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► **To cite this version:**

J. Friedrich, D. Haarer. SPECTRAL DIFFUSION AND RELAXATION OF PHOTOCHEMICAL HOLES ON LOGARITHMIC TIME SCALES. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-357-C7-361. 10.1051/jphyscol:1985764 . jpa-00225093

HAL Id: jpa-00225093

<https://hal.science/jpa-00225093>

Submitted on 4 Feb 2008

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SPECTRAL DIFFUSION AND RELAXATION OF PHOTOCHEMICAL HOLES ON LOGARITHMIC TIME SCALES

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Abstract: Photochemical holes burnt in doped organic glasses evolve on logarithmic time scales. The characteristic time dependent features can be described using the concepts of spectral diffusion. Since the model has no adjustable parameter the results provide detailed insight in the long time relaxation behavior of the glasses.

INTRODUCTION:

Glasses are well described as frozen liquids with a temperature dependent viscosity as given by the Vogel-Fulcher-law

$$\eta = \eta_0 \exp A/k(T-T_0) \quad (1)$$

with parameters η_0 , A , and T_0 . The above equation can be interpreted within the frame of an Arrhenius-law with a temperature dependent barrier

$$V_0 = A/(1-T_0/T) \quad (2)$$

which the system has to overcome for thermally activated structural relaxation processes. At $T = T_0$ the barrier heights diverge formally, indicating that on the average the thermally activated relaxation processes become infinitely slow. T_0 cannot be defined in a straight forward fashion. Within the free volume model of amorphous solids it can be interpreted as the temperature at which the free volume vanishes [1]. Since in an amorphous solid the barrier heights can not be expected to be uniform but are characterized by a distribution, there are still relaxation processes even at very low temperatures. This demonstrates that a glass does not reach equilibrium on experimental time scales. Hence, some of its physical parameters are not well defined as in the case of crystals, but change as a function of time. This was demonstrated five years ago for the specific heat [2]. Very recently, we succeeded in measuring the time dependence of some optical properties, like the area and the width of "persistent" spectral holes. The hole burning technique has proven to be a powerful tool for the investigation of the amorphous state [3]. This is due to the fact that, at low temperatures, the width of a spectral hole may be several thousand times narrower than the inhomogeneous width, which reflects the average intermolecular interaction. Hence, a persistent spectral hole is an extremely sensitive probe for structural (or so called secondary) relaxation processes which can occur on very long time scales. In this paper we demonstrate how one can get detailed quantitative information on the

structural relaxation dynamics of a glass using spectral holes as probes. We investigated quinizarin in alcohol glass, whose photochemistry has been described elsewhere /3/. For comparison we investigated also the photophysical hole burning system tetracene in ethanol /4/.

EXPERIMENTAL RESULTS

Fig.1 shows a survey spectrum of the system quinizarin in an EtOH/MeOH (3:1) glass at 1.3 K. The small dip at 19440 cm^{-1} is the photochemical hole, which is shown on an expanded scale in the insert. Its time evolution is shown in Figs.2 and 3. We found that

- 1) its area decreases linearly on a logarithmic scale
- 2) its width increases linearly on a logarithmic scale
- 3) both relaxation processes occur orders of magnitude slower in deuterated glass
- 4) its degree of polarization remains constant

Fig.4 shows the photophysical hole burning system, tetracene in ethanol. Again, the hole area decays linearly on a logarithmic scale and its polarization is constant throughout the experimental period of roughly 1 week.

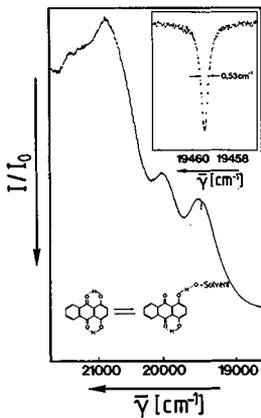


Fig.1: Survey spectrum of quinizarin in alcohol glass: The photochemical hole is shown on an expanded scale. Burning time: 2 min.

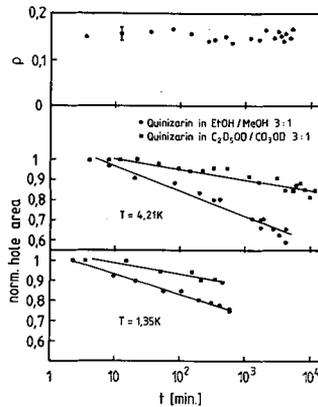


Fig.2: Area and degree of polarization of a photochemical hole as a function of time. System: quinizarin in alcohol glass.

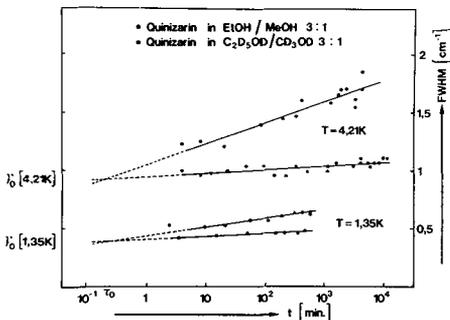


Fig.3: Hole width as a function of time. System: quinizarin in alcohol glass.

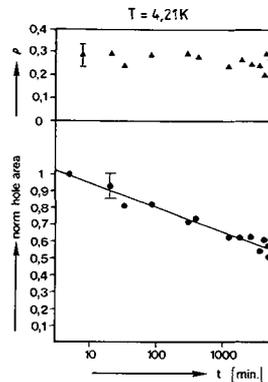


Fig.4: Area and degree of polarization of a spectral hole as a function of time. System: tetracene in alcohol glass.

DISCUSSION

The above results can be interpreted very consistently within the frame of the TLS-model of the amorphous state /5/:

1) The relaxation of the hole area: From low temperature specific heat experiments it is well known that the energies of two level tunneling states (TLS) are uniformly distributed. Consistent with a uniform distribution in energy is a uniform distribution in both parameters, which characterize a TLS, namely the energy asymmetry Δ and the tunnel parameter λ . A consequence of a uniform distribution of Δ and λ is a very asymmetric distribution of tunneling relaxation rates R , roughly given by

$$P(R) \sim R^{-1} \quad (3)$$

Equ.3 is the starting point of our theoretical model /6/. Since the above distribution has to be normalized, there exist two cut-off values R_{\min} and R_{\max} , representing the slowest and the fastest tunneling processes of the system considered. Once R_{\min} and R_{\max} are known the complete dynamics of the TLS-system under consideration is known. For the first time, we could estimate these parameters from hole burning experiments. Our arguments are the following: In both cases, quinizarin and tetracene, the photoproduct is trapped in some tunneling state which is subject to a distribution of relaxation rates according to (3) reflecting the local disorder. At time t one observes mainly those centers relax which are governed by rates on the order $R = 1/t$. Hence, the hole area is given by integrating the above rate distribution from R_{\min} to $R = 1/t$. This integral yields the number of tunneling centers being, at time t , in the photoproduct state, and, thus, is proportional to the hole area. One derives for the hole area $A(t)$ a logarithmic decay law:

$$A(t)/A_1 = 1 - \ln[R_1/R_{\min}]^{-1} \ln t/t_1 \quad (4)$$

A_1 normalizes the decay function at the time t_1 . The slope of the above linear relation is given by the logarithm of the to rates R_1/R_{\min} , $R_1=1/t_1$ is an experimental parameter on the order of 1/min. Hence, R_{\min} can be directly determined from the measured slope. The dispersion of rates R_1/R_{\min} is huge. We get for quinizarin in the protonated and in the deuterated glass, respectively, the values

$$[R_1/R_{\min}]_H = 10^8, \quad [R_1/R_{\min}]_D = 10^{19}.$$

For tetracene in ethanol we found: $R_1/R_{\min} = 10^{11}$.

2) The time evolution of the linewidth: The time evolution of the linewidth occurs on the same time scale as the decay of the hole area. To explain the observed features we employ the concept of spectral diffusion. We consider a molecule, left in the educt state, which has, at a time t_1 , a sharp transition frequency. As time evolves, the molecules relaxing from the product to the educt state create strain fields which lead to a diffusion of excitation energies of the probe molecules in frequency space. As shown by several authors /7,8/, the lineshape of the diffusing molecules is, under certain conditions, Lorentzian. Its width is proportional to the number $n(t-t_1)$ of molecules having 'flipped' within the time interval $t-t_1$:

$$\gamma_D(t-t_1) \sim n(t-t_1) \quad (5)$$

If we consider the case $t_1 = 1/R_{\max}$, then the above equ. represents the full width due to spectral diffusion. Very similar to the procedure outlined above $n(t-1/R_{\max})$ can be determined by integrating Equ.3 from $R = 1/t$ to $R = R_{\max}$. The result is again a logarithmic law with a slope factor which depends on several experimental parameters like the temperature T , the total number of photochemically converted centers N and the concentration C :

$$\gamma_D = f(T, N, C) \ln[R_{\max}/R_{\min}]^{-1} \ln R_{\max} t \quad (6)$$

The measured width γ is the sum of a diffusional width and a time independent width γ_0 which may be the homogeneous width. If one succeeds in measuring separately the diffusional width $\gamma_D = \gamma - \gamma_0$, then it is easy to show /9/ that a reduced plot $\gamma_D(t)/\gamma_D(t_1)$ yields a logarithmic law with a slope factor determined solely by R_{max} , the maximum rate constant:

$$\gamma_D(t)/\gamma_D(t_1) = (\gamma(t) - \gamma_0)/(\gamma(t_1) - \gamma_0) = 1 + [\ln R_{max}/R_1]^{-1} \ln t/t_1 \quad (7)$$

R_{max} can be determined experimentally from the measured slope. In our experiments /9/ we estimated γ_0 from the deuteration effect. As seen in Fig.3, the extrapolated lines of the protonated and deuterated sample show a cross over at a time τ of 12 s. Clearly τ marks the onset of spectral diffusion and thus $\gamma(\tau) = \gamma_0$. Equ.7 allows to give an estimate of the maximum rate constant. For quinizarin in the EtOH/MeOH glass we get $R_{max} = 0.025 \text{ s}^{-1}$. We stress that R_{max} does not show any significant dependence on deuteration.

THE DEUTERATION EFFECT

In case of the quinizarin system it is well known that the hole burning photochemistry is due to a proton transfer reaction, hence, a change in the relaxation rates of the deuterated system is to be expected. Deuteration changes the tunneling matrix element Δ_0 which depends in an exponential fashion on the mass m of the tunneling particle

$$\Delta_0 \sim \exp[-\sqrt{m} \cdot \lambda'] \quad (8)$$

λ' is determined by the barrier height V_0 and the tunneling distance d

$$\lambda' = (V_0 d^2 / 2\hbar^2)^{1/2} \quad (9)$$

It is clear that, if λ' is large, and hence the rate constant small, deuteration may bring about a change of many orders of magnitude. On the other hand, if λ' is small, the deuteration effect will be small and will be hardly noticeable in the logarithmic slope factor. Since the slope factors for both, the decay of the normalized hole area (Equ.4) and the absolute width (Equ.6) are governed by R_{min} , the slowest rate of the total system, a large deuteration effect is expected. This is indeed observed /6/. R_{min} changes by more than 10 orders of magnitude. A most interesting observation is the fact that the isotope effect in the linewidth data (Fig.3) vanish, if they are scaled according to Equ.7. Fig.5 shows that all the data points of Fig.3 lie on the same uniform plot:

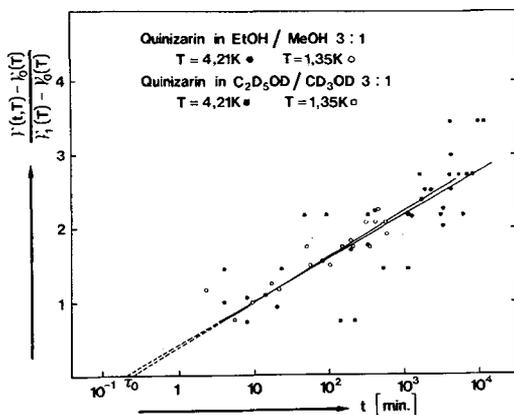


Fig.5: The data of Fig.3, re-scaled according to Equ.7. Note the unified behavior of the data points.

This behavior can be understood on the basis of Equ.7. Due to the rescaling procedure, R_{\min} (and also f) cancel. R_{\max} , however, shows only a small isotope effect as discussed above, which is of negligible influence on the logarithmic slope factor. From the measured isotope effect we can estimate the maximum barrier heights. Assuming tunneling distances on the order of a few Angstroms, one calculates maximum barrier heights on the order of several thousand wave numbers, i.e. much higher than the thermal energy at the glass transition temperature kT_g . Such barrier heights are, however, quite consistent with the Vogel-Fulcher-law (Equ.1), indicating that barrier formation is most likely a collective phenomenon.

POLARIZATION DIFFUSION

From the constant degree of polarization we conclude that on the time scale of the experiment, there is no reorientation of dye molecules left in the ground state. This rules out the possibility that the dye molecules themselves are an active part of the TLS-system of the glass /4/.

ACKNOWLEDGEMENT:

The authors acknowledge a grant from the Stiftung Volkswagenwerk.

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