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Thermal irreversibility in optically labeled low-temperature glasses

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We present an investigation of irreversible features of thermal broadening of persistent spectral holes. The investigation is based on temperature-cycling hole-burning experiments performed with a variety of organic glasses doped with rather different probe molecules. The results show a rich temperature dependence. They can, however, be interpreted in terms of the well-known spectral diffusion models, in which we introduced a freezing condition to account for thermal irreversiblity. There is a tunneling regime for low temperatures and an activated regime for high temperatures. In the tunneling regime the broadening is linear in T; in the activated regime it increases with $T^{3/2}$ and logarithmically with time. From the transition region the quantity md^2, with m being the tunneling mass and d the distance, can be determined.

INTRODUCTION

A characteristic feature of glasses and polymers is their nonergodicity.[1] Nonergodicity means that the system cannot explore all energetically accessible states. Because of large barriers, it is trapped in a small volume in phase space. If the thermal energy is low compared to the barriers surrounding the occupied region in phase space, tunneling processes offer the only possibility to escape from the configurational trap. As the temperature is raised, thermally activated processes may become important and may eventually prevail. Hence, as time goes on or as the temperature is raised, the glass or the polymer starts to explore an increasing volume in its phase space. These processes can only be observed in the case in which the initial microstate can be labeled. Persistent spectral holes offer an excellent possibility to label a certain microstate. If the glass is doped in low concentration with photoreactive dye molecules, frequency labeling of a subensemble out of these dye molecules can be performed by burning a narrow hole into the broad, disorder-dominated absorption band. The microstate of the glass matrix is labeled by those molecules which make up the hole and which happen to have, roughly speaking, the same absorption frequency in the specific microstate considered. As the system starts to explore a larger area in phase space, the frequencies of the labeled molecules no longer coincide. They spread as the temperature increases or as time goes on. This is called spectral diffusion.[2,3] Since, at low temperatures, the original hole may be extremely sharp, small changes can be measured with high accuracy, and, hence, the dynamics of the glass can be monitored.[4]

The phase space of the glass is very conveniently modeled within the so-called two-level-system (TLS) model.[5,6] Within the framework of this model the phase space is made up by an ensemble of double-well potentials (the so-called TLS) with varying energies and barriers. A change in configuration occurs in this simplified phase space via transitions in these TLS modes. These transitions are mediated by lattice phonons. Usually, it is assumed that it is only the two lowest states of such a double well which are important for the dynamics of the glass, an approximation which is certainly very good at extremely low temperatures, for which the model was first developed. At these low temperatures the dynamics is dominated by tunneling processes. At higher temperatures, however, thermally activated processes may occur as well (for a recent review on low-temperature glasses, see Ref. 7).

In this paper we report on a special type of hole-burning experiments, namely, temperature-cycling hole-burning experiments. The first experiment of this type was published in 1982.[8] The special feature of this type of hole-burning experiment is that it is exclusively sensitive to spectral diffusion, whereas a normal hole-burning experiment is, in addition, also sensitive to fast dephasing processes like phonon scattering.[9]

We will show how a freezing condition can be introduced in the spectral diffusion models to account for thermal irreversibility. One can, in principle, expect a rich temperature dependence of the spectral diffusion width as measured in a temperature-cycling hole-burning experiment. This temperature dependence is determined by the pertinent relaxation processes and by the boundaries of the TLS distribution functions. Hence, in most cases there is no unified power law. We will also show that recent experiments by Schulte *et al.*[10] on a series of phthalocyanine-doped polymers fit into the scenery as predicted by our model. Special care is taken to estimate the influence of the experimental boundary conditions on the results, for example, the influence of the experimental time scale, or the chosen burning temperature or whether a deep or a shallow hole is burnt. The paper concludes with a discussion of the approximations used.

EXPERIMENTAL

Sample preparation

The various guest molecules and host glasses are shown in Fig. 1. The doping level of all samples was very low, on the order of 10^{-6} mol/g or less. We investigated three different alcohol glasses, a polymer [poly(methyl methacrylate), PMMA] and a pure hydrocarbon glass (3-methylpentane, 3-MP). The alcohol glasses were mixtures of ethanol-methanol (EtOH-MeOH, 3:1 volume:volume), its deuterated derivative, and a mixture of isopropanol-xylol (P-X, 4:1 volume:volume). In addition, we used a variety of very different probe molecules: photostable molecules (tetracene, Tc) which undergo a photophysical hole-burning reaction,[11,12] photounstable molecules (dimethyl-*s*-tetrazine, DMST) which decompose,[13] tertiary butyl phthalocyanine (PC*), where the photoreaction is considered to be purely intramolecular without changing the shape of the molecule,[14,15] and quinizarin (DAQ), which undergoes a photochemical reaction under participation of the neighboring solvent molecules.[16] Note that apart from their photochemical behavior, the shape and the size of these molecules are also very different.

Experiments

For almost all hole-burning experiments a pulsed dye laser pumped by a nitrogen laser equipped with an intracavity étalon was used. The bandwidth was smaller than $0.02\ \mathrm{cm}^{-1}$. Power levels for burning were on the order of 10 kW/cm^2, and typical fluences were on the order of 100 mJ/cm^2. At 500 mK (Tc in EtOH-MeOH) hole burning was, in addition, performed with an Ar$^+$ laser. In this case the power level was 40 μW/cm^2 with typical burning times of 40 min. We stress that for hole burning below 1 K the power level is crucial due to laser heating.[17] Most experiments were done in a He-flow cryostat, the temperature of which could be varied between 3 and 300 K. In this range the temperature was accurate within 0.1 K. Between 500 mK and 3 K a ^{3}He-type cryostat was used. The temperature control was accurate within 0.01 K. Usually, we waited an hour or so until the recovery dynamics of the hole had sufficiently slowed down before the temperature-cycling experiments were performed. Such a cycling experiment works in the following way: The hole is burnt at the lowest accessible temperature (the burn temperature T_b), and allowed, if necessary, to slow its dynamics. Then, the temperature of the sample is raised to some value T (the excursion temperature), and cycled back again to T_b, where the changes in the width, area, and shape, which the hole suffered through the cycle, are measured. The time scale τ of such a temperature cycle is roughly 100 s. Note that the change in width is decoupled from a change in area (see, for example, Figs. 4 and 7). The two quantities yield different information. The change in area tells us how many molecules have returned from the photoproduct state to the educt state during the cycle. Thus, we obtain information on the distribution of barrier heights which separate these two states.[18] The width, on the other hand, yields information on spectral diffusion, which is governed by the bulk TLS. In this paper we mainly focus on the change in linewidth as a function of excursion temperature. In the following we call this change in width $\Delta\omega_{\mathrm{ir}}$ in order to stress that we are dealing with thermally irreversible features of hole burning.

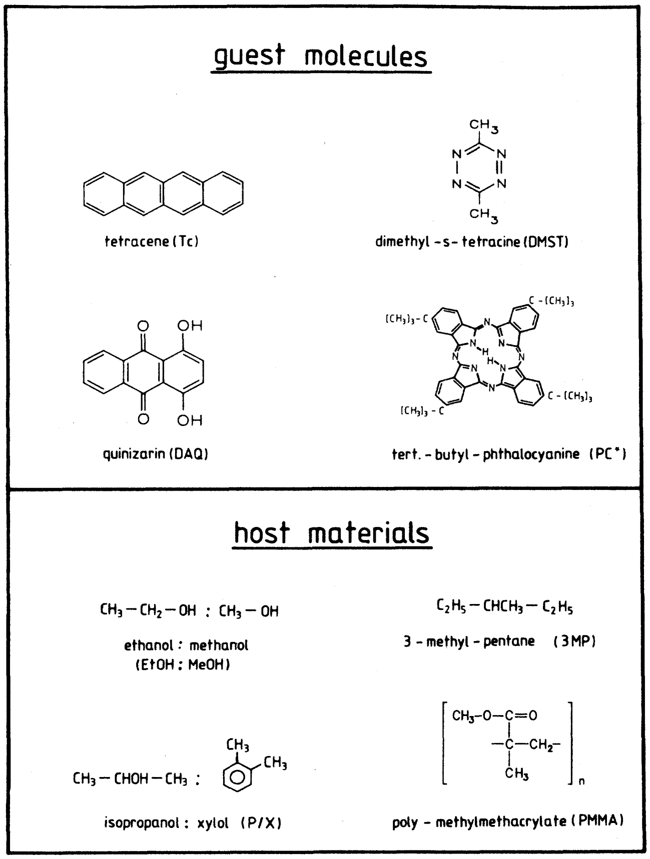

FIG. 1. The various guest molecules and host materials used.

For temperatures above 3 K, $\Delta\omega_{\mathrm{ir}}$ was measured with a high-resolution spectrometer ($0.15\ \mathrm{cm}^{-1}$). Below 3 K, the holes were measured by pressure scanning the dye laser and detecting the transmitted light with a boxcar integrator.

Since we were only interested in the changes of the hole, the depth of the hole was not a crucial quantity. After burning, the holes had a depth of roughly 10%. In order to be sure, however, that the results were independent on the hole depth, we performed the same series of experiments for a shallow (8%) and for a deep (25%) hole, as well as for different burning temperatures [Figs. 8(a)–8(d)]. In any case, we checked very carefully whether the holes were, after burning, Lorentzian or not. For Lorentzian holes the change in width can be simply obtained by subtracting the width measured before the temperature cycle from that measured after the cycle.

RESULTS

In the following we summarize the main points of our results.

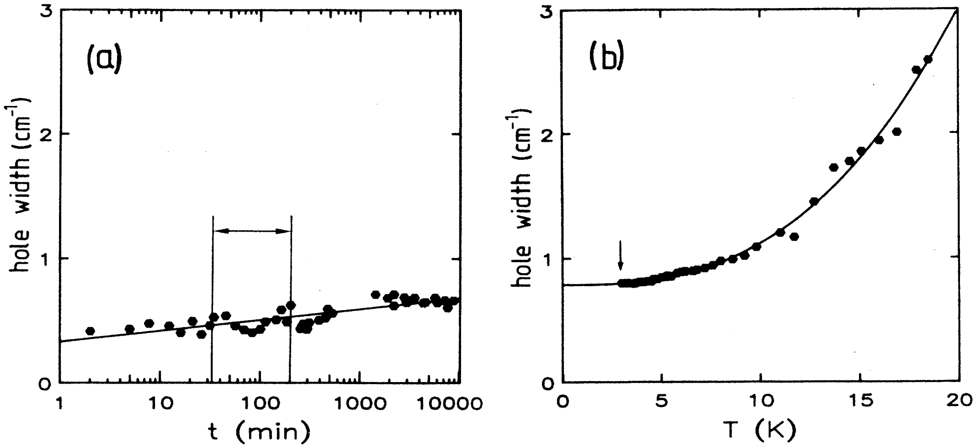

FIG. 2. Comparison between temporal [(a)] and thermal [(b)] effects in spectral diffusion. The measured quantity is the width of an optical hole. The vertical bars in (a) mark the time window in which the temperature-cycling experiments were carried out after hole burning. (a), $T=4.2$ K; (b), burning temperature $T_b=3$ K (arrow). Sample: tetracene in EtOH-MeOH.

(1) The competition between time- and temperature-dependent effects in the spectral diffusion width is of minor importance. Figure 2(a) shows, for Tc in EtOH-MeOH, the spectral diffusion as a function of time. Within 4 orders of magnitude in time, the holes broaden by 0.3 cm $^{-1}$, which is almost a factor of 2. The bars in Fig. 2(a) mark the time window in which the temperature cycles were performed after hole burning. The broadening in this time window has to be compared with the broadening induced by the temperature cycles [Fig. 2(b)]. The latter amounts to about 1.8 cm^{-1} as compared to approximately 0.08 cm^{-1}. Figure 2(b) also shows that the broadening due to temperature cycles can be fitted to a power law $\sim(T^{\alpha}-T_b^{\alpha})$ without underlying any model. For alcohol glasses, α is on the order of 3. We conclude that cycling experiments result in a much steeper temperature dependence than ordinary hole-burning experiments do.[19]

(2) Figure 3 shows a fit to the tetracene data between 500 mK and roughly 20 K. (Note that in this case there are two burning temperatures: 500 mK and 3 K.) The fit is based on a superposition of a one-phonon tunneling process, which dominates below 5 K, a two-phonon tunneling process, which prevails between 5 and 10 K, and a thermally activated process, which dominates above 10 K. The quality of the fit is good. We note that the tran-

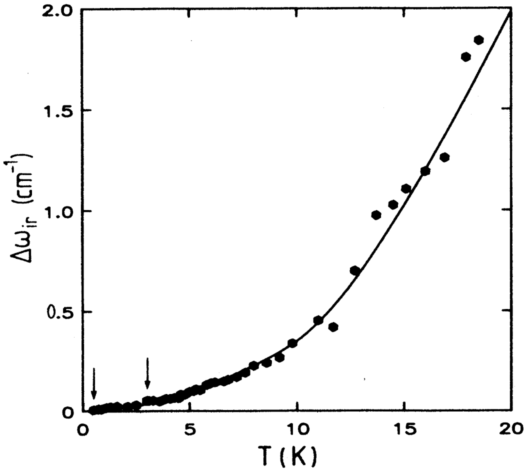

FIG. 3. The change in linewidth $\Delta\omega_{ir}$ as a function of excursion temperature T. Burning temperature: 500 mK and 3 K. Sample: tetracene in EtOH-MeOH. The fit curve is calculated according to Eq. (9) by taking into account a one-phonon tunneling process, a two-phonon Raman-type tunneling process, and an activated process.

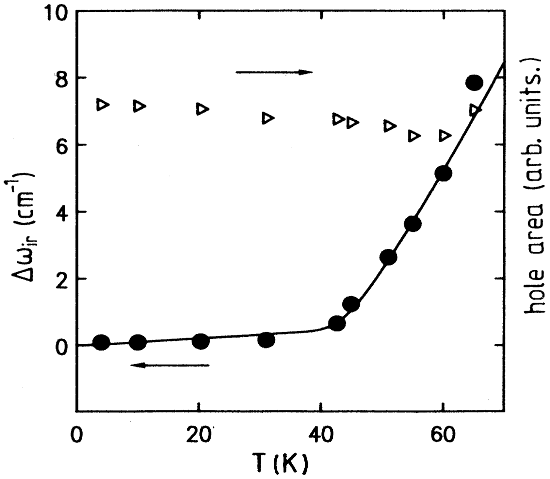

FIG. 4. $\Delta\omega_{ir}$ for tertiary butyl phthalocyanine in 3-methylpentane glass. The fit curve is based on a superposition of a one-phonon tunneling process and an activated process. Note the pronounced transition region around 40 K. Also shown is the hole area A/A_0 as a function of cycling temperature. There is no change in A/A_0 over the whole temperature range of the experiment.

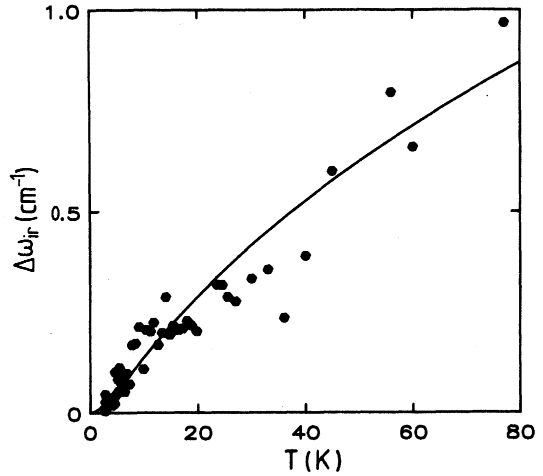

FIG. 5. Irreversible line broadening for quinizarin-doped poly(methyl methacrylate). The fit curve is calculated by assuming activated processes only. Also, it was assumed that there is an upper bound of the TLS density of states around 16 K.

sition from the tunneling to the activated regime is rather smooth.

(3) Figure 4 shows PC* in 3-MP glass. The striking feature is the rather pronounced transition between the tunneling ($T < 40$ K) and the activated regime. Clearly, such a behavior could never have been fitted reasonably well with a single power law. The fit curve is calculated by a superposition of a one-phonon tunneling process and an activated process. There is no evidence for a Raman-type tunneling process. (Note that the hole area does not show any tendency to decay throughout the temperature range investigated. This clearly demonstrates that the hole recovery is totally decoupled from thermally irreversible line broadening.)

(4) Whereas in the organic glasses the irreversible thermal line broadening is strong, it is very small in the polymeric sample (DAQ in PMMA, Fig. 5). Apart from that, the temperature dependence shows roughly a square-root behavior. The fit curve is based on activated processes only.

(5) Figures 6(a)–6(d) summarize the data of the EtOH-MeOH glass samples doped with very different

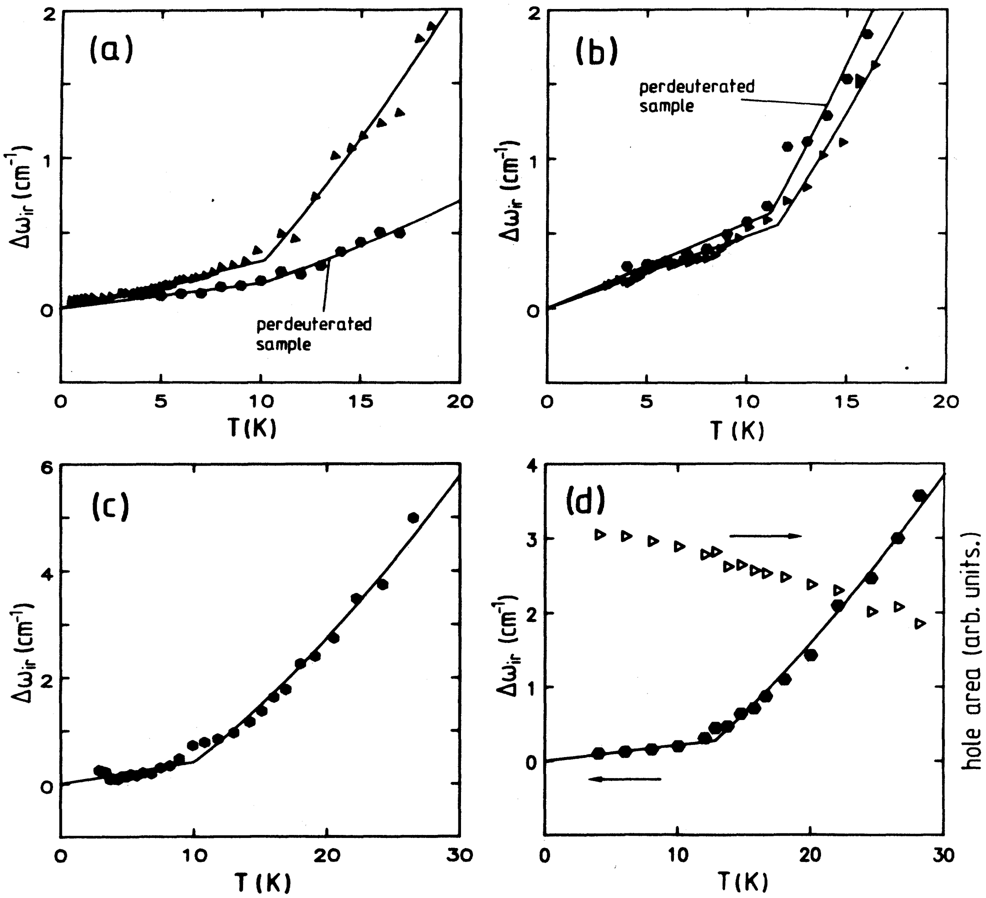

FIG. 6. (a) Influence of glass deuteration on $\Delta\omega_{ir}$. Sample: tetracene in ethanol-methanol glass. (b) Influence of glass deuteration on $\Delta\omega_{ir}$. Sample: quinizarin in ethanol-methanol glass. (c) $\Delta\omega_{ir}$ for dimethyl-*s*-tetrazine in ethanol-methanol glass. (d) $\Delta\omega_{ir}$ for phthalocyanine in ethanol-methanol glass. Also shown is the relative area of the hole as a function of excursion temperature. Note that it decays.

probe molecules. Note the pronounced difference in $\Delta\omega_{\mathrm{ir}}$ upon isotopic substitution for the tetracene sample. In the quinizarine sample the corresponding change is minor but has a different sign. The data in Figs. 6(a)–6(d) are fitted by using a simplified procedure. It is assumed that the low-temperature range is dominated by the tunneling regime, which is characterized by a linear temperature dependence, and that the high-temperature range is dominated by activated processes which follow a $T^{3/2}$ temperature dependence. Of course, this simplified fit procedure does not describe the transition region very well (as would an independent superposition of the various processes), but the fits are reasonably good. Note that the transition occurs for all EtOH-MeOH samples roughly around 12 K, though the absolute magnitude of $\Delta\omega_{\mathrm{ir}}$ may be quite different [e.g., Fig. 6(a)]. In Fig. 6(d) (PC* in EtOH-MeOH) we have, in addition, included the change of the hole area with cycling temperature. We stress that it decays, contrary to the data shown in Figs. 4 and 7.

(6) Figure 7 shows PC* in isopropanol-xylol glass.

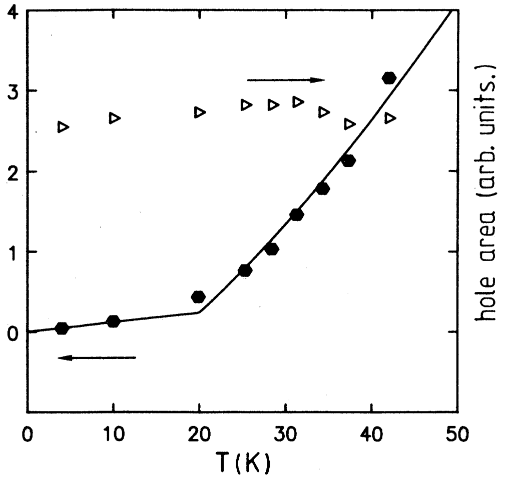

FIG. 7. $\Delta\omega_{\mathrm{ir}}$ (left scale) for phthalocyanine in an isopropanol-xylol glass. Also shown is the relative area of the hole as a function of excursion temperature (right scale). Note that A/A_0 does not decay.

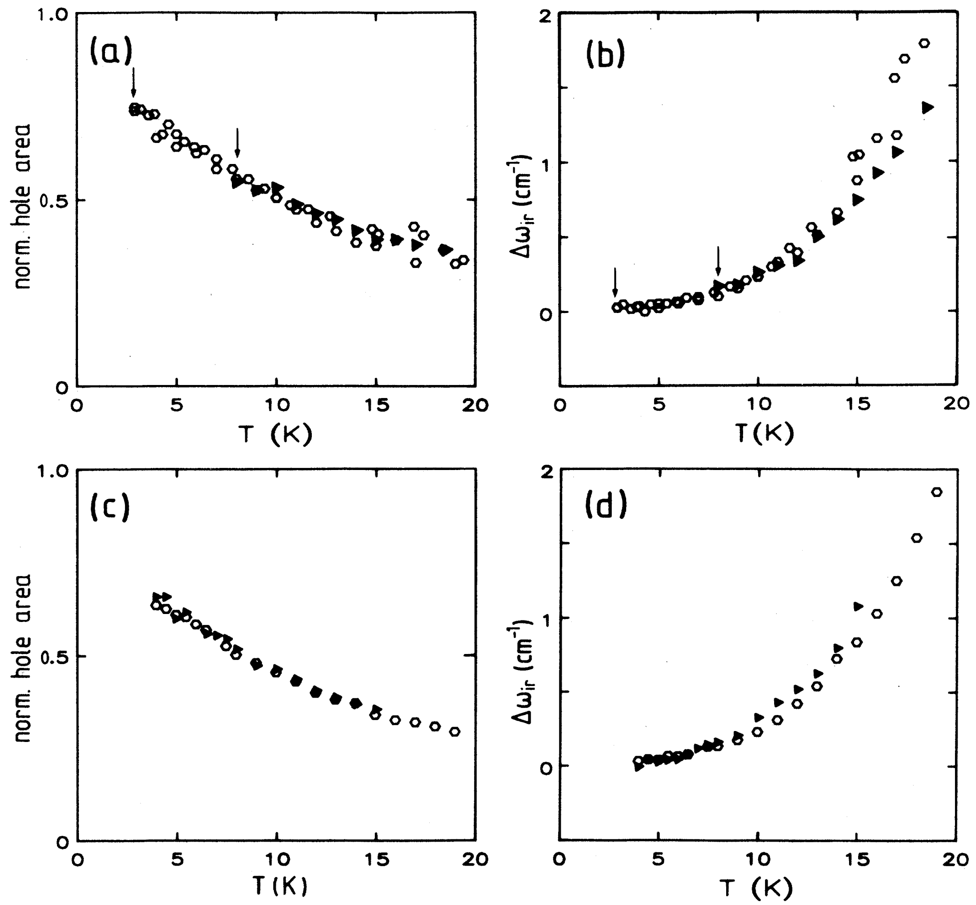

FIG. 8. (a) Recovery of the hole area as a function of excursion temperature for two different burning temperatures (arrows). Sample: tetracene in EtOH-MeOH glass. (b) $\Delta\omega_{\mathrm{ir}}$ for two different burning temperatures (arrows). Sample: tetracene in EtOH-MeOH glass. (c) Recovery of the hole area for a deep and a shallow hole. Sample: tetracene in EtOH-MeOH glass. (d) $\Delta\omega_{\mathrm{ir}}$ for a deep and a shallow hole. Sample: tetracene in EtOH-MeOH glass.

Two features are worth stressing. First, the data can again be well described in terms of a tunneling regime linear in T and an activated regime which increases with $T^{3/2}$. However, the transition region is around 25 K and, hence, is much higher than in EtOH-MeOH. Second, like in 3-MP glass (Fig. 4), there is no hole recovery over the complete temperature range.

(7) In Figs. 8(a) and 8(b) it is shown, for Tc in EtOH-MeOH, that the results do not significantly depend on the burning temperature. The recovery of the hole, as well as the increase of its width, is, within the experimental error, the same for the two burning temperatures shown (3 and 8 K, respectively). The results also do not depend in a significant way on the depth of the hole [Figs. 8(c) and 8(d)]. These are important results because they justify the way we measured the low-temperature data in the tetracene sample (Fig. 3). In this case we used two different cryostats for different temperature regimes.[17]

We stress that our experimental results are plotted in such a way that $\Delta\omega_{\text{ir}}(T=0,\ T_b=0)=0$ [see Eqs. (11) and (13)]. In this case $\Delta\omega_{\text{ir}}(T)$ is an absolute quantity and is independent of the burn temperature.

DISCUSSION

Basic aspects of optical spectral diffusion in glasses

Many aspects of the physics of low-temperature glasses and polymers are very well described, within the framework of the TLS model. This is sort of a mean-field model, where the phase space is made up by an ensemble of rather localized TLS's. A transition in such a TLS mode corresponds to a structural relaxation of the glass or polymer considered. Though the original concept of the TLS model was confined to tunneling processes, we will also allow for activated processes, because the temperature range of our experiment is large. The transition between the tunneling and the activated regime depends strongly, of course, on the special glass considered. Structural relaxation in polymer glasses, for example, occurs under more constraints than in simple small-molecule glasses. We would expect that the number density of TLS's would be smaller and the tunneling masses heavier in polymers due to the constraints imposed by the covalent bonding in the backbone. Such a situation is likely to favor thermally activated structural relaxation processes.

Optical spectral diffusion in doped glasses as measured in a hole-burning experiment can be understood in the following way. At a given temperature, a special subset of dopand molecules is marked in the frequency domain by burning a narrow hole. This hole can be considered a label for the specific microstate which the glass occupies during hole burning. Since the amorphous state is a nonequilibrium state, it may undergo structural rearrangement relaxation as time goes on, or as the temperature increases, or, generally speaking, as a change in some external parameter occurs. This rearrangement leads to a new microstrate, in which the microscopic environments of the frequency-labeled dye molecules differ from the original ones and, hence, the hole has broadened. Monitoring this broadening, i.e., monitoring the spectral diffusion, allows one to study the relaxation of the glassy state.

There are three well-defined time scales which play an important role in the study of optical lines of doped glasses.[2,4,9] These are (i) the dephasing time τ_2^*, (ii) the lifetime τ_1, and (iii) the experimental time scale τ_0.

It is well known that structural relaxation processes in disordered solids have a huge dispersion of rates.[4] Hence, these processes may play a role on all three time scales listed above. Those which occur on the scale of τ_2^* contribute to the homogeneous linewidth. They show up in a two-pulse photon-echo experiment and cannot be distinguished from fast phonon-scattering processes. Those which appear on the τ_1 time scale may determine the width of the fluorescence line. Those which occur on a time scale between τ_1 and τ_0 can only be measured in a hole-burning experiment. Whereas the time scale of an echo or a fluorescence experiment is determined by the pertinent molecular-relaxation times, the time scale of a hole-burning experiment is set by the experimentalist and, hence, this technique can be used to monitor extremely slow relaxation processes.

This discussion stresses the special feature of a cycling hole-burning experiment. Whereas all other techniques, including the usual hole-burning technique, measure contributions from all processes which show up on the relevant time scale, the cycling hole-burning experiment is exclusively sensitive to spectral diffusion as a result of structural relaxation. Hence, to interpret our results, we can immediately start with the spectral diffusion models as developed by Black and Halperin[2] and Reinecke,[3] which are based on earlier results by Klauder and Anderson.[20]

In the case in which an optical line of an impurity molecule in a glass is solely determined by spectral diffusion, its width is given by

$$\Delta\omega=C\left\langle\left|\frac{\Delta}{E}\right|n_f\right\rangle_{E,\lambda}, \tag{1}$$

where C is a coupling constant, Δ the energy asymmetry parameter, and E the eigenvalue splitting of the TLS involved. λ is the tunneling parameter which depends on the barrier height V, the mass m of the tunneling particle, and the tunnel distance d:

$$\lambda=\left[\frac{mV}{2\hbar^2}\right]^{1/2}d\ . \tag{2}$$

The angular brackets in Eq. (1) indicate that the parameters of the TLS, E and λ, are widely distributed, and that an average over the pertinent distribution functions has to be performed.

Let us assume we have labeled a certain microstate by burning a sharp hole at $t=0$, and we probe this hole at a time $t=\tau_0$. Then, n_f is the number of TLS's which have flipped an odd number of times during the interval τ_0. Of course, n_f does not only depend on τ_0, but also on the manipulations imposed onto the system during this interval, e.g., temperature changes. n_f can be calculated from simple rate equations.[2] Equation (1), then, takes the form

$$\Delta\omega=\tfrac{1}{2}C\bar{P}\int_{E_{\min}}^{E_{\max}}dE\,\mathrm{sech}^2\frac{E}{2kT}\int_{\lambda_{\min}}^{\lambda_{\max}}d\lambda(1-e^{-t/T_1})\ . \tag{3}$$

Here, it is assumed that the TLS density of states $\bar{P}$ is uniform between the boundaries $E_{\max},E_{\min}$, and $\lambda_{\max},\lambda_{\min}$, and decreases rapidly outside these limits. $T_1(E,\lambda,T)$ is the TLS relaxation time, which we have not yet specified. Note that regardless of the specific process considered, the dependence of T_1 on λ is strong and, hence, we have to deal with a huge dispersion of relaxation rates $R=T_1^{-1}$, because λ is distributed over a large range. We also stress that Eq. (3) does not account for thermal irreversibility, since, so far, no restriction with respect to the experimental time scale has been introduced.

Equation (3) shows again three interesting time regimes.

(i) The fast experimental time limit

$$\tau_0 \ll T_{1,\min}\ ,$$

where $T_{1,\min}$ is the minimum TLS relaxation time. In this time regime $\Delta\omega$ broadens $\sim t$. For tunneling processes the temperature dependence in this limit was calculated to be $\sim T^4$.[2] For an activated process one would, within the same approximations, expect a temperature dependence $\sim T[\exp(-2\hbar^2\lambda_{\min}^2/md^2kT)]t$. Note, that for optical hole-burning experiments the short-time limit has not yet been verified experimentally, probably due to the fact that the time scale of a hole-burning experiment is slow.

(ii) The slow experimental time limit

$$\tau_0 \gg T_{1,\max}\ .$$

In this limit, the broadening would be linear in T and, of course, independent of time, regardless of the relaxation processes involved. However, this limit is also out of the realm of any experimental verification. From all we know about structural relaxation in organic low-temperature glasses, the slow processes occur on time scales of hundreds of years or more.[4,21,22]

(iii) The logarithmic time regime, characterized by

$$T_{1,\min} \ll \tau_0 \ll T_{1,\max}\ .$$

Unlike cases (i) and (ii), the logarithmic time regime has been shown experimentally to describe the situation in organic glasses very well[4,12,21,22,23] [see Fig. 2(a)].

That Eq. (3) runs into a logarithmic time regime can be easily verified by integrating over rates R instead of λ, and solving the integral under ideal glass conditions,[24] i.e., assuming that the rate constants are either very fast or very slow compared to the experimental time. This is equivalent to a splitting of the TLS ensemble into two categories, namely those which are in the fast experimental time limit and those which are in the slow limit. Under these conditions, one gets from Eq. (3), for tunneling relaxation characterized by rates $R=R_1(E,T)\exp(-2\lambda)$,

$$\Delta\omega=\tfrac{1}{2}C\bar{P}\int_{E_{\min}}^{E_{\max}}dE\,\mathrm{sech}^2\frac{E}{2kT}\times\left[\tfrac{1}{2}\int_{R_{\min}}^{R=1/\tau_0}\frac{dR}{R}(1-e^{-Rt})+\tfrac{1}{2}\int_{R=1/\tau_0}^{R_{\max}}\frac{dR}{R}(1-e^{-Rt})\right]. \tag{4}$$

The first integral yields a negligible contribution, whereas the second integral yields the logarithmic time dependence

$$\Delta\omega=\frac{1}{4}\frac{Cn_0}{\Delta E\,\ln(R_{\max}/R_{\min})}\ln(R_{\max}\tau_0)\times\int_{E_{\min}}^{E_{\max}}dE\,\mathrm{sech}^2\frac{E}{2kT}\ . \tag{5}$$

Here, we have normalized the distribution $P(E,R)$ by introducing the total number n_0 of TLS's and a maximum and a minimum rate, $R_{\max}$ and $R_{\min}$, respectively. ΔE is the energy range of the TLS, $E_{\max}-E_{\min}$. For an activated process characterized by rates $R=R_0\exp(-V/kT)$ the corresponding time-dependent spectral diffusion width would be $\sim[\ln(R_0\tau_0)]^{1/2}$.

The temperature dependence of the spectral diffusion width in the logarithmic time regime would be, due to the scaling properties of the energy integral [Eq. (5)], linear for tunneling processes and $\sim T^{3/2}$ for thermally activated processes.[25] Note, however, that this holds only in the case $E_{\min} \ll kT \ll E_{\max}$, so that the boundaries of the above energy integral can be set to zero and infinity.

In this article we are dealing with thermally irreversible spectral diffusion as measured by hole-burning temperature-cycling experiments. Because a cycling experiment also needs time, it is necessary to compare the time-dependent spectral-diffusion effects with the thermally induced spectral-diffusion effects. This is done in Figs. 2(a) and 2(b). As is clearly seen, the hole broadens in a logarithmic fashion with time, as predicted by the spectral-diffusion model. In the time window where the cycling experiments were done, the hole broadens only by 0.08 cm^{-1}. Comparing this with Fig. 2(b), we can be sure that time-dependent effects can be neglected.

Melting and freezing of TLS and thermal irreversibility

In this subsection we show how a freezing (or melting) condition can be introduced into the spectral-diffusion models to account for thermal irreversibility.

Under ideal-glass conditions the TLS ensemble can, at any temperature, be subdivided into the above-mentioned two groups, namely, the TLS's in fast thermal equilibrium and those which are permanently frozen. The fast TLS's contribute to the width in a dynamic and thermally reversible way. Since the frozen TLS's are, at the temperature given, in a definite microstate, they do not contribute to the width. Under ideal-glass conditions, the transition region between these two categories of TLS's is quite sharp. Suppose the temperature is raised. The relaxation rate will strongly increase and, hence, TLS's from the frozen ensemble move into the equilibrium ensemble. Let us consider a specific class of TLS's among those which have crossed the demarcation line during an increase of temperature. This class of TLS's is characterized by well-defined values of E and λ and, hence, by a well-defined relaxation time $T_1(E,\lambda,T)$, where T is the temperature of the system. When the temperature is cycled back, the contribution of this special class of TLS's to the hole width is reversible as long as $T_1(E,\lambda,T)<\tau$, τ being the experimental time needed to drive the system through the cycle. The ensemble freezes when the relaxation time becomes equal to the experimental time. Hence, a freezing temperature $T_f(E,\lambda)$, for the specific class of TLS's considered, can be determined from the condition

$$T_1(E,\lambda,T_f)=\tau \; . \tag{6}$$

After freezing, this special class of TLS's is static in nature and contributes to the irreversible width.

Let us calculate the contribution from this special class of TLS's to the spectral-diffusion width. When the temperature is cycled back, this class will fall out of equilibrium roughly at T_f. Hence, their contribution $d(\Delta\omega_{\text{ir}})$ to the irreversible width is given by the spectral-diffusion width right at the freezing temperature T_f. From Eq. (3) we have

$$d(\Delta\omega_{\text{ir}})=\tfrac{1}{2}C\bar{P}\,\text{sech}^2\frac{E}{2kT_f}dE\,d\lambda \; . \tag{7}$$

Note that here we have assumed that right above T_f the relaxation time is short enough compared to the experimental time scale so that the exponential in Eq. (3) can be neglected.

To calculate the total amount of irreversible spectral diffusion, we integrate Eq. (7) over the whole temperature range of the cycle, i.e., from T_b to T, under the constraint that, at a given temperature T', only those TLS's are taken into account for which the freezing temperature coincides with T':

$$\Delta\omega_{\text{ir}}=\tfrac{1}{2}C\bar{P}\int_{T_b}^{T}dT'\int_{E_{\min}}^{E_{\max}}dE\,\text{sech}^2\frac{E}{2kT'} \times\int_{\lambda_{\min}}^{\lambda_{\max}}d\lambda\,\delta(T'-T_f(E,\lambda)) \; . \tag{8}$$

Equations (8) and (6) are the basic relations for modeling thermally irreversible relaxation effects. We solve the above integral by transforming to new variables, namely, $x=E/2kT'$ and T_f:

$$\Delta\omega_{\text{ir}}=kC\bar{P}\int_{T_b}^{T}dT'T'\int_{0}^{\infty}dx\,\text{sech}^2x\left|\left[\frac{\partial\lambda}{\partial T_f}\right]_x\right|_{T_f=T'} \; . \tag{9}$$

Here, we have assumed that $E_{\min}\ll kT_b$ and $E_{\max}\gg kT$, T being the excursion temperature. As far as $E_{\min}$ is concerned the approximation seems to be on the safe side. As to $E_{\max}$, the situation is less general. Note, that we lose one power in T in case this approximation fails (see the discussion of the polymer data, Fig. 5).

The temperature dependence for tunneling and activated processes

We are now in a situation to introduce the specific relaxation processes into Eq. (9). At low temperatures, we expect tunneling to dominate. At high temperatures, thermally activated processes prevail. With the aid of Eq. (9) we can calculate the temperature dependence generated by the various processes.

The tunneling regime

For phonon-assisted tunneling, the rate, for a direct process, is given by (see, for instance, Ref. 7)

$$T_1^{-1}=e^{-2\lambda}\left[\frac{\hbar\Omega}{k}\right]^2DE\coth\left[\frac{E}{2kT}\right] \; . \tag{10}$$

Ω is a frequency on the order of a zero-point vibration and D is a parameter which describes the coupling of the phonons to the TLS. Note that Eq. (10) holds for a direct process. Using the freezing condition [Eq. (6)] we can calculate $\lambda(T_f)$. Equation (9) then yields

$$\Delta\omega_{\text{ir}}^{(t)}=\tfrac{1}{2}C\bar{P}k(T-T_b)\int_0^{\infty}dx\frac{x\,\text{sech}^2x}{\cosh x\,\sinh x} \; . \tag{11}$$

The superscript (t) stands for "tunneling." We see that structural relaxation due to tunneling processes leads to a linear dependence of the irreversible width on the excursion temperature. The same result is obtained for the two-phonon Raman process[26] (the calculation is straightforward), but the slope is steeper. Note that Eq. (11) does not depend any more on the experimental time scale τ.

The activated regime

For thermally activated barrier crossing the relaxation rate is of the form

$$T_1^{-1}=R_0\exp(-V/kT) \; , \tag{12}$$

R_0 being an attempt frequency on the order of $10^{12}\ \text{s}^{-1}$. From Eq. (1) we have $V=2\hbar^2\lambda^2/md^2$. Again using the freezing condition Eq. (6) together with Eq. (9), we calculate the following irreversible spectral-diffusion width:

$$\Delta\omega_{\text{ir}}^{(\text{th})}=\tfrac{1}{3}C\bar{P}k^{3/2}\left[\frac{md^2}{2\hbar^2}\ln(R_0\tau)\right]^{1/2}(T^{3/2}-T_b^{3/2}) \times\int_0^{\infty}dx\,\text{sech}^2x \; . \tag{13}$$

The superscript (th) stands for "thermally activated." Contrary to tunneling, thermally activated relaxation processes lead to an irreversible width which increases with $T^{3/2}$. Note also that this contribution depends on the experimental time scale via $[\ln(R_0\tau)]^{1/2}$. However, since this dependence is extremely weak, even changes of several orders of magnitude in $R_0\tau$ have no measurable influence on the experimental results.[18]

Model calculations and comparison with experiments

In this subsection we compare model calculations according to Eqs. (11) and (13) with the experimental results. The different types of glasses, namely alcohol glasses, hydrocarbon glasses, and polymers, show rather specific features, and the question is whether these features can be explained within the framework of the model.

As stated above, all alcohol glasses could be fitted to a power law of the form $\sim(T^\alpha - T_b^\alpha)$, with α being close to 3. However, such a power law would never fit the 3-MP and PMMA data, the latter being described instead by a power law $\sim(T^{1/2} - T_b^{1/2})$. Clearly , a superposition of a one-phonon tunneling process (which dominates below 5 K), a two-phonon tunneling process (between 5 and 10 K), and an activated process (for $T > 10$ K) fits the results in the whole temperature range from 500 mK up to 20 K perfectly well, as demonstrated for Tc in alcohol (Fig. 3). Even the simplified fit procedure which was used for the remaining alcohol glasses is not bad at all. In the hydrocarbon glass (3-MP) a perfect fit is possible by a superposition of a one-phonon tunneling and an activated process. Even the sharp transition region is well represented. Though we do not know any reason why the Raman tunneling process is absent in 3-MP, we note that a similar behavior was found from spin-resonance experiments.[27]

How can the sublinear temperature dependence ($T^{1/2}$) of the PMMA glass be understood in terms of the spectral-diffusion model? First, we stress again that the actual temperature dependence is strongly influenced by the boundaries of the distribution functions for E and λ (or V). We mentioned above that one power is lost as the temperature exceeds $E_{\max}/k$. For tunneling processes this would mean that there is no longer any spectral diffusion in this temperature regime. For activated processes it would mean that the hole broadens with $T^{1/2}$. There is an interesting paper by Kolac *et al.* on specific-heat measurements of epoxy resin.[28] These authors could interpret their results by assuming an upper cutoff of $E_{\max}/k$ around 16 K. They also stress that epoxy resin is very similar to PMMA. Second, for a polymer glass it seems likely that, due to the constraints imposed on the molecule by the covalent bonds in the backbone, the tunnel masses are heavier and, hence, tunneling processes seem to be prohibited to a much higher degree. Consequently the activated regime extends to lower temperatures.

Along these lines of reasoning we calculated the fit curve shown in Fig. 5, which follows a $T^{1/2}$ power law for temperatures above $E_{\max}/k = 16$ K. This value was directly taken from the paper by Kolac *et al.*[28] Note that there is only one free fit parameter, namely, the unit of the measured hole width.

Generally speaking, one can say that, in spite of the special features which the irreversible line broadening as a function of temperatures shows for various glasses, the spectral-diffusion model is quite a satisfactory description.

The transition region between tunneling and activated relaxation

As far as the transition region is concerned there is an interesting outcome of the model. The tunneling relaxation is governed by the tunneling parameter λ, whereas thermal activation is governed by the barrier height V. Since λ does not only depend on V but also on the mass m and the tunnel distance d, the crossover temperature depends on the quantity md^2, which can, as a consequence, be determined from the experiment. To this end, we used the above-mentioned simplified fit procedure with a linear temperature dependence in the tunneling regime and a $T^{3/2}$ dependence in the high-temperature regime. The transition temperature T^* is treated as a fit parameter. This procedure worked surprisingly well. For all ethanol-methanol glass samples we found $T^* = 10 \pm 0.4$ K, which is equivalent to $md^2 = 90 \pm 3$, if m is measured in units of the proton mass and d in Å. For 3-methyl pentane glass the corresponding number is 19. Note that the microscopic structure of both glasses is very different. In the EtOH-MeOH glass there is strong hydrogen bonding, whereas the microstructure of 3-MP glass is governed by van der Waals interactions. For the P-X glass, T^* is around 25 K with md^2 on the order of 36.

The absolute magnitude of irreversible line broadening

Besides the temperature dependence of the thermally induced spectral diffusion, an interesting aspect of the data in Figs. 3–7 is also its absolute magnitude. It is extremely small in the polymer as compared to the alcohol glasses. There is also a remarkable reduction upon deuteration for tetracene in EtOH-MeOH, while for quinizarin this effect is only marginal.

There are two quantities which determine the absolute magnitude, namely the density of TLS states $\bar{P}$ and the coupling matrix element C. We believe that in the polymer it is the density of states which is reduced as compared to the soft glasses. The degrees of freedom in the polymer are restricted due to the covalent bonds along the backbone.

As to the isotope effect in the tetracene sample, it is obvious that it cannot be due to a reduction in the tunneling rates, since it also exists in the activated regime and is only marginal in the quinizarin sample. Moreover, the quantity md^2 is a rather large number and, hence, hydrogen tunneling cannot be involved. (We stress that, with respect to proton tunneling, time- and temperature-dependent spectral diffusion effects show a totally different behavior.[4,21,23]) We attribute the special features of isotopic substitution to a change in the coupling matrix element. Tetracene, for example, has no permanent dipole moment. Hence, its coupling to the TLS's is, to a rather high degree, elastic. The elastic properties, however, are changed by deuteration. Quinizarin, on the other hand, has a strong dipole moment, and, hence, couples mainly via electric forces to the TLS's, which are not influenced by deuteration.

SUMMARY AND CONCLUSION

After having shown that the spectral-diffusion model based on TLS statistics accounts perfectly for the whole variety of special features observed for thermally irreversible line broadening for a series of quite different glasses, we conclude this paper with a few comments on the temperature range accessible to the experiment and on the approximations involved.

As to the temperature range of the experiment, we see that it is quite different for the various samples. For tetracene in alcohol glass it is less than 20 K: it is a little bit larger for dimethyl-*s*-tetrazine in alcohol glass, but it extends over 70 K for 3-MP and PMMA. Whereas the lowest temperature (which is, in our case, always the burn temperature) is determined by the capability of the special setup used, the upper temperature limit is determined by the properties of the sample investigated. There are two independent processes which limit the experimentally accessible range: the recovery of the hole and the spectral-diffusion broadening. In EtOH-MeOH both processes are efficient; hence, the temperature range is small. It is interesting to note that in this glass the photoreaction is, in almost every case we have investigated so far, strongly influenced by photophysical hole burning. This holds even for probe molecules like DMST, which is known to decompose easily under photoexcitation. Even in this case the hole recovers;[29] however, it recovers much more slowly. Consequently, the upper temperature limit is higher than for the tetracene sample. The same arguments hold for PC*. PC* is known to undergo a phototautomeric change of the inner protons, a pure intramolecular photoreaction. As for DMST, one would expect that the hole does not recover. However, as seen in Fig. 6(d), it does, quite in contrast to the 3-MP and the P-X glasses (Figs. 4 and 7). Hence, we have to conclude that in EtOH-MeOH the photoreaction is governed to a large extent by the interaction between probe and solvent (photophysical reaction), whereas in the 3-MP and P-X glasses, it seems that the reaction is due to the well-known phototautomerism of the inner protons, mentioned above.

As to the approximations used in modeling thermally induced spectral diffusion, there are five points we want to stress, which are beyond the scope of the original model.

First, the calculations were performed assuming ideal-glass conditions.[24] It is assumed that most of the pertinent relaxation processes are either very fast or very slow compared to the experimental time scale. This approximation is a good one in case the dispersion of relaxation rates is large. Concerning the huge dispersion of structural relaxation rates in glasses,[4,21,22,23] it seems to be on the safe side.

Second, a uniform distribution of λ values was assumed, as in the original TLS model, and was attributed solely to a distribution of barrier heights. Though other distribution functions for λ were considered in detail,[30] the TLS model works, on a qualitative level, quite well. In our case there was no need to go beyond this model. The assumption that the distribution of λ originates solely from a distribution of V seems to be justified to a large extent. Glasses are characterized by short-range order, hence, there is no possibility for a large variation in d. We stress that for a number of systems the above assumption has been verified experimentally.[18]

Third, we considered activated barrier crossing, which is beyond the tunneling model in its original form. Note, however, that the temperature range of our experiment is huge as compared to the low-temperature specific-heat experiments for which the model was first developed.[5,31]

Fourth, we did not take into account tunneling from thermally occupied levels below the barrier, which would smooth the transition region. Hence, the modeling of the region is rather crude, but the asymptotic behavior seems to be correct.

In conclusion, temperature-cycling hole-burning experiments are most straightforward in measuring spectral diffusion. By taking into account the freezing condition in a proper way, the results can be modeled quantitatively. In some glasses, like EtOH-MeOH, the spectral diffusion is large, and, hence, plays for certain an important role in the so-called quasihomogenous linewidth as obtained from a normal hole-burning experiment.

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