

Investigation of polarization diffusion and relaxation dynamics of low temperature glasses

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We investigated the optical anisotropy and the normalized areas of persistent spectral holes in organic glasses over almost 1 week (4 decades). The systems studied were 1,4-dihydroxyanthraquinone and tetracene in an EtOH/MeOH glass. The areas of the holes decay on a logarithmic time scale, but the anisotropy remains constant. We draw the following conclusions: (i) There is no reorientation of dye molecules in the glass. (ii) Molecules relaxing from the product state reassume the position in the frequency domain and in space which they had before hole burning. (iii) A dye molecule seems to be strongly coupled just to one two level system (TLS).

INTRODUCTION

Glasses are characterized by a large amount of free volume which allows for a diffusive motion of part of the molecules even at very low temperatures.^{1,2} It was suggested that the so-called tunneling modes (TLS) which are the basis of a rather general description of the low temperature properties of glasses,^{3,4} are directly related to voids of free volume which are frozen in as the system is cooled through the glass transition. So far no microscopic description of the tunneling modes has been given.

From a series of recent experiments we know that even at temperatures as low as 1.3 K structural relaxation of glasses can be observed by monitoring the time evolution of photochemical holes over time periods as long as a week (Refs. 5 and 6, and for a review see Ref. 7). It has been found that such processes occur on logarithmic time scales. A quantitative evaluation of the logarithmic laws which was based on the fundamental TLS-distribution function^{3,8} enabled the determination of the minimum and the maximum relaxation rate which differed by more than ten orders of magnitude.

In this paper we investigate the optical anisotropy of photochemical holes as a function of time. The idea is that, if the photoreactive dye molecules have enough free volume, they can undergo some kind of reorientation motion thereby leading to a loss of anisotropy. From the time dependence of the polarization one should therefore gain information whether or not the dye molecules themselves are part of the tunnel modes.

EXPERIMENTAL

We investigated two very different systems: 1,4-dihydroxyanthraquinone (DAQ) which shows photochemical hole burning and tetracene which shows non-photochemical hole burning. In both cases the matrix was an EtOH/MeOH glass (3 : 1, v/v). The concentration was 10^{-5} M.

The holes were burnt either with an Ar⁺ laser (150 μ W/cm²) or with a N₂-pumped dye laser (400 μ J/cm², 30 Hz). Detection was performed with a Spex 1704 mono-

chromator followed by a glan prism. The spectra were scanned either with the probing light polarized parallel (\parallel) or perpendicular (\perp) to the *E* vector of the burning field. The burning time was 4 min in each case. The holes were probed over almost 1 week at a temperature of 4.2 K. Typical spectra for two different states of bleaching are shown in Fig. 1.

RESULTS AND DISCUSSION

We chose the two systems because of their basic difference in the hole burning mechanism. In alcoholic glasses, DAQ undergoes a photochemical⁷—while tetracene undergoes a nonphotochemical transformation.⁹ This difference may have consequences concerning the possible relaxation mechanisms of the optical anisotropy. In the photochemical case one can, in principle, distinguish between two different mechanisms, which might occur on rather different time scales: (i) relaxation of the photoproduct molecules to the educt state. If this process is connected with some reorientation as compared to the state before burning the anisotropy of the hole may change and (ii) polarization diffusion of those dye molecules which were not affected by the laser photochemistry. It is clear that such processes may also lead to a loss in anisotropy.

While the first process (i) is related to a rather special kind of tunnel systems, namely the so-called photochemically induced tunnel systems (TLS_p^{5,6}), the second process (ii) would reflect transitions in the ordinary TLS system of the doped glass. In principle, both tunnel systems may be characterized by rather different TLS parameters such as the energy asymmetry, barrier heights, and tunnel distances.

It is obvious, however, that such a distinction breaks down in case of nonphotochemical hole burning systems. In this case both tunnel systems belong to the same category.

Based on the above considerations we want to answer two questions: Firstly, does a dye molecule change its orientation during the complete photochemical cycle as

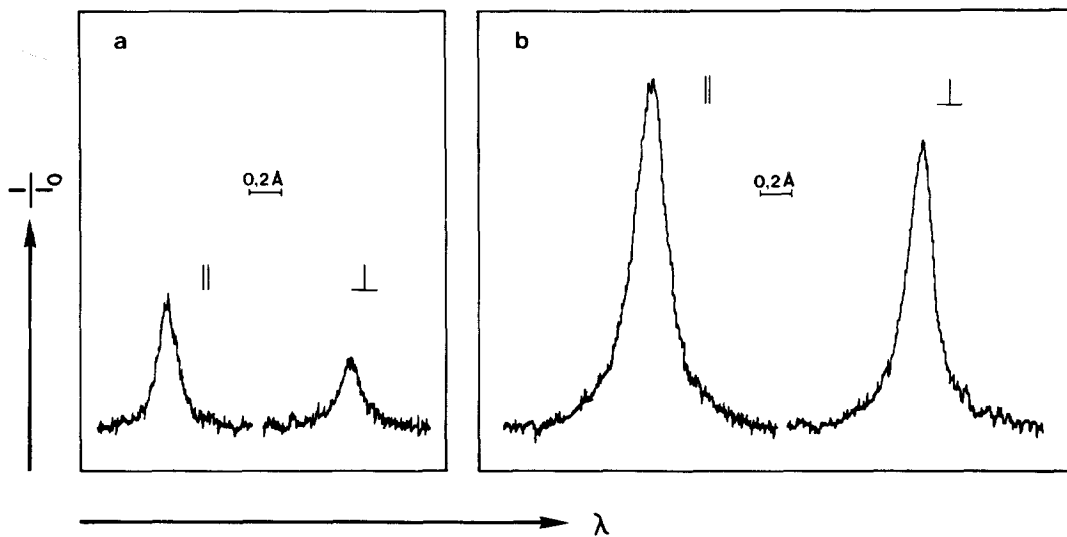


FIG. 1. Photochemical holes detected either parallel (\parallel) or perpendicular (\perp) with respect to the burning field. Two different states of bleaching are shown: (a) burning time 10 s, 0.5 mW/cm², (b) 800 s, 0.5 mW/cm². Sample: quinizarin in EtOH/MeOH at 1.35 K.

shown in Fig. 2 and, secondly, is there any reorientation of the molecules left in the reactant state $|R\rangle$ on the time scale of the experiment?

To answer these questions we measured the areas (A_{\parallel} , A_{\perp}) and the depths (L_{\parallel} , L_{\perp}) of anisotropic holes which were burnt with a linearly polarized laser field, as a function of time. (Since the holes remain Lorentzian throughout the whole experimental time, there are only two independent parameters characterizing the time evolution process of a hole: One can choose, for example, either the width and the depth, or, as we did, the area and the depth.) The time span was almost 1 week (4 decades). Figures 3 and 4 show the time dependence of the hole areas and the degree of polarization ρ , which was determined from the hole depth according to¹⁰

$$\rho(t) = \frac{L_{\parallel}(t) - L_{\perp}(t)}{L_{\parallel}(t) + L_{\perp}(t)}$$

The hole areas A_{\parallel} and A_{\perp} decay on a logarithmic scale indicating that there is indeed a considerable relaxation dynamics of the glass. The degree of polarization however remains constant throughout the whole experimental

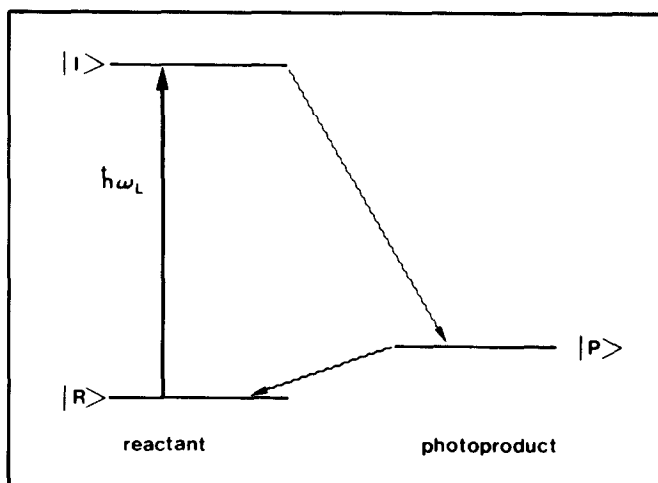


FIG. 2. Level scheme used for the description of the time evolution of photochemical holes. $|R\rangle$ reactant state, $|I\rangle$ photoreactive intermediate, $|P\rangle$ product state.

time. The hole does not lose its anisotropy. An extrapolation of the logarithmic decay laws of A_{\parallel} and A_{\perp} yields in both cases a cross point which lies exactly on the time axis. This tells us that, apart from the degree of polarization, the ratio A_{\parallel}/A_{\perp} is also constant in time.

From these results we draw several interesting conclusions: Since A_{\parallel}/A_{\perp} and L_{\parallel}/L_{\perp} are constant in time, it follows that the number of molecules relaxing into a special spatial configuration with excitation frequency ω is exactly proportional to the number of molecules which were burnt in this configuration. Hence, the molecules relaxing from the product to the educt state return exactly to the positions in space which they had before burning. If we would assume, for example, that the relaxing

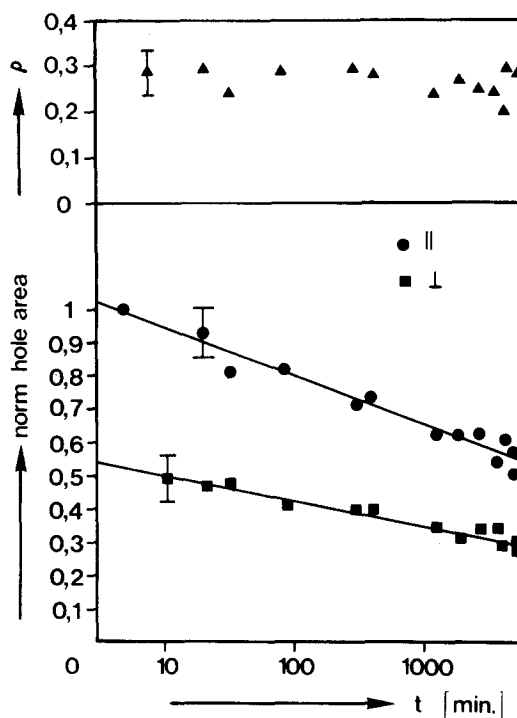


FIG. 3. Degree of polarization ρ (for the line center) and normalized areas of the hole as a function of observation time. \parallel scanning field parallel to the burning field, \perp scanning field perpendicular to the burning field. Sample: quinizarin in EtOH/MeOH at 4.2 K.

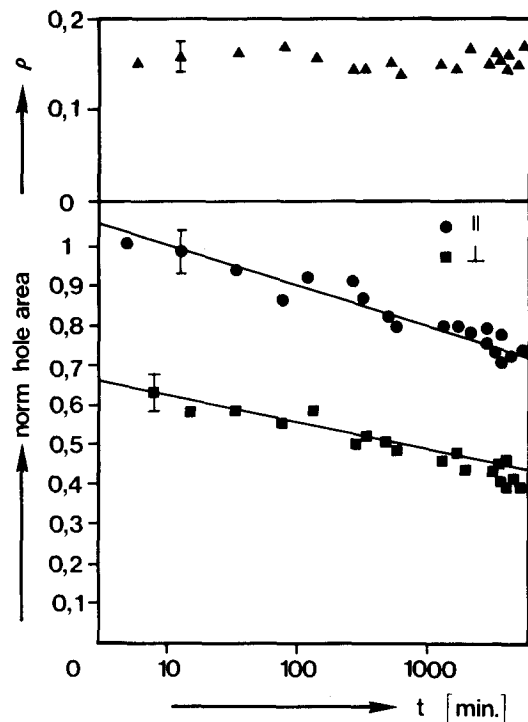


FIG. 4. Degree of polarization ρ (for the line center) and normalized area of the hole as a function of observation time. \parallel scanning field parallel to the burning field, \perp scanning field perpendicular to the burning field. Sample: tetracene in EtOH/MeOH at 4.2 K.

molecules are randomly distributed then, we would have to conclude that A_{\parallel} and A_{\perp} are reduced at the same absolute rate. In this case the degree of polarization would have to increase with time, which is not the case. As to the positions of the relaxing molecules in the frequency domain, we note that they are spread within a narrow range around the frequency which they had before burning. This spread is due to spectral diffusion and is, as was shown recently,¹¹ time dependent.

The above conclusion is a remarkable result because it tells us that the solvent cage seems to be a rather well defined species which does not change in an irreversible fashion during the complete photochemical cycle indicated in Fig. 2. It also tells us that a double minimum potential seems to be a very good description for the phototransformation and the related relaxation processes in both cases, for the photochemical as well as for the nonphotochemical system. The probability that the system relaxes to a third minimum seems to be of minor importance. Finally, we can further infer that a dye molecule is not coupled to several photochemically active TLS but most probably only to one. Otherwise it would be very difficult to understand why a relaxing molecule reassumes its place in the frequency and space domain which it had before burning. Apart from the strong coupling to the photoactive TLS there is, however, an additional weak coupling to the remaining TLS. We consider this type of coupling as responsible for the spectral diffusion.

Another point is worthwhile to be stressed: The data in Figs. 3 and 4 are rather similar. (The magnitude of ρ reflects just the state of bleaching but not a property of

the system investigated.¹⁰) For both systems the decay of the normalized hole areas are linear on a logarithmic time scale and the slopes are nearly of the same magnitude. We showed in a recent paper⁵ that it is possible to derive an analytic expression for the logarithmic decay law which is of the form

$$\frac{A(t)}{A_1(t_1)} = 1 - \left[\ln \frac{R_1}{R_{\min}} \right]^{-1} \ln R_1 t.$$

The derivation is based on the fundamental distribution function of TLS systems.⁸ According to the above equation, a determination of the minimum relaxation rate R_{\min} is possible from the measured slope of the logarithmic decay law. $R_1 = 1/t_1$ is an experimental parameter related to the first data points of Figs. 3 and 4. In our case t_1 is on the order of minutes. From the measured slopes we find

$$[R_1/R_{\min}]_{\text{DAQ}} \approx 10^8, \quad [R_1/R_{\min}]_{\text{T}} \approx 10^{11}.$$

The interesting thing is that DAQ is a photochemical system while tetracene (T) is a nonphotochemical system. In the former case the relaxation rates are determined by the photochemically induced tunnel systems (TLS)_p, while in the latter case they are, according to the hole burning model used,⁹ determined by the ordinary TLS of the doped glass. The logarithmic slope factors for the two TLS systems, however, are very similar.

As to the second question on the reorientation dynamics of the molecules left in the educt state, we can definitely say that, as long as the reorientation leads to a population redistribution within the contours of the hole, the anisotropy should fade as the hole is smoothed out. Since ρ remains constant over the whole experimental period, we can exclude such reorientation processes of the dye molecules.

To be general, however, one has also to take into account the possibility that the possible reorientation dynamics of dye molecules may lead to a uniform population redistribution over the whole inhomogeneous band. If we assume again that the number of molecules which undergo a reorientation relaxation is proportional to the number of burnt molecules, we have to conclude that $L_{\parallel}(t)$ is reduced with exactly the same rate as $L_{\perp}(t)$. Consequently, the hole would appear to be filled but without any loss in anisotropy.

We can, however, safely rule out this latter redistribution process. In both cases, DAQ and tetracene, we found that the hole filling process depends on deuteration of the glass,^{5,12} hence, cannot be due to an orientational relaxation of dye molecules. Consequently, we conclude that if there would be an appreciable amount of reorientation it should be reflected in a loss of the anisotropy. Since there is none, there is no reorientation of dye molecules on the time scale of the experiment. Hence, regardless of the type of burning process, the hole recovery is in all cases, determined by the relaxation of the photoactivated TLS states.

SUMMARY

Our experiments show that the optical anisotropy of spectral holes is constant in time though the decay of the holes reflects a remarkable dynamic behavior of the glass. The features of the decay of the photochemical and the photophysical system are very similar. The results lead to the following conclusions:

(i) Molecules relaxing from the product to the educt state return into the position (frequency and space) which they had before burning. The solvent cage seems to be a well defined species and does not change during a complete photochemical cycle.

(ii) The relaxation process of a glass is well described in terms of a double minimum potential. Relaxation between several minima seems to be absent.

(iii) A dye molecule seems to be coupled just to one photoactive TLS.

ACKNOWLEDGMENTS

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