplitude changes of the signal. To obtain a good signal-to-noise ratio for each probe time t_p , the detection bandwidth was set at the minimum value necessary to avoid instrumental broadening of the holes. The signals, detected in transmission through the sample, were monitored by a photomultiplier (EMI 9658 F) and averaged on a digital oscilloscope (LeCroy 9410, 150 MHz bandwidth).

An example of an averaged probe scan before and after burning a hole is given in Figure 2 for a relatively deep, permanent hole (depth $D = 2.8\%$) and a delay of 30 ms. The burning power density used here was $42 \mu\text{J}/\text{cm}^2$ with a burning time of 20 ms. Holes were probed with an attenuation of a factor 10. The time scale in the figure relates to the trigger time of the oscilloscope, and the hole of interest appears at $t = 10.5$ ms. Holes burnt in previous cycles are visible at the right of the figure; they cancel when the averages of the two

oscilloscope channels are subtracted from each other. This is illustrated in the inset of the figure, where only the central hole scanned at the desired delay time remains. The previously burnt holes are shallower than the hole of interest because the former are not present during all the cycles (here 25) used for averaging.

For a given delay t_d the holewidths were extrapolated to zero burning-fluence density, $Pt/A \rightarrow 0$, by varying the attenuation of the laser beam in a series of experiments, performed on the same spot of the sample at slightly different burning frequencies, with increasing values of Pt/A . To take data at a new delay time, the laser frequency was changed in a large step (of the order of a few angstroms) by varying the diode laser temperature, and the procedure was repeated using a different spot on the sample. The data were subsequently averaged (see above). For every temperature and delay time, about 50–100 holes were measured as a function of Pt/A . Permanent holes were burnt with Pt/A values between $10 \mu\text{J}/\text{cm}^2$ and $10 \text{ mJ}/\text{cm}^2$, whereas

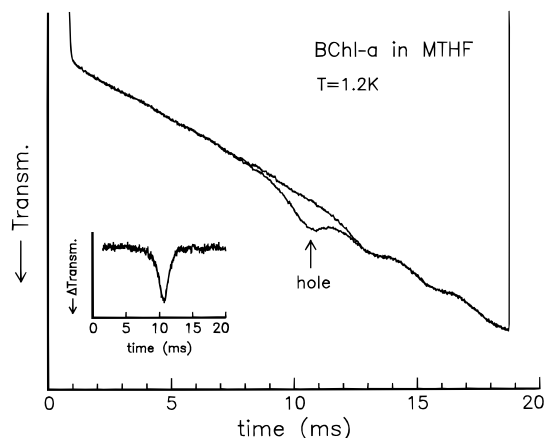


Figure 2. Averaged signals before and after burning holes in the $S_1 \leftarrow S_0$ 0-0 band of BChl-*a* in MTHF with a delay time $t_d = 30$ ms. The time scale in the figure is related to the trigger time of the oscilloscope and is calibrated to the frequency by means of a Fabry-Perot etalon. Previously burnt holes are visible on the right of the hole of interest. The inset shows the resulting hole after subtraction of the two traces.

for transient holes we used about 3 orders of magnitude less burning-fluence densities.

The effective homogeneous linewidth $\Gamma'_{\text{hom}}(t_d)$ of the $S_1 \leftarrow S_0$ 0-0 transition (Q_y) of BChl-*a* was determined from the measured holewidths at $t_d > t_b$ and at $t'_d = t_b$ extrapolated to $Pt/A \rightarrow 0$, $\Gamma_{\text{hole},0} = \lim_{Pt/A \rightarrow 0} \Gamma_{\text{hole}}$, in the following way. For $t_d > t_b$,

$$\Gamma_{\text{hole},0}(t_b, t_d) = \Gamma'_{\text{hom}}(t_b) + \Gamma'_{\text{hom}}(t_d) + 2\Gamma_{\text{laser}} \quad (1)$$

where $\Gamma_{\text{laser}} \approx 50$ MHz is the diode laser bandwidth. For $t_b = t'_d$,

$$\Gamma_{\text{hole},0}(t_b, t'_d = t_b) = 2\Gamma'_{\text{hom}}(t_b) + 2\Gamma_{\text{laser}} \quad (2)$$

Inserting $\Gamma'_{\text{hom}}(t_b)$ found from eq 2 into eq 1, we obtain

$$\Gamma'_{\text{hom}}(t_d) = \Gamma_{\text{hole},0}(t_b, t_d) - \frac{1}{2}\Gamma_{\text{hole},0}(t_b, t_b = t'_d) - \Gamma_{\text{laser}} \quad (3)$$

The frequency profile of the laser and the hole profiles were Lorentzian. For $t_d \gg t_b$, the value of $\Gamma'_{\text{hom}}(t_d)$ is significantly larger than that of $\frac{1}{2}\Gamma_{\text{hole},0}(t_b, t_d) - \Gamma_{\text{laser}}$, the value which is usually taken when $t_d \approx t_b$.⁴⁰

3. Results and Discussion

In Figure 3 a log-log plot of $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of temperature T is shown for BChl-*a* in the four different glasses studied, for two delays $t_d = 15$ μ s (open symbols) and 300 s (closed symbols). The data follow straight lines, all with the same slope of 1.3 ± 0.1 , which is independent of delay time, but with the value of $\Gamma'_{\text{hom}} - \Gamma_0$ depending on t_d :

$$\Gamma'_{\text{hom}} - \Gamma_0 = (\pi T_2^*)^{-1} = a(t_d)T^{1.3 \pm 0.1} \quad (4)$$

where $\Gamma_0 = (2\pi\tau_{\text{fl}})^{-1}$ is determined by the fluorescence lifetime of BChl-*a*, $\tau_{\text{fl}} \approx 4$ ns. The $T^{1.3}$ power law, characteristic for optical dephasing in organic glassy systems,^{13b,14b-e,15,16,18-20,38-41} is independent of t_d .¹⁸ We see in Figure 3 that the data for TEA all fall on the same line independent of delay time, from which we conclude that BChl-*a* in TEA does not undergo observable spectral diffusion (SD) between 10^{-5} and 10^2 s.¹⁸ In the glasses EtOH, MTHF, and diethyl ether, Γ'_{hom} is much larger than in TEA for a given delay and temperature; in addition, Γ'_{hom} increases with delay, which implies that SD is

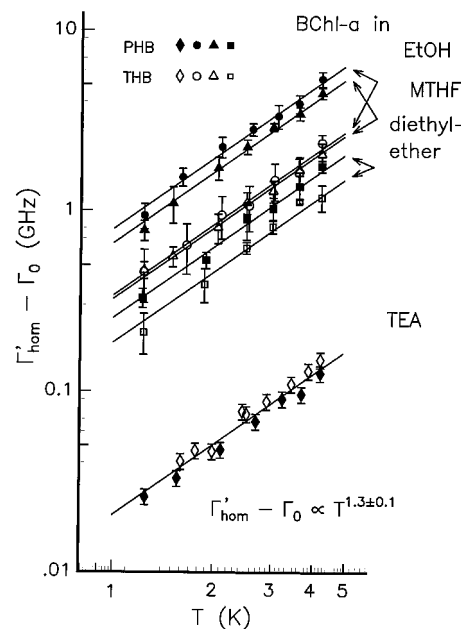


Figure 3. Log-log plot of $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of temperature between 1.2 and 4.2 K, for BChl-*a* in the glasses EtOH (circles), MTHF (triangles), diethyl ether (squares), and TEA (diamonds), at $t_d = 15$ μ s (open symbols) and $t_d = 300$ s (filled symbols).

significant in these glasses. Note that in diethyl ether the amount of SD is less than in EtOH and MTHF, though much more than in TEA. The results prove that SD strongly depends on the nature of the glass. We further observe that the larger the value of Γ'_{hom} for a given delay and temperature in a given glass, the larger the amount of SD in that glass, as compared to another glass with a smaller Γ'_{hom} value under the same conditions. Both this result and the general validity of the $T^{1.3}$ power law appear to indicate that the amount of spectral diffusion is correlated with the amount of optical dephasing.

We would like to comment here on TEA, a glass in which no spectral diffusion was observed, either between 10^{-5} and 10^3 s as determined by hole-burning for BChl-*a*¹⁸ or between 10^{-9} and 10^{-2} s as determined by three-pulse photon echoes for zinc porphyrin.^{26b} The value of Γ'_{hom} for BChl-*a* in TEA at 1.2 K, however, is not just given by the fluorescence lifetime-limited value ($\Gamma_0 \approx 50$ MHz), but is larger by about 25 MHz (see Figure 3). Moreover, we have found that $\Gamma'_{\text{hom}} \propto T^{1.3 \pm 0.1}$ up to $T \approx 7$ K and $\Gamma'_{\text{hom}} \propto \exp(-E/kT)$ for $T > 7$ K with an activation energy $E \approx 35$ cm^{-1} .⁴⁸ Activation energies between 15 and 35 cm^{-1} were also obtained for other organic glassy systems at higher temperatures.^{13b,14b-e,49} The system BChl-*a* in TEA, thus, undergoes "pure" dephasing without observable SD, and, like in a crystal, only very fast fluctuations (within the 4 ns lifetime of the excited state of BChl-*a*) seem to be active in TEA, which we take as an indication that the structure of TEA is rather ordered. From the $T^{1.3}$ dependence, on the other hand, we conclude that TEA is disordered, and the small value of Γ'_{hom} furthermore suggests that either only a few TLSs contribute to the dephasing or the coupling of BChl-*a* to TEA is very weak. We think that structural relaxation in TEA is negligible over time scales longer than T_1 , when doped with BChl-*a* at low concentrations and up to 4.2 K. Nevertheless, we have found that at concentrations $c \geq 5 \times 10^{-4}$ M, SD induced by energy transfer takes place in TEA, even at $T < 4.2$ K.^{50,51} It looks as if a large energy barrier (of ~ 100 cm^{-1}) in TEA first has to be crossed before the TLSs responsible for SD can be activated. Apparently, during "downhill" energy transfer within the 0-0 band enough energy is dissipated and,

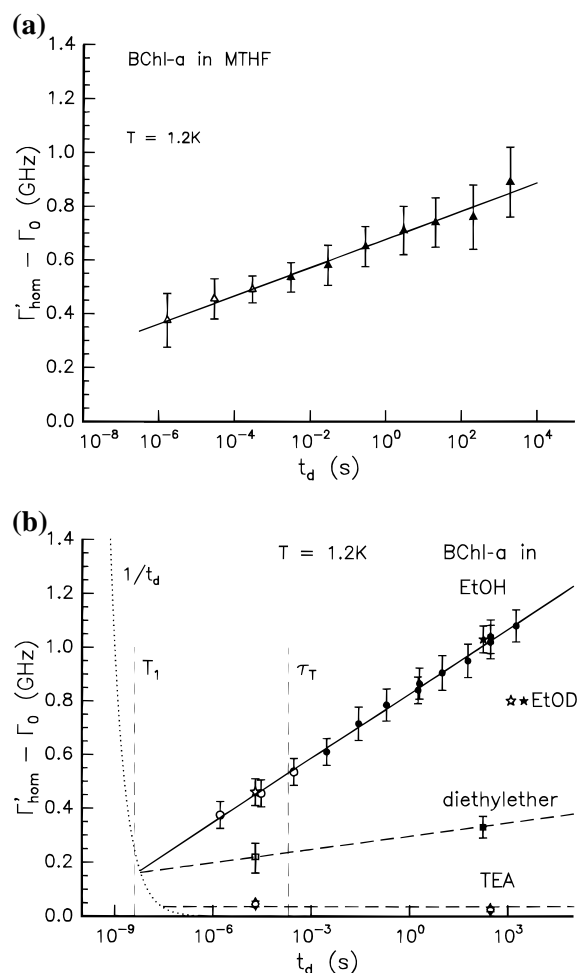


Figure 4. (a, top) $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of the logarithm of delay time for BChl-*a* in MTHF at $T = 1.2$ K. ▲ data points from permanent HB; △ data points from transient HB. (b, bottom) Same as part a for BChl-*a* in the glasses EtOH (●, ○), EtOD (★, ☆), diethyl ether (■, □), and TEA (◆, ◇). The vertical marker lines represent the excited-state lifetime $T_1 = \tau_n \approx 4$ ns, and the triplet-state lifetime $\tau_T \approx 100$ μ s. The dotted curve represents the Fourier contribution $1/t_d$ of the laser pulse length to the “effective” homogeneous linewidth.

therefore, available to overcome this large barrier and flip the TLSs. We are currently investigating this problem.

Let us now focus on the delay time dependence of $\Gamma'_{\text{hom}} - \Gamma_0$, plotted in Figure 4a,b as a function of the logarithm of the delay time t_d between 10^{-6} and 10^3 s for BChl-*a* in MTHF (Figure 4a) and in EtOH, EtOD, diethyl ether, and TEA at 1.2 K (Figure 4b). The slope is steepest for MTHF and EtOH, less pronounced for diethyl ether, and zero for TEA. The dependence is linear in the logarithm of t_d , within the error bars. The two vertical markers in Figure 4b represent the fluorescence lifetime $T_1 \approx 4$ ns, and the triplet-state lifetime $\tau_T \approx 100$ μ s of BChl-*a*. In experiments where $t_d \leq \tau_T$, the hole-burning mechanism in BChl-*a* is transient and caused by population storage in the triplet state;^{18,20} the lifetime of the hole is then equal to τ_T . In experiments where $t_d > \tau_T$, the holes are permanent and probably due to a reorientation of the central magnesium atom of BChl-*a* with respect to the glass when the molecule has been excited.⁴⁸ The holewidths, however, are independent of the particular HB mechanism. In Figure 4b the dotted curve represents the reciprocal of the delay time t_d^{-1} , which is a measure for the Fourier contribution to the holewidth due to the laser pulse length. It determines the short-time limit of the pulsed hole-burning method.

A remark concerning the glasses EtOH and EtOD is in order. Figure 4b shows that the two data points for EtOD measured at

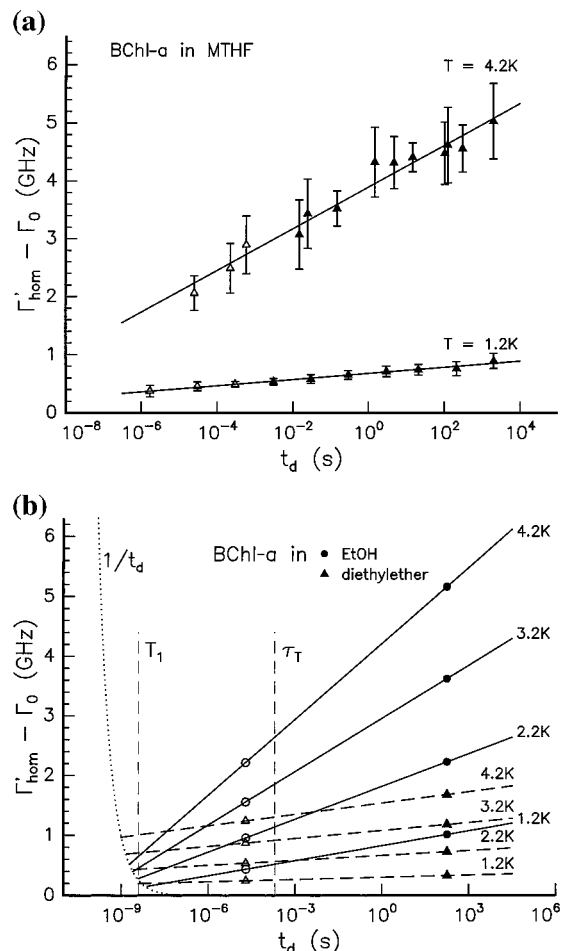


Figure 5. (a, top) $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of $\log t_d$ for BChl-*a* in MTHF at 1.2 and 4.2 K. The data are well fitted with a linear dependence within the error bars. (b, bottom) $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of $\log t_d$ for BChl-*a* in EtOH (●, ○) and diethylether (▲, △) for a number of temperatures between 1.2 and 4.2 K, linear fit. The amount of SD varies much stronger as a function of temperature for EtOH than for diethylether.

$t_d = 10^{-5}$ and 10^2 s fall on the curve for EtOH. According to the literature, “extrinsic” TLSs due to the OH groups are generally held responsible for the occurrence of non-photochemical hole-burning,⁵² and it was conjectured in ref 26b that they may also be responsible for slow spectral diffusion. If the latter were true, one would expect that in a plot like Figure 4b the data points for EtOH would fall on a curve different from that for EtOD. Since this is not the case, we may infer that the rate distribution function of the TLSs should *not* be associated with “extrinsic” TLSs.

To investigate the effect of temperature on spectral diffusion, we have measured the broadening of Γ'_{hom} as a function of t_d for BChl-*a* in MTHF at 1.2 and 4.2 K; see Figure 5a. It is evident that SD increases with temperature, the slope being much steeper at 4.2 K. A similar plot, but for the glasses EtOH and diethyl ether, is given in Figure 5b for a series of temperatures. We see that there is a much larger change in slope as a function of temperature for EtOH (solid lines) than for diethyl ether (dashed lines). Apparently, the increase of SD with temperature depends on the nature of the glass.

In Figures 4 and 5, the values of $\Gamma'_{\text{hom}} - \Gamma_0$ have been fitted by a linear function of the logarithm of t_d , the implication being that the distribution of TLS relaxation rates R is proportional to $1/R$. Within the standard model this implies that the distribution of tunneling parameters of the TLSs is flat¹⁻⁵ and, therefore, the TLS density of states $\rho(E)$ is constant. This leads

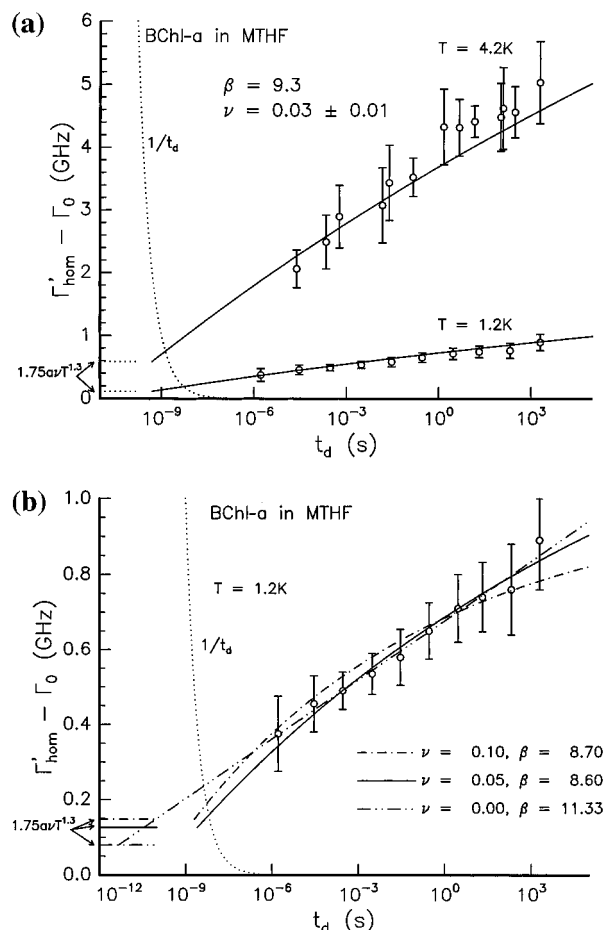


Figure 6. (a, top) $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of $\log t_d$ for BChl-*a* in MTHF at 1.2 and 4.2 K. The curves are fits of eq 5 to the data. The same values of the parameters a , ν , and β fit the data at the two temperatures. (b, bottom) $\Gamma'_{\text{hom}} - \Gamma_0$ as a function of $\log t_d$ for BChl-*a* in MTHF at 1.2 K plotted in an extended vertical scale. Several fits of eq 5 are shown for fixed values of ν between 0.00 and 0.10.

to $\Gamma'_{\text{hom}} - \Gamma_0 \propto T \log t_d^{3-5.46}$ i.e. interrelated linear dependences on T and $\log t_d$. Experimentally, however, one invariably observes a proportionality with $T^{1.3 \pm 0.1}$, which, so far, has been explained by assuming that $\rho(E) \propto E^{0.3}$, where E is the energy splitting of the eigenstates of the TLS.^{8-10,33,44} In an attempt to solve this contradiction, we have modified the assumptions of the standard model.⁴⁶ Instead of taking the distribution of TLS asymmetries ϵ as $P_\epsilon(\epsilon) = \text{constant}$, and the distribution of tunneling matrix elements Δ as $P_\Delta(\Delta) \propto 1/\Delta$,¹⁻³ we have taken $P_\epsilon(\epsilon) \propto |\epsilon|^\mu$ and $P_\Delta(\Delta) \propto 1/\Delta^{1-\nu}$ in ref 46. The latter is the result of numerical calculations based on simulations of glasses by Heuer and Silbey.⁴⁷ They found that $P_\Delta(\Delta) \approx 1/\Delta$ for $\Delta/k_B < 10^{-3}$ K, whereas $P_\Delta(\Delta)$ is best fitted by $1/\Delta^{1-\nu}$, with ν increasing to ~ 0.2 as Δ/k_B increases beyond 1 K. The form of $P_\epsilon(\epsilon)$ is taken to obtain the correct temperature dependence of the linewidth. The new probability distributions lead to the following expression for the time and temperature dependence of $\Gamma'_{\text{hom}} - \Gamma_0$:

$$\Gamma'_{\text{hom}} - \Gamma_0 = 1.75avT^{1+\mu+\nu} + aT^{1+\mu+\nu}\{1 - \exp[-\alpha(\beta + \log t_d)]\} \quad (5)$$

where a is proportional to ν^{-1} and contains a collection of constants, including the chromophore-glass interaction, $\alpha = 2.303\nu/2$ and $\beta = \log(R_{\text{m,eff}})$, with $R_{\text{m,eff}}$ an effective maximum rate averaged over the energy distribution.⁴⁶ The first term in eq 5 represents the predicted two-pulse photon-echo or

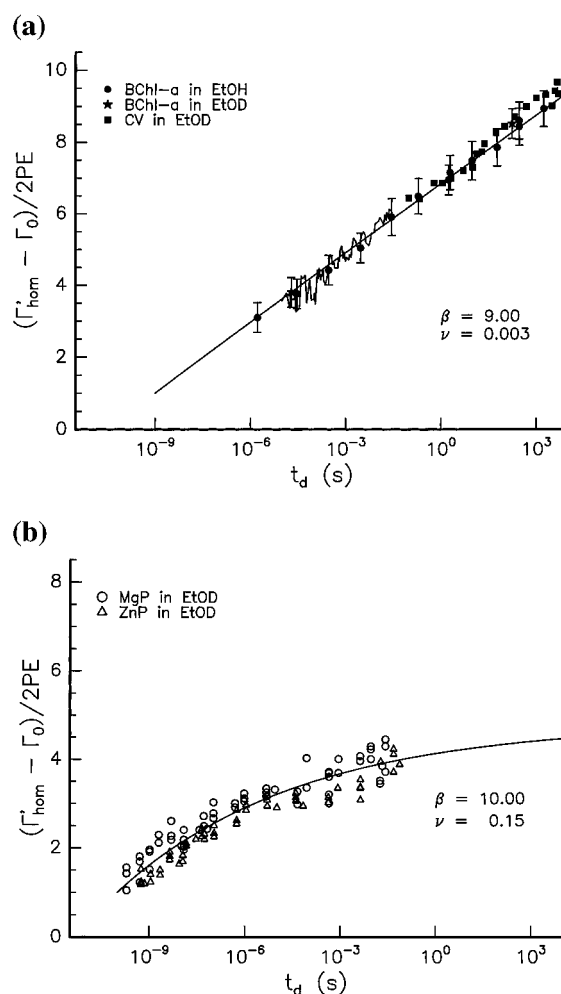


Figure 7. (a, top) $\Gamma'_{\text{hom}} - \Gamma_0/2\text{PE}$ as a function of $\log t_d$ for BChl-*a* in EtOH and EtOD at 1.2 K and for cresyl violet (CV) in EtOD at 1.3 K. The data for CV in EtOD were taken from hole-burning results of ref 17c,d and two-pulse photon-echo results of ref 14e, Figure 4. The curve fits both sets of data with $\nu = 0.005$ and $\beta = 8.75$. (b, bottom) $\Gamma'_{\text{hom}} - \Gamma_0/2\text{PE}$ as a function of $\log t_d$ for zinc porphyrine (ZnP) and magnesium porphyrine (MgP) in EtOD at 1.5 K. The data were taken from three-pulse photon-echo results of ref 26b. The curve fits both sets of data with $\nu = 0.15$ and $\beta = 10.0$. Note that the time scale is shifted to shorter t_d values as compared to part a.

“pure” dephasing term. Obviously, the T and t_d dependences in the second term are intertwined, and Γ'_{hom} depends not only on the distribution function in E but also on the assumed forms of the distribution functions in ϵ and Δ .⁴⁶ In the limit $\nu \rightarrow 0$, $\Gamma'_{\text{hom}} - \Gamma_0$ is linear in $\log t_d$, in agreement with the standard model.

In Figure 6a we have replotted the data of Figure 5a for BChl-*a* in MTHF at 1.2 and 4.2 K and fitted them with eq 5. Within the experimental uncertainty, the curves fit the data well using a single set of parameters, $\beta = 9.3$ and $\nu = 0.03$ for both temperatures. The small value of ν indicates an almost linear fit. The predicted two-pulse photon-echo values are also given. To check the effect of a variation in the parameters β and ν , we have plotted the data taken at 1.2 K again in Figure 6b on an extended vertical scale (compare to Figure 4a). Three different fits are shown with values of ν fixed between 0.00 and 0.10: the larger ν , the smaller β . All three curves go through the data within the error bars, but a fit close to linear ($\nu = 0.00$) seems to be the best. To choose the values of ν and β , we have used the criterion that $R_{\text{m,eff}} = 10^\beta$ should be at least as large as the value predicted for the two-pulse photon-echo decay $(T_2^*)^{-1} = \pi 1.75avT^{1.3}$. This rules out all values of

$\beta < 8.6$ for BChl-*a* in MTHF at 1.2 K, implying that there are fluctuations fast enough to cause dephasing at short times. Note in eq 5 that the smaller the value of ν , the larger the value of μ required for the data to follow a $T^{1.3}$ power law.

In Figure 7a, our hole-burning results for BChl-*a* in EtOH and EtOD at 1.2 K⁵³ are shown together with those of Fayer's group for cresyl violet (CV) in deuterated ethanol (EtOD) at 1.3 K^{17c,d} in a normalized form: $\Gamma'_{\text{hom}} - \Gamma_0$ was divided by the predicted two-pulse photon-echo value $2\text{PE} = 1.75 \alpha \nu T^{1.3}$ for our hole-burning data at $T = 1.2$ K and by the experimental 2PE value at 1.3 K (with the value of Γ_0 subtracted) for the data of ref 17d, $2\text{PE} = 0.172$ GHz (from Figure 4 of ref 14e). The data so obtained were plotted as a function of the logarithm of the delay time, for t_d between 10^{-6} and 10^3 s. From eq 5 we expect that this normalization makes the result independent of the chromophore. Using the same criterion as above for choosing the value of β , we find that one set of parameters, $\beta = 9.00$ and $\nu = 0.003$, fits both sets of data reasonably well. The results indicate that the amount of spectral diffusion (slope) and the number of TLSs active in SD (the absolute value of $\Gamma'_{\text{hom}} - \Gamma_0 / 2\text{PE}$) are about the same for both samples, despite the fact that the probe molecules are very different, one neutral and one ionic. We conclude that SD in ethanol appears to be a property of the glass, independent of the probe molecule, which we would expect. Similar conclusions were reached in ref 17b from the hole-broadening behavior of two ionic dyes (cresyl violet and resorufin) doped in ethanol.

For comparison, we have also taken three-pulse photon-echo data for magnesium (MgP) and zinc porphine (ZnP) in deuterated ethanol (EtOD) at 1.5 K from the literature.^{26b} As for Figure 7a, we have normalized the data by dividing $\Gamma'_{\text{hom}} - \Gamma_0$ by the experimental two-pulse photon-echo values, $2\text{PE} = 0.14$ GHz for MgP and 0.17 GHz for ZnP, and plotted them in Figure 7b as a function of $\log t_d$, for t_d between 10^{-10} and 10^{-2} s. The curve traced through the data is a fit with $\beta = 10.0$ and $\nu = 0.15$. This one set of parameters fits both sets of data rather well. The values of β and ν , however, are much larger than those found for hole-burning in the same glass. This difference is probably related to the different delay-time regions covered by the two techniques, with the three-pulse photon-echo region shifted to shorter times. An explanation for this discrepancy might be found in the glass dynamics simulations of Heuer and Silbey, who calculated the distribution of tunneling parameters in the glass and concluded that $\nu \approx 0$ would be expected at longer times and $\nu \approx 0.2$ at shorter times.⁴⁷ Since the delay times for hole-burning experiments are longer than for three-pulse photon echoes, the former should yield smaller values of ν than the latter, as indeed observed.

From the fits presented in Figures 6 and 7 of our data and those of other groups we conclude that eq 5, which contains the $T^{1.3}$ dependence and a nonlinear dependence on the logarithm of t_d of $\Gamma'_{\text{hom}} - \Gamma_0$, is capable of fitting the hole-burning as well as the three-pulse photon-echo data, but with different values of β and ν for a given glass. Equation 5 also predicts the observed quasi-linear dependence on $\log t_d$ (with ν close to zero) in hole-burning experiments at long delay times.

Finally, in Figures 8a,b we have plotted all delay-time-dependent data for ethanol together in a normalized form (see Figure 7a,b) as a function of $\log t_d$ between 10^{-10} and 10^3 s. Figure 8a is an overlap of Figure 7a,b with the same fitted curves and β and ν parameters. It is surprising that in the delay-time region between 10^{-6} and 10^{-2} s, in which hole-burning (HB) and three-pulse photon-echo data (3PE) are available, there is agreement between the two sets of data, if at all and within the error bars, only between 10^{-6} and 10^{-5} s. Furthermore, the

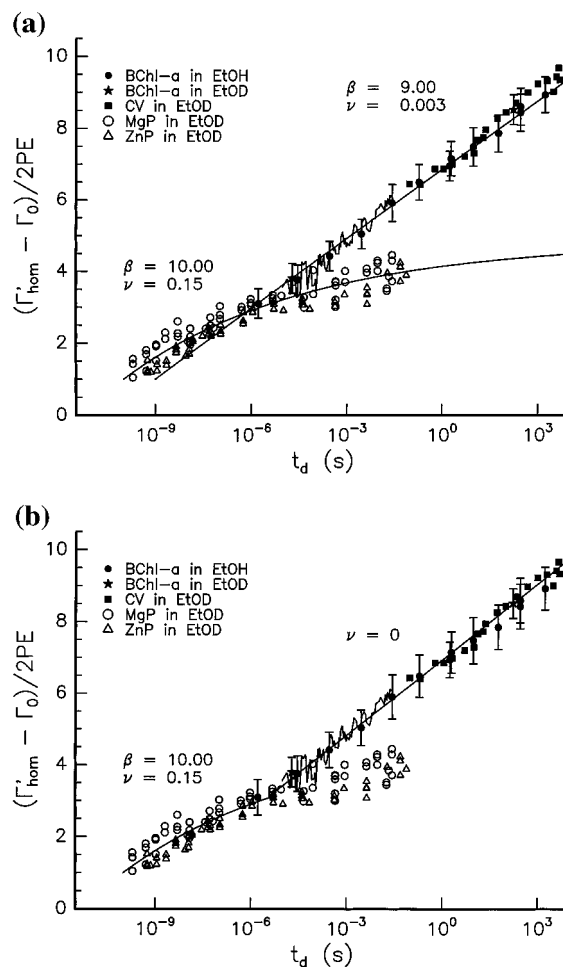


Figure 8. (a, top) Overlap of Figure 7a,b for BChl-*a* in EtOH and EtOD and CV in EtOD^{17c,d} from hole-burning, and ZnP in EtOD and MgP in EtOD from three-pulse photon echoes.^{26b} Notice that the curves cross each other at $t_d \approx 10^{-5.6}$ s. The HB and 3PE data coincide only between 10^{-6} and 10^{-5} s. (b, bottom) Same data as in part a, but the curve was traced with $\nu = 0$ for t_d from 10^3 to $10^{-5.2}$ s, and with $\nu = 0.15$ and $\beta = 10.0$ for $t_d < 10^{-5.2}$ s. A pronounced kink in the curve is observed. The 3PE data at $t_d > 10^{-5}$ s deviate from the curve (see text).

slope of the HB data is much more pronounced than that of the 3PE data, suggesting that the amount of SD is larger for the samples measured by hole-burning. In Figure 8b the same data are plotted as in Figure 8a, but with a slightly different fit. The HB data have been fitted linearly, with $\nu = 0$, whereas the 3PE data have the same fit as in Figure 8a. Both curves cross at $t_d \approx 10^{-5.2}$ s. The 3PE data measured at $t_d > 10^{-5}$ s do not fit the curve.

We do not know yet what the reason is for the discrepancy between the hole-burning and the 3PE data. Since there are no HB data at $t_d < 10^{-6}$ s so far, we do not know either what type of curve these data would follow at shorter delay times: that of the 3PE data with a kink in the curve, or a straight line following smoothly the HB curve? For the final test of the theoretical model⁴⁶ more data are needed, not only for ethanol but also for other glasses like MTHF and polymers (e.g. PMMA and polystyrene) doped with different guest molecules, over at least 9 or 10 decades in delay time.

We would like to comment here on results reported by Zimdars and Fayer that were recently published⁵⁴ while the present paper was being prepared. In this article the discrepancies between the hole-burning data of Fayer's group^{17d} and the 3PE data of Wiersma's group^{26b} are also discussed, and a heuristic model is proposed to fit the data and explain the

disagreement. Their model is based on the assumptions that (1) the coupling between the chromophore and the glass can vary as a function of the fluctuation rate R of the TLSs and (2) the uncharged and nonpolar metal porphines couple to TLS strain dipoles, while the charged and polar cresyl violet (CV) also couples to TLS electric dipoles. If this model were applied to our hole-burning data on BChl-*a* in ethanol, we would, in first instance, expect a behavior similar to that of the 3PE results on metal porphines in ethanol,^{26b} since both types of molecules belong to the same family. But this is not the case. In contrast, our HB results between 10^{-6} and 10^3 s are like those obtained for CV in ethanol. A way to explain this within the model of Zimdars and Fayer is to note that BChl-*a* is non-centrosymmetric and has a dipole moment, unlike the metal porphines. Therefore, it will couple to the TLS electric dipoles in the same manner as CV. However, we believe that this argument fails for two reasons: (1) If the model were correct, CV and BChl-*a* would have different spectral diffusion, since they have unequal dipole moments. However, as shown in Figure 7a, the results for these two molecules scale in exactly the same manner. (2) The metal porphines have a large (state-dependent) polarizability and thus an induced dipole moment due to the asymmetric and polar glass environment. Consequently, they will interact with the TLS electric dipoles, in contradiction to the assumptions in ref 54. In addition, we have found the same type of (quasi-) linear logarithmic dependence of Γ'_{hom} on delay time for other glasses and molecules. This suggests that the coupling of the chromophore to the modes of the glass is not dependent on rate in the manner assumed by Zimdars and Fayer, at least not in the range from 10^{-6} to 10^3 s. We believe, therefore, that the difference between the HB and the 3PE results remains a puzzle.

If we examine the fit of our model⁴⁶ to the hole-burning data for CV^{17d} and compare it to the fit of the model of Zimdars and Fayer,⁵⁴ it is not surprising that the latter reproduces the data more accurately because it contains at least five parameters (two separate rate distributions and a parameter to scale the results), whereas our model contains only three (ν , β and a parameter to scale the results). Our interest here was not to get an absolutely exact fit, but to test whether our model,⁴⁶ which was originally suggested by a previous theoretical and computational study,⁴⁷ can fit the data reasonably well with a small number of parameters.

4. Conclusions

We have studied the "effective" homogenous linewidth Γ'_{hom} of the $S_1 \leftarrow S_0$ 0–0 transition of BChl-*a* at low concentration ($c \approx 1 \times 10^{-5}$ M) in a number of organic glasses as a function of temperature and delay time. Time-resolved spectral holes were burnt and probed with delay times varying over 9 orders of magnitude, from 10^{-6} to 10^3 s. Whereas significant spectral diffusion (SD) was found for the glasses MTHF and EtOH, much less was observed for diethyl ether, and none for TEA in the same time interval. We conclude that SD depends markedly on the glass chosen.

The increase of Γ'_{hom} with temperature obtained from permanent ($t_d = 300$ s) as well as from transient ($t_d = 15$ μ s) holes follows a $T^{1.3 \pm 0.1}$ power law between 1.2 and 4.2 K and extrapolates for $T \rightarrow 0$ to the fluorescence lifetime-limited value Γ_0 in all samples. Such a T dependence, typical for doped organic glasses, is independent of the experimental time scale. The amount of SD, therefore, increases with temperature according to the same power law.

In a first approximation, Γ'_{hom} appears to vary linearly with the logarithm of delay time, as predicted by the standard model,^{3–5} which also predicts a constant density of TLS states,

$\rho(E) = \text{constant}$, and a linear T dependence of Γ'_{hom} . If, however, the distributions of TLS asymmetries and tunneling matrix elements are assumed to be different⁴⁷ from those of the standard model, a $T^{1.3}$ dependence on temperature is simultaneously expected with a nonlinear dependence on the logarithm of the delay time. The model of ref 46 not only appears to fit our dephasing data for BChl-*a* in MTHF and EtOH as a function of both temperature and delay time but also fits time-dependent hole-burning data from the literature for cresyl violet in EtOD^{17c,d} reasonably well with values of ν close to zero. When the model is used to fit three-pulse photon-echo data for zinc and magnesium porphine in EtOD,^{26b} larger values of ν (~ 0.15) are needed. We do not know yet to what to attribute the discrepancy between the hole-burning and three-pulse photon echo data in the region between 10^{-5} and 10^{-1} s. Finally, by comparing results in ethanol doped with various probe molecules, we conclude that the number of active TLSs in the glass and the amount of SD are not influenced by the probe.

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