

Spectral diffusion of a photochemical proton transfer system in an amorphous organic host: Quinizarin in alcohol glass

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Experimental data describing the time evolution of photochemical holes in organic glasses are reported. The photochemical system is 1,4-dihydroxyanthraquinone (quinizarin) in ethanol/methanol glasses; its photochemistry is based on proton or deuteron transfer processes. The experiments show a logarithmic increase of the hole widths in a time domain between minutes and about 10^4 min. The experimental results yield a pronounced deuteration effect and little variation with temperature between 1.35 and 4.2 K. The data are interpreted in a semiquantitative way using current theories of spectral diffusion in amorphous solids. The fastest measured photochemical rates are on the order of seconds, leaving a "time independent" linewidth of about 0.4 cm^{-1} at 1.35 K.

I. INTRODUCTION

Glasses are, by definition, nonequilibrium systems and, hence, the determination of their macroscopic physical properties can pose serious experimental problems. This is especially true for parameters, which depend on slow relaxation processes and, whose experimental analysis can only be performed on a long time scale. In this case the pertinent experimental parameters can depend on the time scale of the experiment. A typical example is the time dependence of the specific heat, which increases, as has been shown experimentally, on a logarithmic time scale.¹⁻⁴

For the microscopic description of the glassy state, one usually assumes, that the intermolecular potentials are not as well defined as in the case of single crystals, but can be described by potentials with random parameters. A consequence of the random nature of glassy systems is the fact, that at "zero temperature" the glass is not in an absolute minimum of its free energy; it is instead in a "local minimum," allowing relaxation processes through tunneling even at the absolute zero.

A very successful theoretical approach for understanding the experimental parameters of the glassy state was its description with the aid of double well potentials.¹ These potentials are characterized by a distribution of the pertinent parameters, namely the energy asymmetry Δ and the tunneling parameter λ . This description is mostly referred to as the description with "two level systems" (TLS). The available information stemming from specific heat experiments justifies the assumption of a "flat" distribution of both parameters Δ and λ ,¹

$$P(E)dE = P'(\Delta, \lambda) d\Delta d\lambda = \bar{P} d\Delta d\lambda \quad (1)$$

with \bar{P} being a constant.

It had been recognized several years ago, that certain optical properties of glasses may be influenced by the dynamics of the TLS degrees of freedom⁵ (for a review, see Refs. 6 and 7). This was based on various experimental observations, the most important being, that the optical homogeneous linewidths of impurity molecules in glasses, as measured by hole burning or fluorescence line narrowing (FLN), were very large compared to the corresponding linewidths in

single crystals. They also showed a different temperature dependence, where the linewidth varies comparatively little with temperature, showing power exponents between one and two in contrast to exponential or T^7 dependencies, which are known from crystalline materials. The experimental work was followed by various theoretical models,^{5,8-13} which are mostly based on the TLS model of the glassy state.

In this article we want to focus on optically detected relaxation processes in glasses, which have been investigated with the method of photochemical hole burning (PHB). This method is, in contrary to FLN and coherent transient techniques, well suited for measuring slow relaxation processes, since the optical line shape of holes can be observed over long time periods. The photochemical system is 1,4-dihydroxyanthraquinone (DAQ) in ethanol/methanol (3:1; v/v) glasses. Its low temperature photochemistry, which is based on proton transfer, has been described elsewhere.¹⁴⁻¹⁶

The main features of the photochemical process are given in Fig. 1, showing a conversion of an intramolecular hydrogen bond to an intermolecular bond. Figure 1 also gives the pertinent reaction scheme. The initial state is labeled $|R\rangle$; it is photochemically converted to the product state $|P\rangle$ via the intermediate state $|I\rangle$. The dark reaction from $|P\rangle$ to $|R\rangle$ has been found to be rather small.¹⁷ Its time dependence has been investigated in detail. A quantitative data evaluation showed, that a model based on photochemically induced two level systems ($|R\rangle$ and $|P\rangle$) with a distribution function as given in Eq. (1) was adequate for the data analysis.¹⁷

This paper focuses on the time dependence of the linewidth of photochemical holes in the PHB system of DAQ in alcohol glasses. With the aid of the measured isotope effect based on sample deuteration, it will be possible to link the observed spectral diffusion to tunneling processes which involve the photochemical proton transfer system. The corresponding tunneling levels will be referred to as TLS_p ; they should be distinguished from the "normal" TLS which have been involved to account for the observed thermodynamic anomalies. We argue that the introduction of the TLS_p is justified by the experimental findings yielding typical relaxation times for the fastest processes, which are

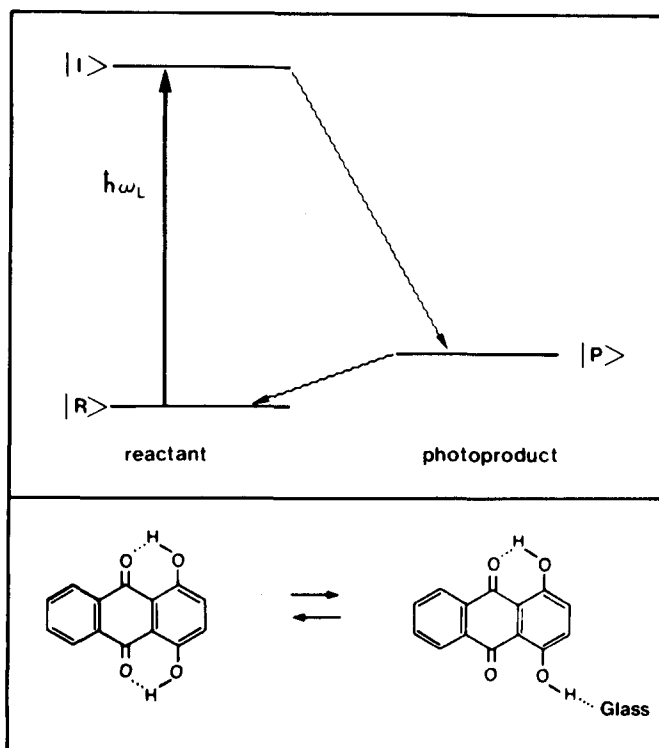


FIG. 1. Upper part: Three level scheme describing the proton transfer reaction of 1,4-dihydroxyanthraquinone (quinizarin) in alcohol glasses. $|R\rangle$ is the ground state of the reactant, $|P\rangle$ is the ground state of the photoproduct, and $|I\rangle$ is a photoreactive intermediate. Lower part: Schematic scheme for the proton transfer reaction.

orders of magnitudes slower (minutes) than the corresponding processes of the "normal TLS".³⁰ The two states of the TLS_p correspond to the two different photochemical ground states which are depicted in Fig. 1. From previous experiments¹⁸ one can conclude that they are well separated in energy as compared to kT .

II. LINE BROADENING OF PERSISTENT OPTICAL HOLES IN GLASSES

The optical linewidth of an "impurity center" in an amorphous host can be caused by the following processes (for a review, see Ref. 7). (i) Elastic scattering of phonons or other lattice excitations of the glass (such as fractons¹⁹) by the impurity. (ii) Spectral diffusion processes with a wide range of rate constants.

In order to separate the different line broadening mechanisms, we make the following definition. We define line broadening processes which occur on a time scale of

$$t \leq T_1 \quad (2)$$

as dynamic processes. Based on the same reasoning, we define the slow line broadening mechanisms with

$$t > T_1 \quad (3)$$

as adiabatic.²⁰

T_1 is defined as the lifetime of the excited electronic state.

The above definition of dynamic and adiabatic linewidths make quite obvious, that "fast" optical experiments, such as FLN or coherent transient experiments, may yield results which are quite different from those as mea-

sured by hole burning experiments. It is obvious, that both slow and fast processes contribute to the hole burning experiments and hence, we have the following relation:

$$\gamma_{PHB} \geq \gamma_h, \quad (4)$$

where γ_h is the "homogeneous" linewidth which is only due to dynamic line broadening processes. γ_{PHB} is the optical linewidth in the adiabatic limit. It is assumed, that the above linewidth parameters are measured under appropriate experimental conditions, in which trivial line broadening mechanisms, such as power broadening or photochemical saturation broadening are ineffective.⁷

This paper deals with specific aspects of spectral diffusion processes. These processes can be due to different microscopic mechanisms. For the investigated photochemical system two mechanisms have to be considered:

(i) Ground state tunneling processes of either solvent or impurity molecules. These processes lead to a change of the microscopic matrix-molecule configuration and, hence, to a change in the optical energies of the various "sites" via strain mediated coupling. Spectral diffusion processes of this kind redistribute the various photochemical sites under the inhomogeneous line profile. Hence, one of its characteristic feature is the conservation of the integrated hole area.²¹

(ii) Back reaction processes from the photochemically induced state $|P\rangle$ to the reactant state $|R\rangle$ (Fig. 1). These processes reverse the PHB photochemistry and, hence, reduce the integrated hole area. They also lead to a line broadening with a mechanism similar to the one described under (i). The back reaction induces strain fields which, in turn, lead to changes of the optical energies of the dye molecules.

Based on the large measured deuteration effect of the line broadening mechanism and on the time scales involved, we argue, that the observed spectral diffusion phenomena are mainly governed by the photochemically induced states TLS_p .

III. EXPERIMENTAL

1,4-Dihydroxyanthraquinone (DAQ) was doped into EtOH/MeOH glass (3:1) at a concentration of 2×10^{-5} mol/mol. Part of the experiments were performed with the perdeuterated glass (C_2D_5OD/CD_3OD) with equal DAQ concentration. The hole burning photochemistry was performed either with an N_2 -pumped dye laser (Moletron DL14P) with a pulse duration of about 7 ns and a spectral width of 0.02 cm^{-1} or with an Ar^+ laser ($14 \mu W/cm^2$) of comparable linewidth. The PHB hole widths did not show signs of power broadening up to pulse power levels of 5 kW/cm^2 . The holes could either be measured using a Spex spectrometer (1402) with a resolution of 0.15 cm^{-1} or by pressure scanning of the pulsed dye laser. The sample was immersed in liquid helium, whose temperature could be varied between 1.3 and 4.2 K. At 4.2 K the time evolution of the holes could be measured over a week. Under pumped helium conditions (1.3 K) the experiment was limited to an observation time of 18 h.

IV. RESULTS

A. Absolute hole width

Figure 2 shows the hole width at 1.35 K as a function of

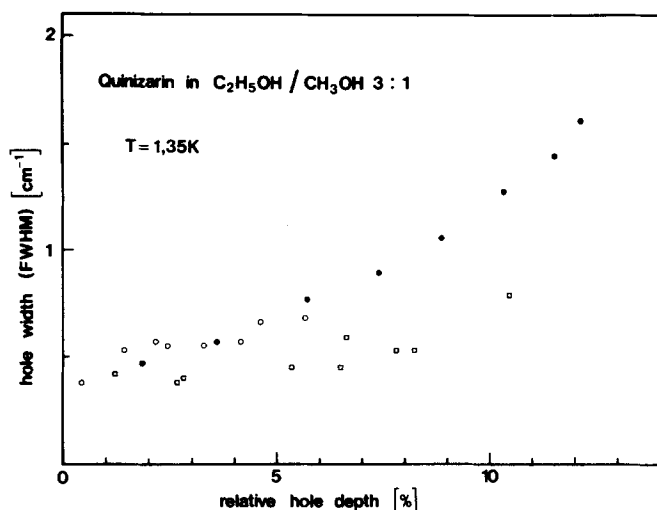


FIG. 2. Hole width as a function of the relative hole depth for various laser power levels. Full circles: Ar-ion laser: $140 \mu\text{W}/\text{cm}^2$. Open circles: Ar-ion laser: $14 \mu\text{W}/\text{cm}^2$. Squares: Pulsed dye laser $5.5 \text{ kW}/\text{cm}^2$.

the relative hole depth. The relative hole depth is a measure of the percentage of photochemically transformed molecules at a given frequency interval. The "real" hole width is extrapolated for values of the hole depth approaching zero.²² Figure 2 shows several experiments performed with pulsed and cw excitation at various power levels. All experiments extrapolate to a hole width of about 0.45 cm^{-1} . It should be noted, at this point, that the width γ , which reflects the dynamical processes of the system, is $1/2$ of the measured hole width. It is rather interesting, that our measured linewidth is more than two orders of magnitude larger than the Heisenberg lifetime limit, which one would expect for $T \rightarrow 0$. The lifetime of DAQ is about 6 ns for the protonated species and 12 ns for the deuterated species.²³

B. Time evolution of the optical linewidth

Figure 3 shows the widths of various photochemical holes, whose original depth was about 6%. The figure shows the time dependencies of both, protonated and deuterated samples for the two temperatures of 1.35 and 4.21 K, respectively. We summarize the noteworthy features:

(i) The hole widths increase within experimental error on a logarithmic time scale.

(ii) The time dependence of the hole width shows a pronounced isotope effect. The hole width of the deuterated sample increases at a much slower rate as compared to the hole width of the protonated sample. This reflects the fact, that spectral diffusion processes will, most likely, be linked to tunneling processes of the photochemically induced TLS.

(iii) An extrapolation of the measured logarithmic dependencies leads to a "crossover" between the two curves belonging to protonated and deuterated samples. The crossover point appears, for both temperatures, at a characteristic time τ_0 of about 12 s . The corresponding linewidths γ_0 are 0.93 and 0.4 cm^{-1} , respectively.

(iv) Figures 4–7 show the time evolution of the line shapes for both, protonated and deuterated samples for the temperatures 4.21 and 1.35 K, respectively. Each figure displays the hole in an early, intermediate, and late stage of the observed time interval. As can be seen from the line fits, the

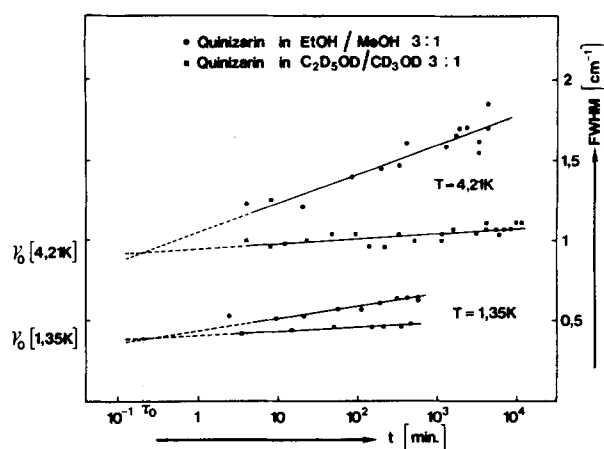


FIG. 3. Time dependence of the hole width for protonated (circles) and deuterated (squares) samples. The pronounced isotope effect is evident. γ_0 is a time independent contribution to the linewidth. τ_0 marks the onset of spectral diffusion. Experimental parameters: Protonated sample (4.2 K): Ar⁺ laser, $170 \mu\text{W}/\text{cm}^2$, burning time 6 min. Deuterated sample (4.2 K): Pulsed dye laser, repetition rate: 20 s^{-1} , energy per pulse: $89 \mu\text{J}/\text{cm}^2$, burning time 5 min. Protonated sample (1.35 K): pulsed dye laser, repetition rate: 30 s^{-1} , energy per pulse: $80 \mu\text{J}/\text{cm}^2$, burning time 2 min. Deuterated sample (1.35 K): pulsed dye laser, repetition rate: 30 s^{-1} , energy per pulse: $40 \mu\text{J}/\text{cm}^2$, burning time 6 min.

shapes of the holes remain Lorentzian throughout the experimental observation time (up to 1 week).

V. DISCUSSION

A. Spectral diffusion and time dependence of the linewidths

The basic concepts of spectral diffusion are outlined in a paper by Klauder and Anderson²⁴ (see also Ref. 25): The frequency distribution $I(\omega)$ of an ensemble of interacting dipoles (e.g., spins or pseudospins) is approximately given by the number of configurations of energy $\hbar\omega$. The calculation

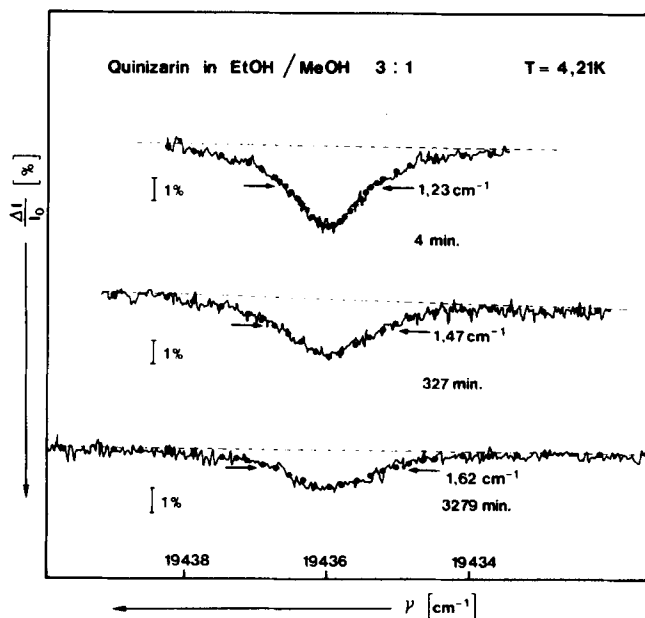


FIG. 4. Line shapes of photochemical holes at 4.21 K for various times, corresponding to the data points of Fig. 3. The full circles represent a fit to a Lorentzian line shape. The relative depth is indicated. Sample: Quinizarin in EtOH/MeOH glass.

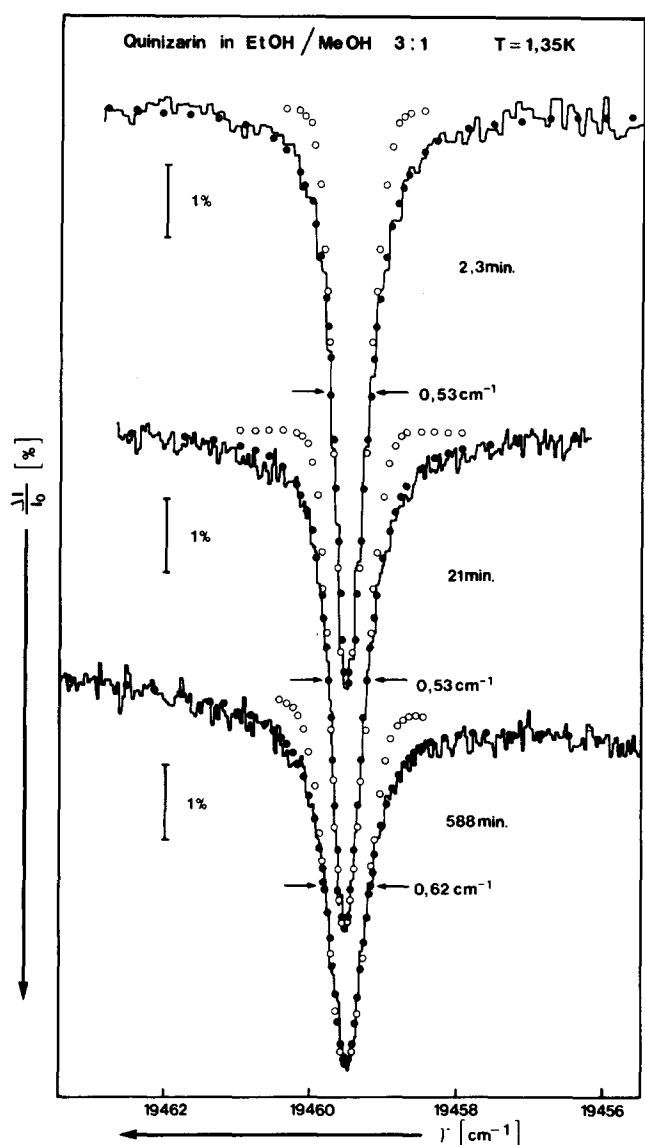


FIG. 5. Line shapes of photochemical holes at 1.35 K for various times, corresponding to data points of Fig. 3. The full circles represent a fit to a Lorentzian, the open circles to a Gaussian line shape. Sample: Quinizarin in EtOH/MeOH glass.

leads to a Lorentzian line shape, whose width is proportional to the number n of spins per unit volume. Even though most diffusion problems lead to a Gaussian line profile it can be shown that, in the special case considered, a Lorentzian "inhomogeneous" line profile can be expected. In our case of optical spectral diffusion we deal with molecular states which are photochemically produced. As time progresses, a certain number $n(t)$ of product molecules per unit volume will relax to the educt state. These relaxation processes do indeed occur, as has been shown by experiments, which document a reduction of the integrated hole area.¹⁷ There is no doubt, that such relaxation processes, which change the local geometry of the involved protons, give rise to strain fields and thus lead to strain mediated spectral diffusion. Since these processes occur on a time scale which is much longer than T_1 , they are called adiabatic and their linewidth contribution is classified as inhomogeneous.

The theory of strain mediated spectral diffusion was applied to TLS pseudospins by Black and Halperin²⁶ and to

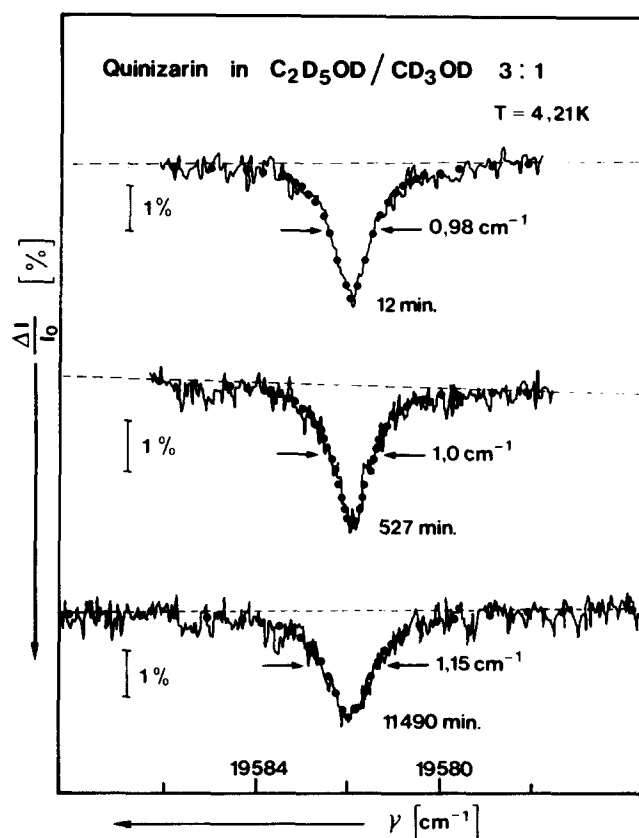


FIG. 6. Line shapes of photochemical holes at 4.21 K for various times, corresponding to data points of Fig. 3. The full circles represent fits to a Lorentzian line shape. Sample: Quinizarin in deuterated ethanol/methanol glass.

optical transitions by Reinicke.⁸ We start with equations derived by the above authors to interpret our results. If one assumes, that one has tunneling atoms in an amorphous matrix, then these tunneling particles create strain fields which are, in lowest order, of dipole type. The strain fields can change the energy levels of probe molecules from $\hbar\omega'$ to $\hbar\omega' \pm \epsilon$. After a time t has elapsed $n(t)$ molecules per unit volume may have tunneled and, hence, the transition energies $\hbar\omega'$ of the probe molecules have spread out forming a band with a width of $\gamma_D(t) = 2\langle|\epsilon|\rangle$, which is due to diffusion processes. A calculation shows that $\gamma_D(t)$ is proportional to $n(t)$. The latter number may also depend on the temperature and, hence on gets^{8,24-26}

$$\gamma_D(t, T) = C(\Delta/E)n(t, T). \quad (5)$$

C represents an electronic-elastic deformation potential with tensor character which does not depend on time and temperature and which can, in our case, be regarded as a constant factor. E and Δ are the energy and the energy asymmetry parameters as used for describing TLS systems.⁴ Both quantities are related to each other by

$$E = \sqrt{\Delta^2 + \Delta_0^2}, \quad (6)$$

with Δ_0 being the tunneling matrix element. The above considerations do not depend on the specific nature of the tunnel systems involved. In our present model we make the *ad hoc* assumption that the induced strains are mainly related to the photochemical tunnel systems TLS_p . This assumption is

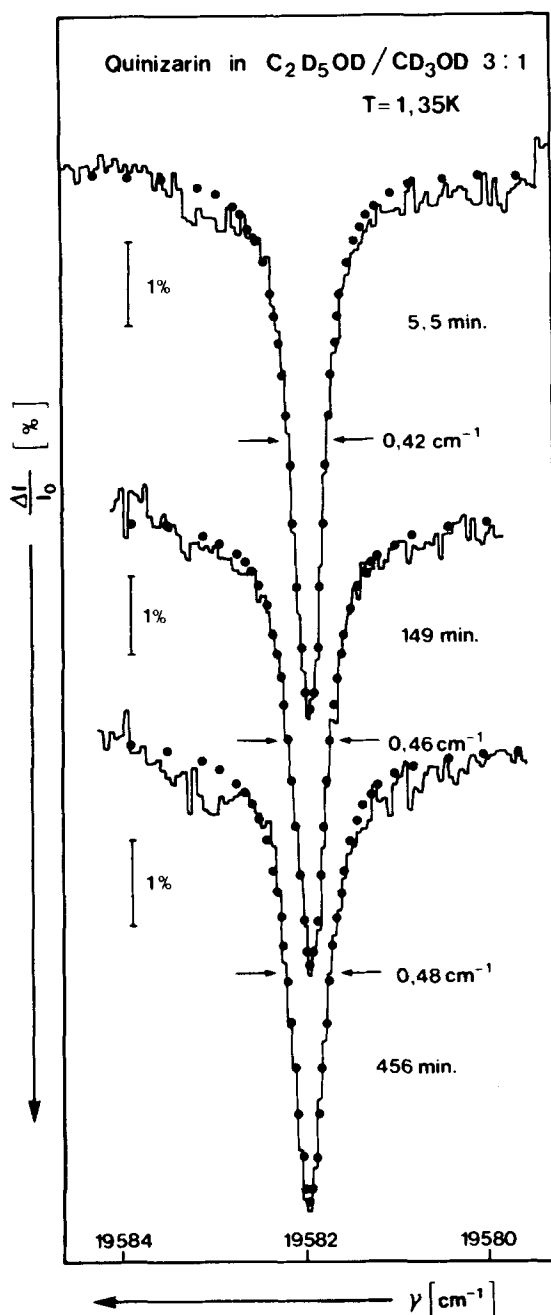


FIG. 7. Line shapes of photochemical holes at 1.35 K for various times, corresponding to data points of Fig. 3. The full circles represent fits to a Lorentzian line shape. Sample: Quinizarin in deuterated ethanol/methanol glass.

based on the observation that the time scales of the photochemical back reaction¹⁷ and of the spectral diffusion (this paper) are of the same order of magnitude. We would like to point out, however, that even the assumption that the spectral diffusion is governed by photophysical processes, would lead to the same results. In the latter case, however, the ensemble average of Δ and E would have to be discussed in more detail. For our photochemical system we can safely assume high tunneling barriers for the photochemically induced TLS_p, and, hence, we make the assumption of small Δ_0 values. This assumption is justified by the long time scale of our experiment. Then Eq. (6) simplifies to $E = \Delta$. Since $E \gg kT$ we can neglect "dark reaction" processes from $|R\rangle$ to

$|P\rangle$ and, hence, the measured optical linewidth can, after a time t has elapsed, be written as

$$\begin{aligned}\gamma(t, T) &= \gamma_0(T) + \gamma_D(t, T) \\ &= \gamma_0(T) + C \cdot n(t, T).\end{aligned}\quad (7)$$

$\gamma_0(T)$ is the linewidth without spectral diffusion; it is, in our model, time independent. Equation (7) is based on the following assumptions: The laser photochemistry leads, for short burning times τ , to a Lorentzian dip in the optical site distribution function $N_0(\omega')$ centered at the laser frequency ω_L :

$$N_\tau(\omega') = N_0(\omega') \times \left\{ 1 - \alpha \sigma (I / \hbar \omega_L) \phi \tau \cdot \frac{\gamma_0}{2\pi} \cdot \frac{1}{(\omega' - \omega_L)^2 + \gamma_0^2/4} \right\}.$$

α is the Debye-Waller factor, σ the molecular absorption cross section, ϕ the photochemical yield, and I the laser intensity.⁷ If we consider an infinitesimal frequency interval within the above distribution, say around ω'_0 , then it will spread out due to flipping of the involved pseudospins of the photochemical TLS forming a Lorentzian band with width $\gamma_D(t, T)$. Since this spread occurs for all frequencies ω' of the above distribution we simply have to convolute this distribution with a Lorentzian given by

$$L_D(\omega - \omega') = \gamma_D(t, T) / 2\pi [1 / \{(\omega - \omega')^2 + \gamma_D^2(t, T)/4\}].$$

This yields again a Lorentzian line with a width of

$$\gamma(t, T) = \gamma_0(T) + \gamma_D(t, T).$$

We can estimate $\gamma_0(T)$ from our experiments by interpreting the data in a physically meaningful way: Fig. 3 shows the linewidth data of a protonated and deuterated sample, respectively. We recognize, that the measured time dependencies are faster for protons than for deuterons reconfirming our tunneling model. If we extrapolate the data back to the short time regime, assuming, that the logarithmic law holds, then the data for protons and deuterons cross over at a critical time τ_0 . This limiting time τ_0 is roughly identical at both temperatures 1.3 and 4.2 K, respectively. At times shorter than τ_0 the simple physical picture of tunneling states is bound to be invalid, since, for $t < \tau_0$, the deuterons would have to tunnel faster than the protons. Since this is not consistent with the present tunneling model, we define τ_0 as the smallest relevant time of our time scale describing the measured increase in linewidths. This defines the "time origin" of the photochemically induced spectral diffusion as follows:

$$\gamma(\tau_0, T) \equiv \gamma_0(T).\quad (8)$$

Equation (8) also defines a linewidth prior to the onset of measurable spectral diffusion.

We point out, that the way of determining τ_0 and γ_0 from our experimental results is not rigorous but yields estimated values. This is due to the fact, that the logarithmic law is confined to a certain time range (see below). In principle, τ_0 may be a function of temperature and may also be rather different for the protonated and the deuterated species. Below we derive a relation for τ_0 which shows, why it is, in our case, independent of both, temperature and isotopic substitution.

One can eliminate the unknown parameter C [Eq.(7)] by

calculating the ratios of the linewidths $\gamma(t, T)$ and $\gamma_1 \equiv \gamma(t_1, T)$ as measured after the time intervals t and t_1 , respectively, and readily gets

$$\frac{\gamma(t, T) - \gamma_0(T)}{\gamma_1(T) - \gamma_0(T)} = \frac{n(t, T)}{n_1(T)}, \quad (9)$$

with $n_1 \equiv n(t_1, T)$ representing the number of photochemically induced TLS per unit volume, which have undergone a tunneling reaction within the time interval t_1 after the hole burning process. For calculating the time dependence of the total number of TLS_p systems, which have tunneled in the time interval between hole burning and detection of the hole at a given time t , one has to integrate over an appropriate distribution $p(R)$ of relaxation rates R which characterize the TLS_p:

$$p(R) = \frac{\bar{P}}{2} \cdot \frac{1}{R \sqrt{1 - R/R_{\max}}}, \quad (10)$$

Eq. (10) was calculated by Jäckle.²⁷

At this point a comment should be made concerning the distribution function $p(R)$ of our model. We make the basic assumption that the distribution of the TLS_p is identical to the one describing the normal TLS. Our reasons are the following: First, this assumption explains the experimental findings of a logarithmic time evolution of the optical width (Fig. 3). Second, the considered reaction occurs in an amorphous host material, and, hence, it is reasonable to expect a broad distribution of tunneling parameters and energy asymmetries. A broad distribution of these parameters leads to Eq. (10).

R_{\max} is the maximum relaxation rate and \bar{P} is a constant. We can calculate the number $n(t, T)$ of relaxed centers per unit volume by simply integrating Eq. (10) between $R = 1/t$ and R_{\max} .¹⁷ One readily gets

$$n(t, T) = n_0 \{ \ln 4R_{\max}/R_{\min} \}^{-1} \ln 4R_{\max} t. \quad (11)$$

The above equation takes into account, that if one observes the system for a time t , the slowest rate constants which play a role are on the order of $R = 1/t$. The above equation holds for $1/R_{\max} \ll t \ll 1/R_{\min}$, where R_{\min} is a lower limit of the possible relaxation rates.

The factor $\{ \ln 4R_{\max}/R_{\min} \}^{-1}$ in the above equation is a normalization factor which we have introduced to account for the fact, that the total number density of relaxed molecules must be equal to the number density n_0 of photochemically converted centers. One can insert the above result into Eq. (7) and thus gets a logarithmic increase of the linewidth with a deuteration dependent slope. Figure 3 shows linewidth data for the protonated and the deuterated system at two temperatures. As we can see, the logarithmic law seems to be rather well fulfilled. A logarithmic increase of the optical width with time was also derived recently by Hunklinger *et al.*²⁸

As to the absolute magnitude of the logarithmic slope (Fig. 3), we point out, that it is not directly related to any microscopic parameters. It depends, in our model, on various experimental parameters via the quantities n_0 and C .

As discussed in a recent paper¹⁷ the deuteration effect enters solely via R_{\min} . This has the following reasons: Only in tunneling systems with high barriers and large tunneling dis-

tances (as is the case for systems characterized by R_{\min}) deuteration may bring about changes in the involved tunneling rates which are large enough to show up in the logarithmic slope factor of Eq. (11).

For a quantitative evaluation of the logarithmic law, we use Eqs. (9) and (11) and get

$$\frac{\gamma(t, T) - \gamma_0(T)}{\gamma_1(T) - \gamma_0(T)} = 1 + \left[\ln \frac{4R_{\max}}{R_1} \right]^{-1} \ln R_1 t. \quad (12)$$

Equation (12) is very similar to the time evolution of the hole area, with the exception that in the latter case the logarithmic slope was determined by R_{\min} , whereas in the above equation, it is determined by R_{\max} .

Equation (12) leads to some interesting conclusions: We note that any changes of the experimental parameters such as temperature, d substitution, etc., must show up in the slope factor. If the variation of the experimental parameters, however, does not bring about order of magnitude changes in the rate constants, the slope factor remains roughly constant due to the logarithmic dependency.

Equation (12) allows an estimate of R_{\max} . At $t = \tau_0$, $\gamma(t, T) = \gamma_0(T)$ and, hence,

$$R_{\max} = 1/4\tau_0. \quad (13)$$

This is of course a rough estimate but it yields the correct order of magnitude.

It should be noted, that the τ_0 value which follows from a data extrapolation is on the order of tens of seconds and, hence, corresponds to a long time compared to typical time constants in microwave and ultrasonic experiments^{26,29,30} (for a review see Ref. 31). The reason for such a slow process may be, that we are investigating a photoproduct state, which was created with "high energy" photons and whose back reaction in the dark will be characterized by high barriers.

From Eq. (13) it follows, that τ_0 is, as has been found experimentally, independent of temperature. One can further conclude, that it is, in our case, almost independent of deuteration. These conclusions are based on the following arguments: The temperature dependence of a direct relaxation process of tunneling systems varies as $\text{ctgh } E/2kT$, hence, is rather small, if $E \gg 2kT$ as expected for photochemically induced TLS.

As far as the sample deuteration is concerned, it changes the tunneling matrix element Δ_0 via a change in the mass m of the tunneling particle (for example see Ref. 32)

$$\frac{\Delta_0(\text{H})}{\Delta_0(\text{D})} \sim e^{-\lambda'(\sqrt{m_{\text{H}}} - \sqrt{m_{\text{D}}})}. \quad (14)$$

A strong influence is only expected for large values of λ' , i.e., for small tunneling rates.¹⁷ Since τ_0 is determined by the fastest rate R_{\max} (small λ') it is clear, why deuteration is only of minor importance for its magnitude. If we plot, instead of the linewidth, the reduced linewidth [Eq. (12)], then all the data points should fall on the same plot. As can be seen from Fig. 8, this is fulfilled within the accuracy of the experiment.

B. Line shapes

Figures 4–7 show that the line shapes remain Lorentzian within good approximation over the whole experimen-

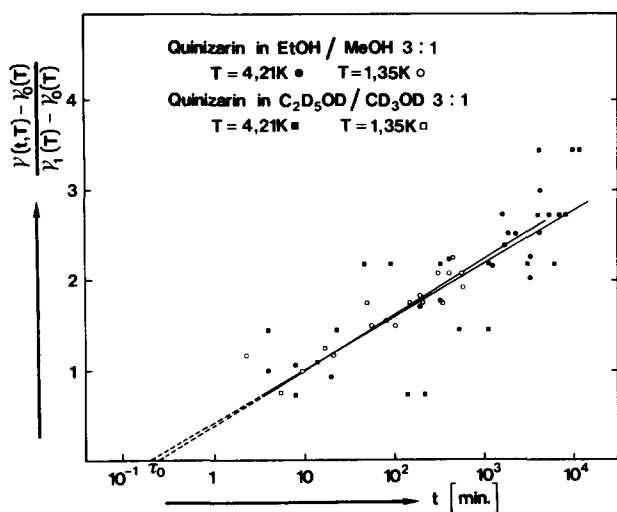


FIG. 8. Linewidth contribution due to spectral diffusion as a function of time. The data are normalized to the linewidth measured at 10 min after hole burning. The plot contains all data points of Fig. 3. The straight lines are calculated by least square fits for the temperatures 4.21 and 1.35 K, respectively.

tal period (20 h at 1.3 K and 1 week at 4.2 K). From this we conclude, that all contributions to the hole have to be of a Lorentzian shape. As far as the spectral diffusion contribution is concerned, a Lorentzian line shape is expected as long as the strain fields created by the relaxing species are of dipole type.²⁴ Since the time scale of the observed spectral diffusion process is very slow compared to T_1 , it can be characterized as adiabatic and thus be called an inhomogeneous linewidth contribution.

The above analysis has shown, that the major contribution to the linewidth is, within the first 10 min of the experiments, γ_0 . The absolute value of γ_0 is about two to three orders of magnitude larger than the T_1 limit of the optical linewidth (Heisenberg limit). Therefore the question has to be discussed, how the observed optical linewidth can be understood. At the present time, there are two possible answers: One, the γ_0 value is due to very fast T_2 -scattering processes due to phonon or fracton scattering. We would have to assume, that the scattering processes in our system are roughly a factor of 30 faster than those observed for molecules like porphyrin.³³ The second possibility would be to assume a second type of spectral diffusion process, which would have to be much faster than the one investigated in this paper and, whose slowest contribution would have to be faster than our experimental time resolution.

VI. SUMMARY

We have shown, that the optical linewidths of DAQ in alcohol glasses, as measured by PHB, increase slowly on a logarithmic time scale. We have also measured an isotope effect for samples in which the protons of the matrix and of the photoactive group of the dye molecule (DAQ) were replaced by deuterons. The linewidth increase of the protonat-

ed system is faster, than the increase of the deuterated system, reflecting a proton tunneling mechanism of the observed spectral diffusion process. The results could be described by a model involving photochemically induced tunnel systems.

Based on the observed isotope effect, we were able to measure the maximum spectral diffusion rate R_{\max} , whose inverse is on the order of seconds. This complements recent experimental data on the same photochemical systems yielding values for the slowest rates R_{\min} .¹⁷

ACKNOWLEDGMENTS

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