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Tunneling dynamics of doped organic low-temperature glasses as probed by a photophysical hole-burning system

W. Köhler, J. Meiler, and J. Friedrich
Physikalisches Institut und Bayreuther Institut für Makromolekülforschung, Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany

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We studied the photophysical hole-burning system tetracene in alcohol glass. The relaxation dynamics of the hole obeys logarithmic time laws. The analysis of the logarithmic laws yields information on the dispersion of the relaxation processes involved. Experiments with deuterated alcohol glass show that the spectral diffusion is governed by proton-tunneling processes. From the observation of two isoabsorptive points and the fact that the integrated absorption of the product is less than that of the hole, it is concluded that the photoreaction is most probably due to a light-induced rotation of the probe molecule in the glass. The barrier heights of the product state are sampled between 3 and 25 K and are shown to follow closely the tunneling model. We finally report on thermally induced spectral diffusion processes which are shown to follow a nonlinear power law in temperature.

I. INTRODUCTION

Low-temperature glasses have been a growing field of scientific research for more than a decade.[1,2] Most of the experimental work has been done on inorganic glasses, and most of the information came from specific-heat, microwave, and ultrasound, as well as thermal-conductivity experiments.[2,3] It was not until recently that optical methods, like spectral hole burning and fluorescence line narrowing, were increasingly used to get insight into the dynamics of low-temperature glasses.[4–6] In fact, most of the research on organic glasses has been done with the hole-burning method. Optical hole burning offers the possibility of measuring system parameters, for instance, extremely long relaxation times;[7–9] for a review see Ref. 10. In most cases, hole burning can be applied only to doped glasses. That is, the optical properties of a dye molecule dissolved at low concentration in the glass are used to probe the dynamics of the system. On long time scales (long compared to the T_1 time of the probe molecule) the dynamics of the hole is determined by the dynamics of the disorder modes of the glass, the so-called two level systems (TLS).[11] Doping of the glass may also introduce a new type of disorder modes, which are extrinsic in nature. We denote these extrinsic modes by TLS_p (p: photoinduced).[7,8,10]

In this paper we present experiments on a photophysical hole-burning system, namely tetracene in ethanol-methanol glass. Photophysical hole burning was discovered by Kharlamov *et al.*[12] and is characteristic for all those systems where the probe molecule itself is not affected by the burning process. Hayes and Small[13] were the first who linked the hole-burning process in these systems to a coupling between the probe molecule and the disorder modes of the glass. A fast tunneling process in the electronically excited state of the coupled system was assumed to lead to hole formation. Yet, the detailed nature of the reaction was not explained.

By investigating the system tetracene in alcohol glass we want to learn something about the interplay between the probe molecule and the glassy host system. The following questions are addressed in more detail.

(a) What is the nature of the intrinsic TLS modes of the alcohol glass and how does their dynamics show up in the dynamics of the hole?

(b) What are the time scales of relaxation of the spectral hole?

(c) What is the nature of the photoproduct state?

(d) What is the temperature dependence of the thermally induced spectral diffusion processes?

II. EXPERIMENTAL

The concentration of the samples used was 1.5×10^{-4} mol/l. The holes investigated on long time scales (Fig. 1) were burnt at 475.1 nm and, for the deuterated sample, at 474.6 nm, using a nitrogen-pumped dye laser. For the protonated sample, which was much easier to burn, the energy density per pulse was 40 μJ/cm^2 at a repetition rate of 40 counts per sec and a burning time of 5 min. For the deuterated sample the energy density per pulse was 80 μJ/cm^2 and the burning time was 20 min at the same repetition rate. Both holes were burnt to exactly the same relative depth (6%). The temperature was kept at 4.2 ± 0.01 K over the whole experimental time period.

To investigate the spectral distribution of the photoproduct [Fig. 2(a)] hole burning was performed with the 4764.68-Å line of an Ar$^+$ (15 mW/cm^2). The total burning time was 60 min. During this time the band was scanned several times [Fig. 2(b)]. In order to create an appreciable amount of photoproduct the temperature chosen for this experiment was 10 K.

All holes were detected in transmission using a high-resolution spectrometer (<0.15 Å). Areas and widths were determined by fitting the data on line to a Lorentzian.

The temperature-cycling experiments were performed in the following way. First, the hole was burnt at the lowest temperature accessible in this experiment (T_b).

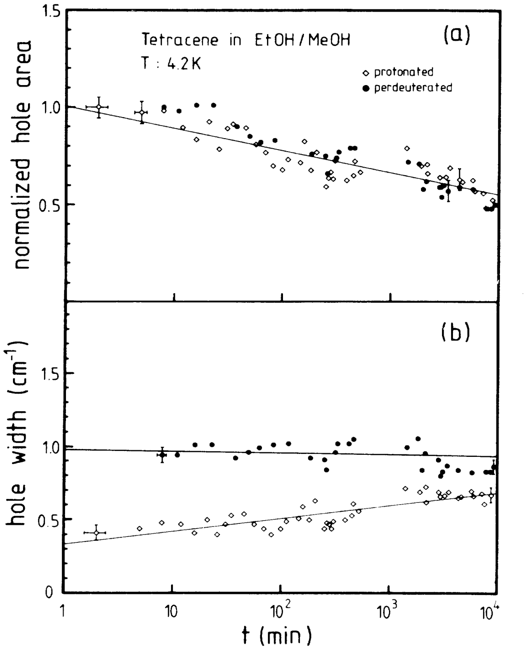

FIG. 1. (a) Hole area and (b) hole width as a function of time. System: tetracene in protonated and perdeuterated alcohol glass.

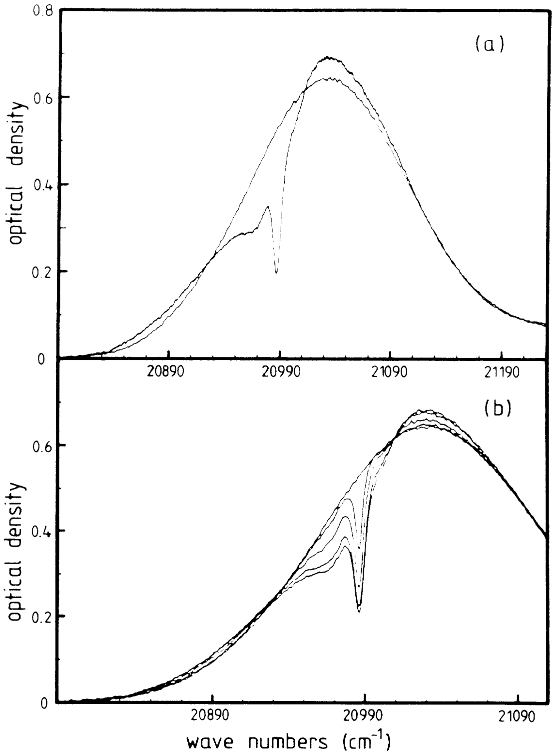

FIG. 2. (a) The spectral distribution of the "photoproduct" and (b) occurence of two isoabsorptive points. Note that the area of the hole is significantly larger than that of the product (a).

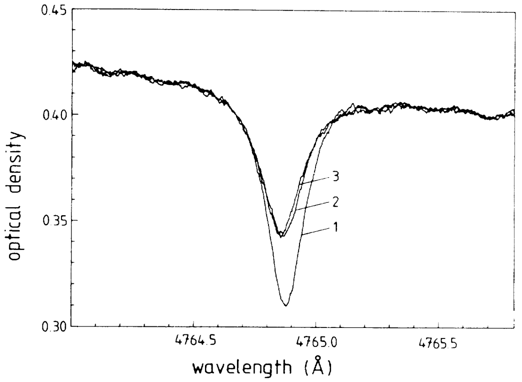

FIG. 3. Reduction of the hole area by cycling the system between the burn temperature $T_b = 3$ K and $T = 8$ K (curves 1 and 2). If the same cycle is repeated twice no further reduction occurs (curve 3).

Then, the temperature was raised to some value T and cycled back to T_b, where the area and the width were measured again. The area changed significantly only with the first cycle between T_b and T. Additional cycles had no influence. Clearly, such an experiment samples the distribution of barrier heights of the photoproduct state.

III. RESULTS

The main results of this study can be summarized as follows.

(1) At 4.2 K, the hole is not stable. It recovers on a logarithmic time scale. The recovery dynamics are independent of whether the glass is deuterated or not [Fig. 1(a)].

(2) The width of the hole increases on a logarithmic time scale. Contrary to the recovery dynamics, the time evolution of the width is strongly influenced by glass deuteration: in a perdeuterated glass, there is no detectable change in the linewidth within a period of one week [Fig. 1(b)].

(3) The photoproduct is distributed over an appreciable range of the inhomogeneous band [Fig. 2(a)]. There are

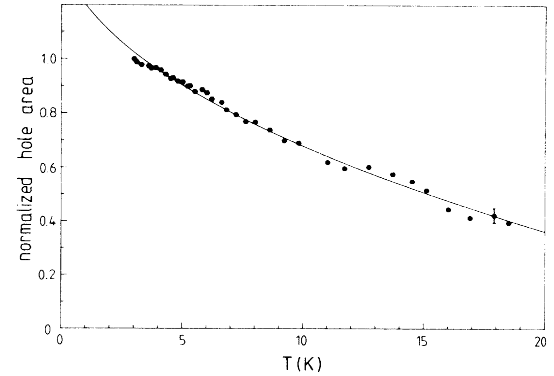

FIG. 4. Hole area as a function of cycling temperature. The fit curve is calculated using a distribution function of barrier heights $\tilde{P}(V_0) \sim (V_0)^{-1/2}$ [see Eq. (7)].

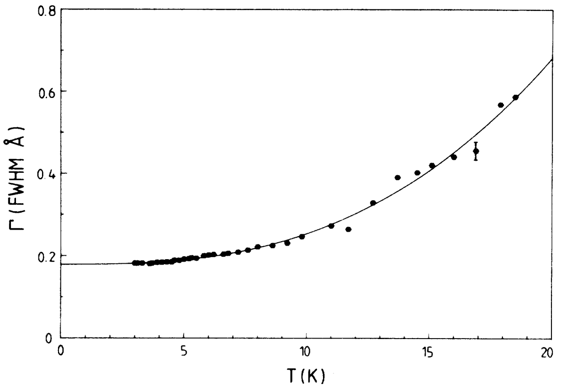

FIG. 5. Hole width (measured at the burning temperature T_b) as a function of cycling temperature, T.

two isoabsorptive points [Fig. 2(b)]. It is obvious [Fig. 2(a)] that the hole-burning reaction leads to a loss of integrated oscillator strength: The "area" of the photoproduct is less than that of the hole.

(4) Figure 3 shows that the area of a hole changes in cycling the temperature between the burning temperature T_b and some temperature T. Repeated cycling between T_b and T has, however, no further influence on the area.

(5) The area (always measured at the burning temperature T_b) is well described by a function $\sim[1-(\alpha kT/V_{0\max})^{1/2}]$, with T being the cycling temperature, $V_{0\max}$ the maximum barrier height, and α a constant (Fig. 4).

(6) The linewidth (measured at T_b) increases as a function of the cycling temperature T in a nonlinear fashion (Fig. 5).

IV. DISCUSSION

A. Logarithmic relaxation laws and nature of the tunneling systems

1. Hole recovery

From Fig. 1 it is obvious that the hole recovery, as measured by the time-dependent hole area $A(t)$, as well as the time evolution of the linewidth are well described by logarithmic laws. Logarithmic time patterns very generally arise in case the relaxation rates R depend in an exponential fashion on some parameter Λ, which is subject to a rather uniform distribution. (A uniform distribution of the tunneling parameter, for instance, is the basic ingredient of the TLS model.[3,11] Under these conditions one gets from $R\sim e^{-2\Lambda}$ a distribution of rates according to

$$P(R)=P_0/R \ , \tag{1}$$

with P_0 being a constant. Normalization of this distribution can be achieved by assuming cutoff values as given by a maximum and a minimum rate constant, $R_{\max}$ and $R_{\min}$, respectively. If the rate dispersion of the system is large, then, at a certain time t, one observes only a very small fraction of the system relaxing with rate constants roughly given by $R=t^{-1}$.

As to the hole area as a function of time it can be calculated by calculating the number of centers being at time t in the photoproduct state $|P\rangle$ (Fig. 6). At 4.2 K, the product state relaxes via tunneling, hence the rates are distributed according to Eq. (1). Integration of Eq. (1) from $R=R_{\min}$ to $R=1/t$ yields the number of centers being in $|P\rangle$ at time t. Carrying out this integration one arrives at a logarithmic time pattern

$$\frac{A(t)}{A_1}=1-s\ln R_1 t \ , \tag{2}$$

with A_1 being the hole area at time t_1. Equation (2) holds for $R_{\min}^{-1} \ll t \ll R_{\max}^{-1}$.[7,10]

The slope factor s is the quantity which is measured. Within the frame of the model it is given by

$$s=\left[\ln\frac{R_1}{R_{\min}}\right]^{-1} . \tag{3}$$

s is a measure of the rate dispersion of the process considered. For tetracene in protonated and perdeuterated alcohol glass we find from the measured slope a dispersion $R_1/R_{\min}$ on the order of 10^{10}. R_1 is an experimental parameter and corresponds to the fastest rate which can be determined experimentally. In our case R_1^{-1} is on the order of minutes. $R_{\min}$, of course, is a system parameter.

We stress that, unlike in most other decay patterns with long-time tails,[14] s is well defined in terms of microscopic rates. Knowing the details of the microscopic relaxation process, it can be calculated from first principles. As to the physical origin of the large dispersion of rates, we recall that R describes a tunneling relaxation from a photoproduct state $|P\rangle$, which is generated via the hole-burning process, to the educt state $|E\rangle$ (Fig. 6). $|P\rangle$ and $|E\rangle$ form a special kind of tunneling system, which we denote by $\mathrm{TLS_p}$, and which is intimately related to the dopant molecule. Then, Λ is the corresponding tunneling parameter

$$\Lambda=(mV_0/2\hbar^2)^{1/2}x \ , \tag{4}$$

m is the mass of the tunneling species and x the distance

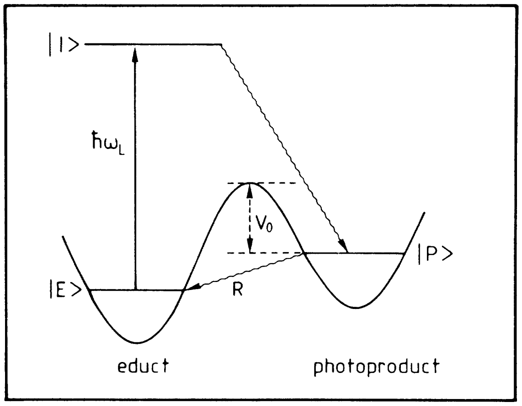

FIG. 6. Schematic representation of the $\mathrm{TLS_p}$ system consisting of the educt state, $|E\rangle$, and the product state, $|P\rangle$, decoupled by the barrier V_0.

(Fig. 6). Characteristic for a photophysical hole-burning process obviously is the fact that the barrier height V_0, which stabilizes $|P\rangle$ against $|E\rangle$, is subject to a large variation because of the amorphous nature of the glass matrix. This variation seems to be the main cause for the huge dispersion of rates, as deduced from the measured slope.

The absence of any significant deuteration effect in the hole-recovery dynamics [Fig. 1(a)] leads to the conclusion that the species involved in the tunneling processes considered is rather heavy as compared to a proton. As to the nature of the tunneling species and, hence, the nature of the photoproduct state, we give a detailed interpretation in Sec. IV B.

2. Line broadening

The relaxation processes which lead to line broadening are obviously very different from those which are responsible for hole filling. We observe a significant isotope effect in the slope factor, from which we conclude that the relaxation processes involved are proton-tunneling processes. To distinguish these processes from the hole-recovery processes we denote their parameters with lower-case letters (r,λ, etc.).

As outlined in several recent papers[8,9,10] line-broadening processes on long-time scales (the so-called spectral diffusion) can be calculated in a similar way as the hole recovery: We assume that a probe molecule is interacting with some kind of TLS ensemble characterized by a distribution of relaxation rates between the bounds $r_{\max}$ and $r_{\min}$. For $t > r_{\max}^{-1}$ part of the TLS ensemble equilibrates, giving rise to new configurations. These configurations lead to a fluctuation of the absorption frequency of the probe molecule via strain and/or electric-field-mediated coupling.[15–17] It was shown[15] that the contribution to the width due to these processes is proportional to the number density n of TLS having equilibrated within the time interval t. If these equilibration processes occur on time scales larger than the T_1 lifetime of the probe molecule, the line broadening is inhomogeneous in nature; if they occur on time scales larger than the experimental time scale, the line broadening becomes time dependent. In case tunneling processes, characterized by a tunneling parameter λ, are involved, one gets the same rate distribution function as discussed above [Eq. (1)]. We note that the rate distribution for the standard tunneling model differs from Eq. (1) by having a singularity at $r = r_{\max}$.[18] This singularity would lead to a deviation from a logarithmic time pattern for times close to $r_{\max}^{-1}$, which is not observed. The singularity arises from taking into account symmetric TLS. For symmetric TLS $\Delta_0 = E$ holds, with $\Delta_0 = \hbar\omega_0 e^{-\lambda}$ being the tunneling matrix element and $\hbar\omega_0$ being an energy on the order of the zero-point energy.[11] Hence, at a given energy, symmetric TLS are characterized by the maximum rate constant. Using $r/r_{\max} = \Delta_0^2/E^2$ we can rewrite the distribution of the tunneling model[18] in the form

$$P(E,r) \sim E/r(E^2-\Delta_0^2)^{1/2} .$$

For an asymmetric TLS, Δ_0 is always smaller than E, and hence, in this case, the distribution has no singularity at $r = r_{\max}$.

From Fig. 1 it is obvious that the fastest processes we measure occur on time scales of minutes. The influence of such slow processes on the eigenvalues of a TLS is extremely small. For a rough estimation we use the simpel relation

$$r = r_0 e^{-2\lambda}$$

where r_0 is on the order of ω_0.[11] Then, Δ_0 is given by

$$\Delta_0 = (\hbar^2 r r_0)^{1/2} .$$

Inserting for $\hbar r_0$ a typical energy of 1000 cm^{-1} (note, that we have proton tunneling) we estimate for Δ_0 a value on the order of 10^{-5} cm^{-1}. Hence, Δ_0 can be neglected in the above distribution, as long as E is much larger than this number. Since the total width of the distribution is orders of magnitude larger than 10^{-5} cm^{-1}, we think that $P(E,r) \sim r^{-1}$ is, for the problem considered, an adequate distribution function.

To calculate the number density $n(t)$ we integrate this distribution from $r = t^{-1}$ to $r_{\max}$. The result is a logarithmic time pattern for the hole width:

$$\gamma = \gamma_0 + B \left[\ln \frac{r_{\max}}{r_{\min}} \right]^{-1} \ln r_{\max} t . \tag{5}$$

Like Eq. (2), Eq. (5) holds only in the time window $r_{\max}^{-1} \ll t \ll r_{\min}^{-1}$. γ_0 is a time-independent contribution. It could, for example, be the homogeneous width. The simple superposition of these two parts is possible as long as the corresponding line-broadening mechanisms lead to a Lorentzian shape.[15] A Lorentzian line shape is indeed measured at all times. In most cases the hole whose time dependence is measured, is subject to some amount of artificial broadening (e.g., due to saturation and/or sample heating, etc,), and, hence, γ_0 is not the homogeneous width. This seems to be the case for the deuterated glass [Fig. 1(b)]. Because of the low hole-burning efficiency a higher power and a much longer burning time was necessary. We believe that, due to the large amount of irradiated energy, the hole shows saturation broadening. As to the low hole-burning efficiency of the deuterated glass, there is, as of yet, no clear understanding of this fact.

Equation (5) shows that the slope factor is again determined by the dispersion of the rates, i.e., by $r_{\max}/r_{\min}$. However, the slope depends on additional parameters which are summarized in the constant, B. Hence, a quantitative evaluation of the slope factor in terms of $r_{\max}$ or $r_{\min}$ is not possible, unless one has an independent information on γ_0.

For the protonated glass we measured the homogeneous linewidth by determining the width of the hole as a function of its area and extrapolating to area zero.[19] We found for $T = 4.2$ K a homogeneous width of 0.4±0.05 cm^{-1}. From Fig. 1(b) we see that the very first data point, taken at a time τ_0 after burning, is already very close to this value. Hence, from Eq. (5), with $\gamma(\tau_0) = \gamma_h = \gamma_0$, we find $r_{\max} = \tau_0^{-1}$, with τ_0 being on the order of minutes.

Obviously, the relaxation processes leading to spectral diffusion broadening of the hole seem to be rather slow for the systems considered. At the moment, we do not know how to reconcile this result with the rather fast glass dynamics as measured by ultrasound and microwave experiments for some inorganic systems[20,21] We stress, however, that we received results in the same order of magnitude for several systems[8,22] using other methods to determine γ_0.

As to the system considered here the critical question is, of course, whether the homogeneous width can be determined from hole-burning experiments at all. For some organic glass systems, at least, it was shown that hole-burning and photon-echo experiments give basically the same results.[23,24] This means, that, considering the slow experimental time scale of hole-burning experiment, the spectral diffusion processes cannot occur on time scales much faster than seconds.[25]

3. Isotope effect

As to the time dependence of the parameters of the hole we expect that Eq. (5) is of a rather uniform character, because the system parameters, as given by the ratio $r_{\max}/r_{\min}$, show up in a logarithmic fashion, and, hence, only minor changes in the slope factor are expected in case this ratio is changed by some manipulation. However, this argument breaks down in case $r_{\max}/r_{\min}$ is altered in an exponential fashion. Obviously, this is the case for isotopic substitution [Fig. 1(b)]. Hence, we have to conclude that the TLS dynamics, which lead to line broadening is based on hydrogen tunneling. The most probable candidate is the hydrogen atom of the hydroxy group which forms hydrogen bonds to neighboring molecules. Also, rotational tunneling of the methyl groups is a possibility. It is worthwhile to be stressed that the isotope effect shows up only because its influence on the extremely slow processes, characterized by $r_{\min}$, is orders of magnitude larger than on $r_{\max}$.[8,9]

To summarize this paragraph we conclude that in doped glasses there are at least two rather different TLS systems, both of which originate from rather localized motions. One is extrinsic and is related to the probe molecule. It seems to be responsible for the phototransformation and for the hole recovery. The other is intrinsic. It is responsible for spectral diffusion and is closely related to hydrogen tunneling. The dispersion of rates for the two TLS, $R_{\max}/R_{\min}$ and $r_{\max}/r_{\min}$, respectively, may be quite different.

B. The photoproduct state

Many papers on photophysical hole burning have been published (for reviews see Refs. 4, 5, and 6) but, up to now, no clear picture of the nature of the "photoproduct" emerged. For tetracene in alcohol glass we try to give an answer to this problem. Our arguments are based on a few simple experiments.

First of all we stress that, according to the discussion above, the photoproduct state does not seem to be related to the intrinsic TLS modes of the glass. Figure 2(a) shows the interesting fact that there is no conservation of area within the inhomogeneous band, when burning occurs: The area of the hole is significantly larger than the corresponding area of the photoproduct. Hence, it seems that oscillator strength is not conserved. We checked the possibility whether several, maybe very different, products may be formed by the burning process. It seems that this is not the case. There are two isoabsorptive points [Fig. 2(b)], as were found recently for a different photophysical hole-burning system.[26] This tells us that the photoreactive system is closed and, hence, the whole product has to be found in the band considered.

The simplest way to reconcile the various experimental facts is to assume that the hole-burning process is a light-induced rotation of the probe molecule within the host lattice. It is possible that this process includes a concommittant distortion of the amorphous lattice in the immediate neighborhood of the impurity molecule.

Suppose hole burning is done with polarized light, as is the case in our experiment, then, the photoactivated ensemble of probe molecules is anisotropic. If we would assume, for example, that the burning process leads to a more isotropic distribution, we could lose $\frac{2}{3}$ of ingerated hole area. In our experiment approximately 50% gets lost.

The idea of a light-induced rotation of the guest molecule fits to the observed lack of any deuteration effect in the hole-recovery dynamics [Fig. 1(a)]: According to the discussion above the mechanism of the back reaction from the product to the educt state is most probably a rotational tunneling. Since the masses involved in this process are heavy compared to hydrogen, no isotope effect is observed. Moreover, we conclude that the barrier heights involved have to be low in order to observe any relaxation on measurable time scales. The distribution of barrier heights is discussed in the following section.

C. Distribution of barrier heights

If we cycle the hole once between the burn temperature T_b and some higher temperature T we find that the hole area decreases. If we repeat this experiment a second time no further change occurs. We interprete this result as follows: The barrier heights V_0 which stabilize the product against the educt are distributed over some range because of the random interaction between probe molecule and glass matrix. If the temperature is raised from T_b to T all those centers having barrier heights between $\alpha k T_b$ and $\alpha k T$ return to the ground state by an activated barrier crossing and fill the hole. (α is a scaling factor which is estimated below.) According to these ideas the hole area as a function of cycling temperature T is a measure for the distribution of barrier heights between product and educt state.

We stated above that a rather uniform distribution of the tunneling parameter Λ leads to logarithmic features in the recovery dynamics which were experimentally verified. Based on such a distribution of Λ we can calculate the distribution of barrier heights. Keeping, for the moment, the tunneling distance x fixed, we have from Eq. (4)

$$\Lambda \sim (V_0)^{1/2} \tag{6}$$

and hence

$$\tilde{P}(V_0) \sim (V_0)^{-1/2} . \tag{7}$$

Knowing the distribution function of barrier heights, the area of the hole after cycling the temperature between T_b and T can be calculated by integrating the distribution between $V_0 = \alpha k T_b$ and $V_0 = \alpha k T$. One gets

$$A(T)/A_0 = \frac{1-(\alpha k T / V_{0\,\mathrm{max}})^{1/2}}{1-(\alpha k T_b / V_{0\,\mathrm{max}})^{1/2}} . \tag{8}$$

We have normalized the distribution assuming a maximum and a minimum barrier height $V_{0\,\mathrm{max}}$ and $V_{0\,\mathrm{min}}$, respectively. A_0 is the hole area at the burning temperature T_b. In deriving Eq. (8) we have further assumed that $V_{0\,\mathrm{max}} \gg V_{0\,\mathrm{min}}$ and that there exists no correlation between V_0 and x. In this case, Eq. (7) holds also in case x is distributed. Figure 4 shows a fit of Eq. (8) to the relative hole area A/A_0. The fit is quite good. We draw the following conclusions.

(1) Obviously, the extrinsic two-level systems ($\mathrm{TLS_P}$) system formed by the product and educt state are well described by the basic features of the tunneling model.

(2) For the first time a distribution of barrier heights of low-temperature tunneling states is determined experimentally over an appreciable range. The results show that the theoretical distribution as derived from the tunneling model fits the experimental results quite well.

To estimate the parameter α, we note that during the experimantal time scale $t(\approx 100\ \mathrm{s})$ all those product states may relax which are characterized by rates $R > 1/t$. Since we consider a thermally activated barrier crossing we estimate the maximum barrier height which can be crossed at a temperature T of being on the order of $V_0 = kT \ln \nu_0 t$. ν_0 is the attempt frequency, which may be on the order of $10^{11}\ \mathrm{s}^{-1}$. Then, the factor α is given by $\ln \nu_0 t$, which is on the order of 30. The measured curve extrapolates to $V_{0\mathrm{max}}/\alpha = 25\ \mathrm{cm}^{-1}$, from which we estimate $V_{0\mathrm{max}}$ to be on the order of $800\ \mathrm{cm}^{-1}$. (Note that in an earlier publication[27] the calculation was carried out with $\alpha = 1$.)

D. Thermally induced spectral diffusion

As shown by Fig. 5, the annealing of a photophysical hole is accompanied by an irreversible line broadening. We call this type of broadening thermally induced spectral diffusion and interpret it in the following way: We consider an ensemble of probe molecules which absorb at the same frequency and which interact with a frozen-in ensemble of TLS states. As the temperature is raised from T_b to T, part of the TLS undergoes a thermally induced barrier crossing and gives rise to new configurations of interacting TLS, which get frozen in as the temperature is cycled back to T_b. The new configurations lead to a spread of the sharp resonance frequency of the ensemble of probe molecules considered, in a similar way as discussed in Sec. IV A for the spectral diffusion due to spontaneous TLS relaxation. This experiment very clearly demonstrates the nonequilibrium nature of the glass: The properties of the hole are "path dependent." The cycling process leads to a different state of the glass. At the moment we do not offer a quantitative explanation of this phenomenon. However, we think it is worthwhile to stress that the observed temperature dependence of this irreversible line broadening is much stronger than linear.

V. SUMMARY

We investigated the photophysical hole-burning system tetracene in alcohol glass (EtOH/MeOH 3:1). At constant temperature (4.3 K) the hole relaxes on logarithmic time scales. Different processes are responsible for the hole recovery and for the line broadening (spectral diffusion).

The hole recovery originates from the relaxation of extrinsic TLS (which are responsible for the hole-burning process) while the spectral diffusion originates from intrinsic TLS. The intrinsic TLS are intimately related to hydrogen tunneling. The features of the phototransformed state and, hence, the features of the extrinsic TLS can be well described by a light-induced rotation of the probe molecule within the amorphous lattice. This accounts for the lack of any deuteration effect in the hole recovery for the observed loss of oscillator strength, and for the occurence of two isoabsorptive points.

Temperature cycling experiments enabled a probing of the distribution of barrier heights which was shown to follow a $V_0^{-1/2}$ distribution. Temperature cycling leads also to thermally induced spectral diffusion which shows up as an irreversible temperature-dependent line broadening. Our experiments show that for the system considered this broadening increases much stronger with temperature than linear broadening.

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