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TIME- AND TEMPERATURE-DEPENDENT RELAXATION FEATURES OF SPECTRAL HOLES*(Presented by K. K. Rebane)*

We investigated configurational relaxation of doped organic glasses by monitoring the changes of spectral holes as a function of time and temperature. The configurational changes occur either by tunneling processes or by thermally activated processes. At extremely low temperatures the tunneling processes prevail, leading to logarithmic features in the relaxation function from which information on the dispersion of relaxation rates can be obtained. The activated processes determine the temperature dependence. It is shown that the distribution of activation barriers follows closely a $1/\sqrt{V}$ -dependence, which can be measured in a most direct way. We demonstrate that the time- and temperature dependent relaxation features show scaling behavior.

Introduction

Glasses can be viewed as liquids which are trapped in a high dimensional configurational space. The nature of the glass transition is not yet very well understood and there are different approaches to this problem. It is, however, generally assumed that at very low temperatures, configurational relaxation is extremely small, so that a glass can be considered as being trapped at a certain point in configuration space. This is, for example, a direct outcome of the Vogel-Fulcher-Tamman law (eq. 1).

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

which states that the viscosity η tends to infinity as T falls below T_0 . One can interpret eq. (1) as an Arrhenius-law with a temperature dependent barrier which diverges as T approaches T_0 [1,2]. In this paper we demonstrate that, even at extremely low temperatures, glasses and amorphous polymers are not confined to a definite point in configuration space but can sample small areas around the point where they were originally trapped by cooling through the glass transition. The configurational changes can occur either as a function of time at constant temperature, or as a function of temperature on time scales fast compared to the intrinsic time scale of the low temperature glass relaxation. Our experimental approach is based on the spectral hole burning technique which was shown to be quite a sensitive method to investigate relaxation dynamics of low temperature glasses [3,4].

Experimental

We present results on several, very different types of hole-burning systems: tetracene and quinizarin-doped alcohol glasses and quinizarin-doped PMMA glass. The quinizarin-doped glasses are photochemical hole-burning systems while the tetracene-doped glasses are photophy-

sical hole-burning systems. In the photochemical systems the hole-burning reaction is assumed to occur via a proton rearrangement process. In the photophysical systems the hole-burning reaction does not lead to a change of the dopand molecule at all. Instead, we will demonstrate with a few simple experiments that, in this case, the reaction is most likely due to a light-induced rotation of the tetracene molecule within the amorphous host matrix [4].

The holes were burnt at liquid He-temperatures using an Ar⁺-laser with an intensity of about 200 $\mu\text{W}/\text{cm}^2$ and burning times between 2 and 10 min. Several features of the holes were investigated:

- i) the change of its area and its width as a function of time;
- ii) the change of its area and its width as a function of temperature.

These latter experiments are a type of annealing experiments. The hole is burnt at low temperatures (T_b); then the temperature is raised to an excursion temperature T , which is the variables of this experiment, and cycled back again to T_b , where the hole is measured again;

- iii) the spectral distribution of the photoproduct and the concomittant change in oscillator strength.

The holes were probed by a high resolution spectrometer (0.16 cm^{-1} in 2nd order) and were processed on line by a computer.

Results

Logarithmic features in the time evolution of spectral holes. Fig. 1 and 2 show the time evolution of spectral holes of quinizarin and tetracene-doped alcohol glasses for an observation period of one week. We see that the area of the hole as well as the width evolve linearly on a logarithmic time scale.

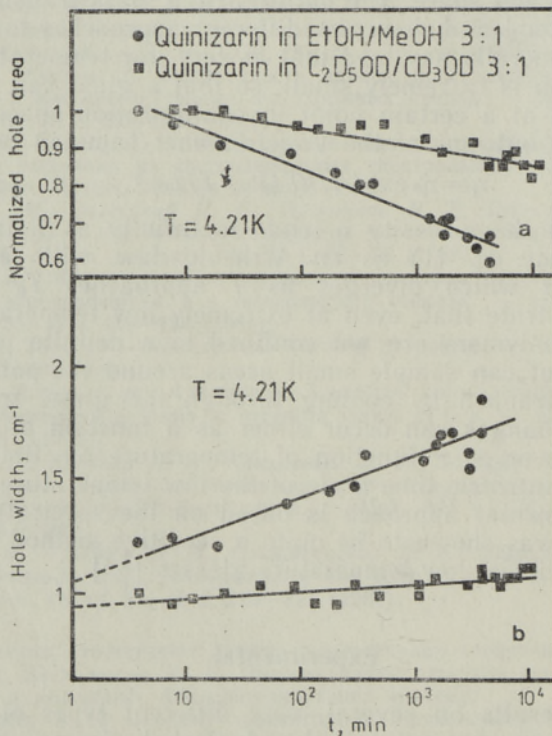


Fig. 1. Hole area (a) and hole width (b) as a function of time after burning. System: quinizarin in protonated and perdeuterated alcohol glass.

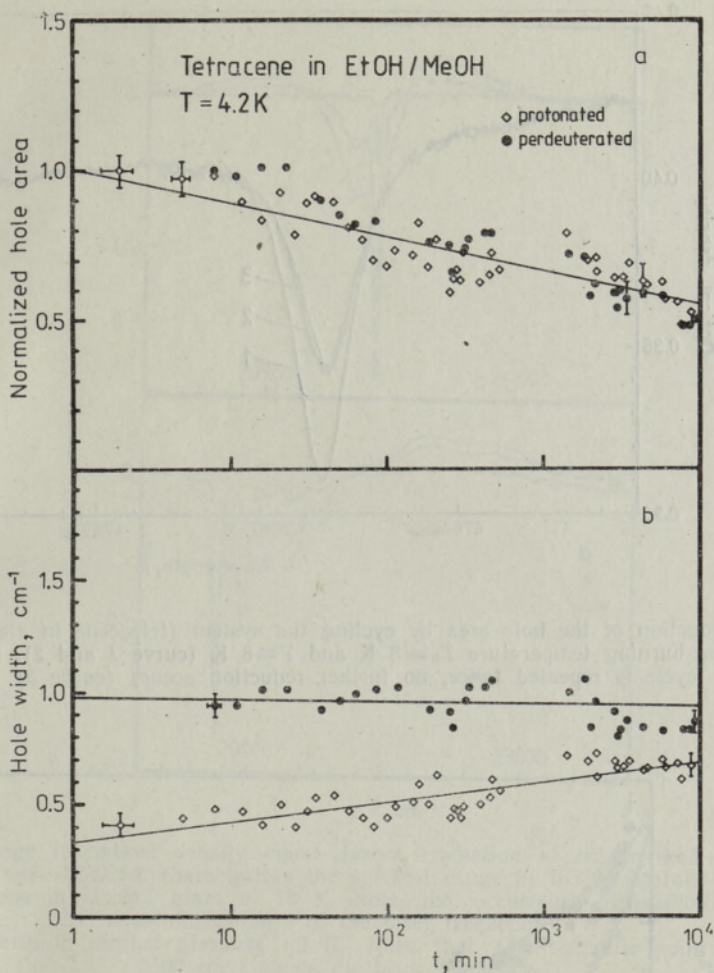


Fig. 2. Hole area (a) and hole width (b) as a function of time after burning. System: tetracene in protonated and perdeuterated alcohol glass.

Deuteration effect. Deuteration of the alcohol glass has a significant influence on the relaxation of the holes. In the quinizarin-doped system, the time evolution of both the area and the width slows down dramatically, while in the tetracene-doped system only the width is affected.

Sampling of barrier heights. Fig. 3 shows that, for a given excursion temperature (in this case 8 K), it is only the first cycle which leads to a reduction of the hole area. A second or third cycle does not lead to any further change. This suggests that for any excursion temperature there exists a related barrier height. Centers with barriers below that height relax, while those with barriers above that height are unaffected. Hence, varying the excursion temperature leads to a sampling of the distribution of barrier heights.

Annealing effects. Fig. 4 shows the thermal relaxation behavior of tetracene in alcohol glass and of quinizarin in PMMA glass. It can be seen that the thermally induced reduction of the hole area is well described by

$$A(T) \sim 1 - \sqrt{aT}, \quad (2)$$

where a is a fit parameter. This formula holds for both the photophysical

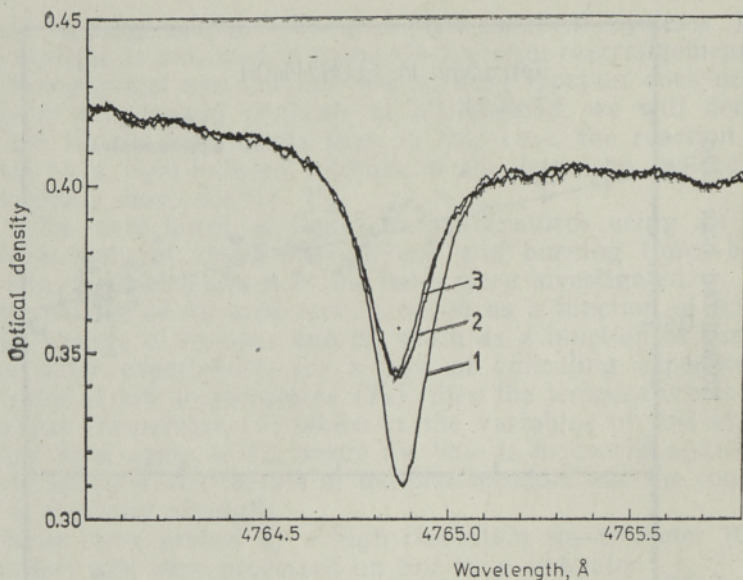


Fig. 3. Reduction of the hole area by cycling the system (tetracene in alcohol glass) between the burning temperature $T_b=3$ K and $T=8$ K (curve 1 and 2). If the same cycle is repeated twice, no further reduction occurs (curve 3).

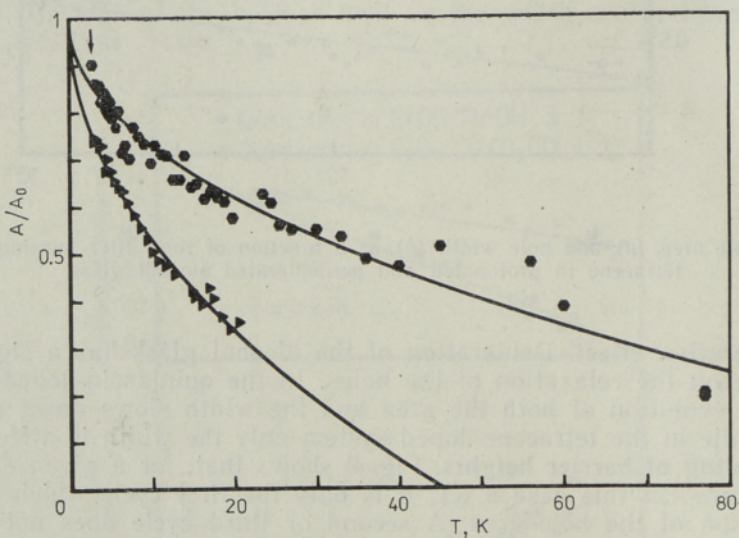


Fig. 4. Hole area as a function of cycling temperature. Note that all data points are measured at the burning temperature T_b . Systems: quinizarin in PMMA and tetracene in alcohol glass (lower trace).

and the photochemical systems. However, the slope of the annealing curve is much steeper in the photophysical case. We conclude, from this observation, that the maximum barrier height, in this system, is much lower.

The photoproduct. Fig. 5 shows the spectral distribution of the photoproduct for tetracene and quinizarin in alcohol glass. In both cases we

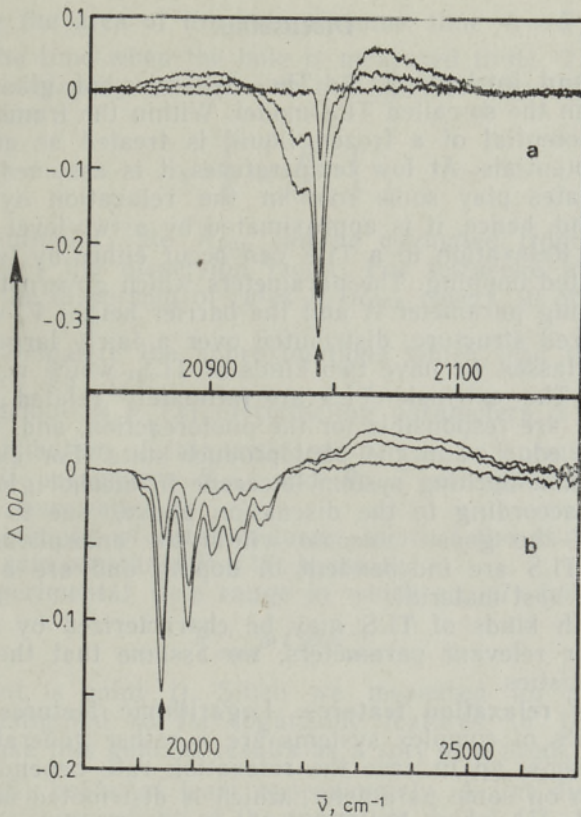


Fig. 5. Change in optical density upon laser irradiation at the marked positions (arrows). $\Delta OD > 0$ characterizes the spectral range of the photoproduct.
a — Tetracene in alcohol glass at 10 K. Note the occurrence of isosbestic points within 30 cm^{-1} of the laser frequency.
b — Quinizarin in alcohol glass at 4.2 K. Note that the isosbestic point is found 2500 cm^{-1} above the laser frequency.

plotted the change in optical density after laser irradiation. $\Delta OD > 0$ characterizes the photoproduct, while $\Delta OD < 0$ characterizes the burnt educt. We see that both systems are characterized by isosbestic points. The occurrence of an isosbestic point tells us that there is only one photoproduct state. In the quinizarin case the isosbestic point is shifted from the burning frequency to higher energies by some 2000 cm^{-1} . This is a clear evidence of the photochemical nature of the photoreaction which was suggested to be a proton transfer reaction. In the tetracene case there are two isosbestic points close to the burning frequency and well within the inhomogeneous band. We conclude that the photoreaction is closed, i.e. that all the product has to be found within the inhomogeneous band. This is a characteristic feature for a photophysical system [3]. In both systems the integrated area of the photoproduct is less than the area of the burnt hole. When this can be easily understood in the photochemical case where the molecule itself and, hence, the oscillator strength is changed, it is more difficult to understand in the photophysical case. The only obvious interpretation we can think of is that the photophysical hole-burning reaction is due to a light-induced rotation of the guest molecule within the host matrix [4]. Thereby, an anisotropic ensemble of molecules, photoselected by polarized laser light, may be transformed to a different state of orientation and, hence, one can, in principle, lose much of the original oscillator strength.

Discussion

Extrinsic and intrinsic TLS. The dynamics of glasses is usually modelled within the so-called TLS-model. Within the frame of this model the random potential of a frozen liquid is treated as an ensemble of double-well potentials. At low temperatures it is assumed that only the two lowest states play some role in the relaxation dynamics of the double well and, hence, it is approximated by a two-level system and is called a TLS. Relaxation in a TLS can occur either by tunneling or by thermal activated hopping. The parameters which govern these processes are the tunneling parameter Λ and the barrier height V , which are, due to the disordered structure, distributed over a fairly large range.

In doped glasses we have two kinds of TLS, which we call extrinsic and intrinsic. The extrinsic TLS are intimately related to the dopand molecule. They are responsible for the photoreaction, and, hence, the two states are the educt- and the photoproduct state. For example, in the photophysical hole-burning system tetracene in alcohol glass, the extrinsic TLS are, according to the discussion above, due to two different orientations of the guest molecule within the amorphous host lattice. The intrinsic TLS are independent of doping and are a characteristic quantity of the host material.

Though both kinds of TLS may be characterized by very different ranges of their relevant parameters, we assume that they both follow the same statistics.

Logarithmic relaxation features. Logarithmic features in the relaxation dynamics of complex systems are a rather general phenomenon. They always show up in case the relaxation rate depends in an exponential fashion on some parameter, which is distributed uniformly over a sufficiently broad range [3, 4, 6]. Since at 4 K, the relaxation processes occur via tunneling, the corresponding parameter is the tunneling parameter

$$\Lambda = \left(\frac{1}{2} \frac{V}{\hbar^2} m \right)^{1/2} d, \quad (3)$$

which depends on the barrier height V , the mass m of the tunneling particle and the tunneling distance d .

The relaxation rate for tunneling processes is given by

$$R = R_0 e^{-2\Lambda}. \quad (4)$$

A distribution of Λ leads to a distribution p_R of the rates R . If we assume, for a moment, that the distribution of Λ is flat in the relevant parameter range, i. e.

$$p_\Lambda(x) = \bar{p}, \quad (5)$$

then we find immediately

$$p_R(x) \sim \frac{1}{x}. \quad (6)$$

Eq. (6) leads to logarithmic time-dependent features in the relaxation behavior of the glass [3]. For example, the decay law of the hole can be determined by calculating the number of centers being at time t in the photoproduct state. This can easily be done by integrating eq. (6) from a minimum rate R_{\min} to a rate $R=1/t$, yielding

$$\frac{A(t)}{A_1} = 1 - s \ln R_1 t \quad (7)$$

with A_1 being the area of the hole at some time $t_1=R_1^{-1}$ (t_1 may, for example, be the time when the hole is measured first). The slope factor s , which is the quantity measured in this kind of experiments, turns out to be of the form

$$s = \left[\ln \frac{R_1}{R_{\min}} \right]^{-1}. \quad (8)$$

Hence, the minimum rate R_{\min} can be estimated from the measured slope. We call s the dispersion factor. For tetracene in alcohol glass we find that the dispersion of rates R_1/R_{\min} covers 10 orders of magnitude.

We just summarize the approximations which lead to the logarithmic decay law eq. (7):

- i) the distribution $p_\Lambda(x)$ of tunneling parameters Λ is flat;
- ii) the distribution of rate constants p_R can be normalized by introducing cut off parameters R_{\max} and R_{\min} , corresponding to the maximum and minimum rate;
- iii) the dispersion of rates is large so that the number of centers relaxing with rate constants $R=1/t$ is small;
- iv) the experimental time range in which eq. (7) holds is given by

$$R_{\min}^{-1} \gg t \gg R_{\max}^{-1}. \quad (9)$$

Most important is point i). Since we measured for all glasses and polymers investigated so far logarithmic features in their relaxation kinetics, we take this general results as a sort of a proof that p_Λ is flat, i.e. that eq. (5) holds, at least approximately. A flat distribution of Λ is also the basic ingredient of the tunneling model [7]. The exact form of the distribution is rather unimportant, because, in case the dispersion is large, deviation from the log-features are far outside the experimentally available range. As to the time-dependent line broadening, we merely note that a similar calculation can be done in this case [3], starting from the well-known fact that the irreversible linewidth γ_D is proportional to the number density of configurational changes $n(t-t_0)$ having occurred within the time range $t-t_0$ after burning [8, 9, 3]:

$$\gamma_D = cn(t-t_0). \quad (10)$$

To calculate $n(t-t_0)$, we assume that the polymer or glass can sample a small area in configuration space around its original point where it has been trapped. We assume that this motion in configuration space occurs via independent, rather local displacement of certain atoms, molecules or small groups of atoms. At low temperatures, atoms (or groups of atoms) can move from one minimum to the other by tunneling processes. Again, a flat distribution of the tunneling parameter accounts for almost all experimental data. Hence, the rates of configurational relaxation are distributed according to eq. (6). This, again, leads to logarithmic features in the time-dependent line broadening:

$$\gamma(t-t_0) = \gamma_0 + c \left[\ln \frac{R_{\max}}{R_{\min}} \right]^{-1} \ln R_{\max} t. \quad (11)$$

γ_0 is the time-independent contribution to the width and c can, in our experiments, be considered as a constant. Again, the slope factor depends on the dispersion of rates. For a quantitative evaluation, however, the constant c has to be known.

This treatment of hole-broadening shows that not only the dynamic processes, like phonon scattering, but also the extremely slow processes,

like structural relaxation, can significantly contribute to the observed width [10]. We also stress that the time-dependent logarithmic features in optical line-broadening were considered by D. A. Fushman [11].

The deuteration effect. The quinizarin — as well as the tetracene system (Fig. 1 and 2) show a strong influence of glass deuteration on the line-broadening. However, only the quinizarin system shows an influence of deuteration on hole-filling. Since the quinizarin reaction is a light-induced proton transfer, a deuteration effect is expected when the reaction is reversed and the hole is filled. In case of the tetracene reaction we argued above that it is most likely a rotation of the guest molecule in the host matrix. Since, in this case, deuteration of the host glass does not change masses involved in the hole-filling reaction, there is no isotope effect.

We conclude from these experiments that hole-filling and line-broadening are due to relaxation of different types of TLS. The hole-filling is caused by the relaxation of the photoactive extrinsic TLS, whereas the hole-broadening is due to the relaxation of the intrinsic TLS, which obviously are proton-tunneling systems.

Deuteration of the alcohol glass slows down the glass relaxation in a dramatic way. This can be understood from eqs. (7), (8) and (11). The arguments are as follows: The tunneling matrix element depends, in an exponential fashion, on the square root of the mass of the tunneling particle:

$$\Delta_0 \sim \exp \{-\sqrt{m}\Lambda'\} \quad (12)$$

with Λ' depending on the barrier height and the tunnel distance (see eq. (3)).

$$\Lambda' = \frac{d}{\hbar} \sqrt{V_0}. \quad (13)$$

In case Λ' is large (which holds for the slow rates), Δ_0 may be changed by order of magnitudes if m is changed by a factor of 2. Since R_{\min} , which characterizes the extremely slow processes in the TLS relaxation, appears in the slope factor of the area as well as of the width (eq. (8) and (11)), we can understand the significant change in the slope factor upon deuteration, which shows up even in the logarithmic form.

We treated the photoproduct and the educt state (i.e. the extrinsic TLS) as a two-level system which obeys the same statistics as the two-level systems of the configurational changes of the host glass, i.e. the intrinsic TLS. That this treatment is correct, seems to be justified by the experimental results. However, the nature of these two kinds of TLS as well as their relevant parameter ranges are quite different, as is obvious from the measured deuteration effect in the tetracene doped glass: while the configurational changes, which lead to line-broadening, originate from proton-tunneling (as documented by the observed deuteration effect), a quite different process has to be responsible for the hole-filling reaction. Since the photoreaction is due to a light-induced rotation of the dopand molecule, as argued above, the relaxation process which leads to hole-filling is most probably due to a rotational tunneling of the guest molecule in the amorphous host [4].

Annealing effects. In this section we want to explain the irreversible changes of the area of a hole burnt at low temperatures as a function of the excursion temperature. We employ again the concept of independent two-level systems. As far as the area is concerned, it is clear that the configurational changes are related to the back reaction from the product to the educt state. In the photophysical system this corresponds

to a thermally induced reorientation of the guest molecule in the matrix, whereas in the photochemical case it corresponds to a rearrangement of an external hydrogen bond between probe molecule and solvent to an internal hydrogen bond [12].

Again, we have to calculate the number of TLS centers having changed their position, but this time the variable is not the time, it is, instead, the excursion temperature [4].

We start this calculation on the basis of what we have already learned from the time-dependent experiments, namely the assumption of a flat distribution of the tunneling parameter Λ (eq. 3). Since Λ depends on the barrier height V , we can determine the distribution of barrier heights from eq. (3) and (5). We get

$$p_V(x) \sim \frac{1}{\sqrt{x}}. \quad (14)$$

We can normalize this distribution assuming again cut off values V_{\max} and V_{\min} , corresponding to the maximum and the minimum barrier height. Eq. (14) holds even in case we assume a distribution in the tunneling distances as long as d and V are independent. The observed irreversible changes occur via thermally activated crossing of the barriers involved. For the following, one could, in principle, distinguish a variety of different cases, determined by the relative magnitude of the burning temperature T_b , the excursion temperature T , and V_{\max} and V_{\min} . For most of the cases of thermally induced hole recovery which we have investigated, it turns out that the situation is best described by

$$V_{\min} < \alpha T_b, \quad \alpha T < V_{\max}, \quad (15)$$

α being a factor which is discussed below.

Since we burn the holes around 3 K, relation (15) implies that we have extremely small barriers in the systems considered. For the following we assume that all changes are brought about by activated processes, the rates of which depend in an exponential fashion on the barrier involved.

$$R = R_0 e^{-V/hkT}, \quad (16)$$

R_0 being the attempt frequency, which may depend on temperature.

In case the typical time scale of the experiment (i.e. the time scale to cycle the system between T_b and T) is t , all those TLS characterized by rates $R^{-1} \leq t$ can cross the barrier and contribute to a reduction of the hole area. Hence, for a given excursion temperature, there is a marginal barrier height V_T which can be crossed, namely

$$V_T = kT \ln R_0 t. \quad (17)$$

From eq. (17) we conclude that it is only the excursion temperature which determines the marginal barrier height, because all other dependencies, e.g. on the experimental time or on the attempt frequency, appear under the logarithm and, hence, their variation does not show up. The log-factor can be easily estimated. Assuming for R_0 something like 10^{12} s^{-1} and for t a typical scale of 100 s, we get

$$\ln R_0 t \approx 30. \quad (18)$$

Hence, the sampled barrier height (i.e. the marginal barrier) is accurate within

$$\frac{\Delta V}{V} = \frac{1}{\ln R_0 t} \frac{\Delta t}{t}. \quad (19)$$

For $\Delta t/t \approx 1$ the uncertainty in the barrier height is on the order of $V/30$.

We can calculate the number of centers, which are, at a certain excursion temperature T , still in the product state, by integrating the properly normalized distribution function (eq. 14) from the marginal barrier height V_T (eq. 17) to V_{\max} . This integral yields the area of the hole as a function of the excursion temperature. For convenience, we normalize the result to the extrapolated area A_0 of the hole at the temperature $T=0$, to get the quantity $A(T)/A_0$, which is measured

$$\frac{A(T)}{A_0} = 1 - \sqrt{\frac{k \ln R_0 t}{V_{\max}}} T. \quad (20)$$

According to eq. (20), the parameter α of eq. (2) can be identified with $\frac{k \ln R_0 t}{V_{\max}}$. The fit curves in Fig. 4 are calculated according to this equation. As can be seen, the fit is quite good. Since $\ln R_0 t$ can be estimated (see eq. 18), the fit yields a value for the upper bound of the barrier distribution V_{\max} . For tetracene in alcohol glass V_{\max} is of the order of 800 cm^{-1} , while for quinizarin in PMMA it is of the order of 3000 cm^{-1} in both, the polymer and the alcohol glass. The difference in the maximum barrier heights reflects the difference between a photophysical and a photochemical hole-burning systems. Obviously, in the special photochemical system considered here; namely quinizarin in PMMA glass, the barrier height of the photoproduct is strongly determined by the nature of the amorphous state, in agreement with the fact that the photoproduct state corresponds to a hydrogen bond between probe molecule and amorphous host matrix [10].

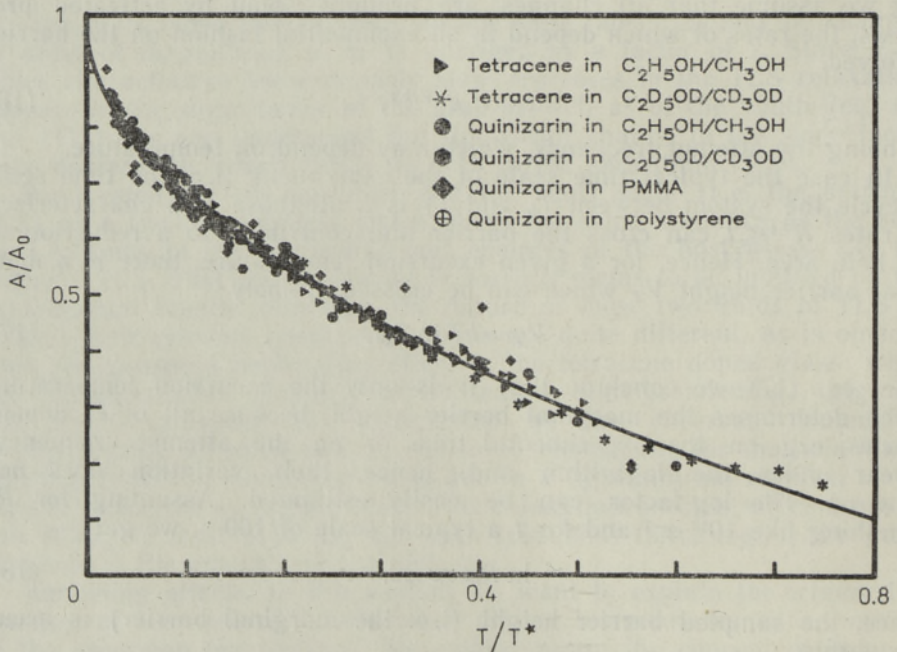


Fig. 6. Hole area as a function of a reduced temperature T/T^* (see the text). The scaling behavior is quite obvious. The systems investigated are shown in the figure.

Scaling behavior. Eq. (20) shows scaling behavior. We can introduce a system specific temperature T^* , given by

$$T^* = V_{\max}/k \ln R_0 t, \quad (21)$$

and plot the temperature in units of T^*

$$\frac{A(T/T^*)}{A_0} = 1 - \sqrt{T/T^*}. \quad (22)$$

This yields a master curve on which all our data points should fall. Fig. 6 shows the result, which is quite convincing. We stress that very different systems, glasses and polymers, with very different parameters T^* have been investigated (see Fig. 4).

We summarize this paragraph by stating that both the time-dependent and the temperature-dependent features of the relaxation phenomena of amorphous solids can be understood on the same physical basis, namely that the distribution of the tunneling parameter Λ is flat, which implies that the barrier heights are distributed according to eq. (14). Though the experimental points follow eq. (22) quite well, we stress that we would expect a deviation from the theoretical curve in case

$$aT < V_{\min}; \quad (23)$$

V_{\min} does not appear in our calculation because we assumed that it is small compared to V_{\max} .

We also denote that discrete structures in the barrier height distribution, as could, for example, be the case in proteins, would drastically change the annealing behavior.

Summary

We investigated time-dependent and temperature-dependent relaxation phenomena of doped organic glasses and polymers. We showed that the relaxation function is dominated by logarithmic features due to a large dispersion of rates. The dispersion factor was interpreted in terms of the ratio of the maximum to the minimum relaxation rate which could be determined from the experiment. It was shown that this ratio covers 10 orders of magnitude. Deuteration slows down the relaxation enormously. We conclude that in alcohol glass there are configurational changes due to hydrogen tunneling processes.

As to the thermally induced configurational changes of the doped glasses leading to hole-filling, we concluded that the relevant barriers follow a $V^{-1/2}$ distribution, in agreement with the tunneling model.

To get an idea about the nature of the photoreactive processes involved, we investigated the spectral distribution of photoproducts. In the photophysical hole-burning case the «photoreaction» is most likely a light-induced rotation of the guest molecule in the host matrix. All the product is found in the same spectral range as the educt. For quinizarin in alcohol- and PMMA-glass we definitely showed that the reaction is photochemical in nature. The product is shifted by more than 2500 cm^{-1} towards higher energies; hence, it is well outside the inhomogeneous band.

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SPEKTRAALSÄLKUDE AJAST JA TEMPERatuurIST SÖLTUVA RELAKSATSIOONI ISEÄRASUSED

On uuritud lisandiga orgaaniliste klaaside konfiguratsioonilist relaksatsiooni, registreerides spektraalsätkude muutusi aja- ja temperatuurifunktsioonina. Konfiguratsioonilised muutused toimuvad kas tunnelprotsesside või termiliselt aktiveeritud protsesside kaudu. Äärmiselt madalatel temperatuuridel prevaleerivad tunnelprotsessid tingivad relaksatsioonifunktsiooni logaritmsõltuvuse, millest saab informatsiooni relaksatsioonikiiruste dispersiooni kohta. Aktiveeritud protsessid määravad temperatuurisõltuvuse. On näidatud, et aktivatsioonibarjääride jaotus on lähedane $1/\sqrt{V}$ -sõltuvusele, mida saab vahetult mõõta, ning demonstreeritud ajast ja temperatuurist sõltuvate relaksatsioonikarakteristikute mastaap-invariantset iseloomu.

B. КОХЛЕР, И. ФРИДРИХ

ВРЕМЕННАЯ И ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТИ РЕЛАКСАЦИИ ПАРАМЕТРОВ СПЕКТРАЛЬНЫХ ПРОВАЛОВ

Путем наблюдения изменения спектральных провалов как функции времени и температуры изучена конфигурационная релаксация примесных органических стекол. Конфигурационные изменения происходят вследствие туннельных или термических активационных процессов. При экстремально низких температурах туннельные процессы преобладают, что ведет к логарифмическим законам релаксации, откуда может быть получена информация о дисперсии скоростей релаксации. Активационные процессы определяют температурную зависимость. Показано, что распределение активационных барьеров близко к зависимости $1/\sqrt{V}$, которая может быть измерена наиболее прямым путем. Продемонстрировано, что параметры релаксации, зависящие от времени и температуры, обнаруживают свойство скейлинга.