

LOGARITHMIC DECAY OF PHOTOCHEMICALLY INDUCED TWO-LEVEL SYSTEMS IN AN ORGANIC GLASS

W. BREINL, J. FRIEDRICH and D. HAARER

Physikalisches Institut der Universität Bayreuth, 8580 Bayreuth, Federal Republic of Germany

Received 1 March 1984

The recovery dynamics of photochemically labeled, metastable sites are investigated via photochemical hole burning in the visible spectral range. It is shown that, in a glass matrix, the recovery follows a logarithmic law. The experimental data are interpreted with the concept of two-level systems (TLSs). This interpretation is supported by the observed large isotope effect. The tunneling rates for protons and deuterons and the heights of the pertinent tunneling barriers are discussed.

Recent progress in site-selective optical spectroscopy has increased the spectral resolution in amorphous materials by several orders of magnitude. This immense increase in resolution has created novel tools for investigating low-energy excitations in amorphous solids, such as the two-level systems (TLSs) [1] which have been introduced for interpreting specific heat anomalies [2–4] and anomalies in ultrasonic absorption [5][†]. In this article the method of photochemical hole burning (PHB) is used as a sensitive optical probing technique for measuring low-temperature tunneling processes. The observed logarithmic decay laws of photochemical states are, for the first time, linked to the tunneling dynamics of amorphous solids. The evidence for tunneling phenomena is supported by isotopic effects.

Photochemical hole burning has also been used recently for experimental investigations of optical relaxation processes in amorphous organic solids [7–10] and for measuring time dependent photochemical changes [11]. The theoretical understanding of the observed optical linewidths is based on various models which use the notion of low-lying excitations in amorphous solids [12–14].

In the following the time dependence of the tunneling of photochemically labeled sites of dye molecules in an amorphous organic host material is investi-

gated. The photoreactive "sites" are protons and deuterium atoms of the dye molecule quinizarin (1,4-dihydroxyanthraquinone, DAQ). The dye molecules are dissolved in an alcohol glass matrix (EtOH/MeOH, 3:1) in a concentration of 2×10^{-5} mole/mole. The photochemical labeling of the dye sites is performed with narrow-band laser excitation. The mechanism of the laser photochemistry is believed to be due to the breaking of an intramolecular hydrogen bond and the formation of an intermolecular hydrogen bond as is symbolically shown in fig. 1. Optical experiments have shown, that the proton transfer photochemistry leads to a photoproduct which absorbs at energies which are several hundred wavenumbers above the reactant state [15].

The low-temperature laser photochemistry at the frequency ω_L leads to the disappearance of absorbers at energies of approximately $\hbar\omega_L$ and thus to a "dip" in the absorption spectrum which is referred to as the photochemical hole. Fig. 1 shows a photochemical hole at 19436 cm^{-1} after a few minutes of laser irradiation with either a N_2 -pumped dye laser or an Ar-ion laser. The total irradiation energy was typically about 100 mJ/cm^2 . The insert in fig. 1 shows the hole on an expanded energy scale immediately after the laser photochemistry (monochromator resolution 0.15 cm^{-1}). The full circles correspond to a Lorentzian line profile reproducing the measured curve within experimental error.

[†] For a comprehensive review of amorphous solids, see ref. [6].

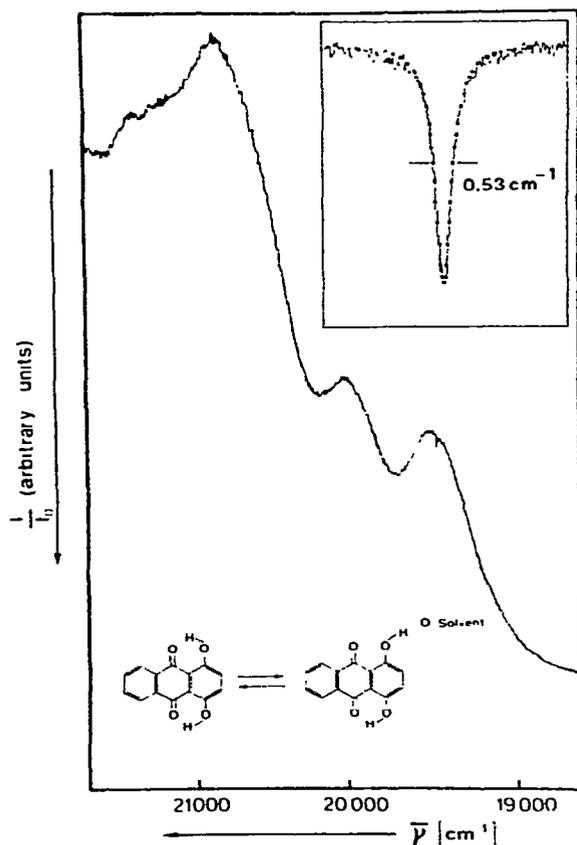


Fig. 1. Absorption spectrum of 1,4-dihydroxyanthraquinone in an EtOH/MeOH (3:1, v/v) glass at 1.35 K. The dip at 19436 cm^{-1} is the photochemical hole, measured 2 min after hole burning. An expanded scale is shown in the insert (spectrometer resolution 0.15 cm^{-1}). The full circles correspond to a calculated Lorentzian line profile.

As to the temporal changes of the photochemical hole, there are basically two recovery mechanisms: first, ground-state tunneling processes, corresponding to a redistribution of sites of those optical centers (and their microscopic environment) which were not affected by the laser photochemistry. These processes broaden the photochemical hole via spectral diffusion [16], yet without changing its area. The redistribution processes have been discussed previously in terms of the pertinent TLS parameters [17]. The second mechanism, which affects the photochemical hole, is the back-reaction of the photoproduct, i.e. the back-transfer of the hydrogen or deuterium atom. The change in

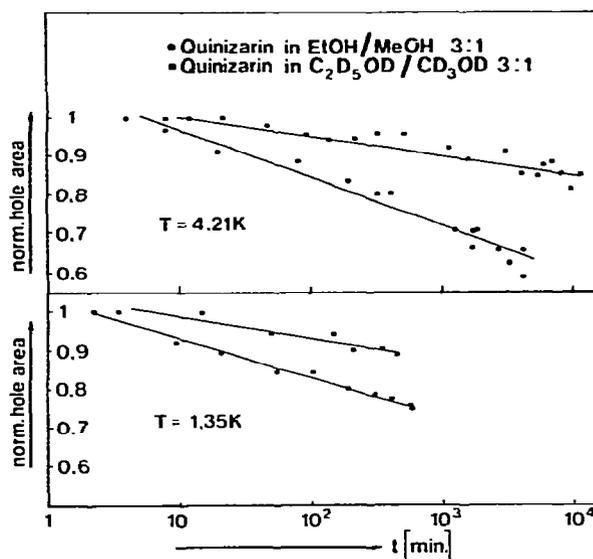


Fig. 2. Decay of the normalized hole area for the protonated and deuterated sample at two different temperatures. The first data point of the protonated sample at 1.35 K corresponds to the hole of fig. 1.

integrated hole area which is investigated in this paper, is solely due to this process.

The experimental data for the decay of the hole area are shown in fig. 2 on a logarithmic time scale for both, deuterated and protonated material and for two different temperatures. A logarithmic law describes the decay processes within experimental error. In our opinion, there is an analogy between our experiments and the experiments of Fox et al., who observe a logarithmic recovery of the microwave echo amplitude in As_2S_3 glass [18]. A remarkable feature of the data is the pronounced isotope effect in the decay dynamics of the hole area.

Our discussion of the observed logarithmic recovery process, including the isotope effect, will be based on theories of tunneling processes in amorphous systems: Since the light induced proton transfer reaction is matrix controlled, it is reasonable to introduce the concept of photochemical TLS, characterizing the educt and the product ground state with a wide distribution of barrier heights and energy asymmetries, in analogy to the "ordinary" TLS of the glassy state. This distribution results in a wide variation of the back-transfer rates R of the proton or deuteron, which we

assume to be governed by tunneling processes at the temperatures of the experiment. Since typical energies of the photochemical TLS are known to be well above the thermal energy of the sample, the tunneling rates are, in our experiment, rather independent of the temperature (see fig. 2). With these assumptions the distribution of back transfer rates follows from the theory of TLS states in glasses [3,4,19]:

$$P(R) = \frac{P_0}{2} \frac{1}{R(1 - R/R_{\max})^{1/2}}. \quad (1)$$

P_0 is a constant and R_{\max} is the maximum relaxation rate.

It is evident that, for various experimental observation times, various relaxation rates of the distribution are probed. The longer the time period t during which one observes the system, the smaller will be the pertinent relaxation rates R of the system according to the relation

$$R = 1/t. \quad (2)$$

In order to answer the question as to how many photochemical states have tunneled back to the educt state, one has to integrate eq. (1) and obtains the following relation

$$N = \frac{P_0}{2} \int_R^{R_{\max}} \frac{dR}{R(1 - R/R_{\max})^{1/2}} \\ = \frac{P_0}{2} \ln \left(\frac{1 + (1 - R/R_{\max})^{1/2}}{1 - (1 - R/R_{\max})^{1/2}} \right). \quad (3)$$

It has to be pointed out, that the distribution [eq. (1)] of relaxation rates is not normalized. The normalization can be achieved by introducing a limiting value for R . This value, R_{\min} , corresponds to a cutoff value in barrier heights. With this definition of R_{\min} and with the total number of photochemical states contributing to the photochemical hole being N_0 , the number of molecules being in the educt state after the time t has elapsed, is given by

$$\frac{N}{N_0} = \left[\ln \left(\frac{1 + (1 - R_{\min}/R_{\max})^{1/2}}{1 - (1 - R_{\min}/R_{\max})^{1/2}} \right) \right]^{-1} \\ \times \ln \left(\frac{1 + (1 - 1/R_{\max} t)^{1/2}}{1 - (1 - 1/R_{\max} t)^{1/2}} \right). \quad (4)$$

In the time regime, $R_{\max}^{-1} \ll t \ll R_{\min}^{-1}$, the normalized hole area can be calculated from eq. (4) as

$$A/A_0 = 1 - [\ln(4R_{\max}/R_{\min})]^{-1} \ln(4R_{\max}t). \quad (5)$$

Eq. (5) yields a logarithmic decay law with a slope determined by the ratio between the fastest and the slowest rate. Since, however, the time scale of our experiment is long compared to R_{\max}^{-1} , we do not observe, when we start our probing experiment at t_1 , the total hole area A_0 . Instead we observe just a fraction of it, namely $pA_0 = A_1$. Centers with $R > 1/t_1$ have already tunneled back to the educt state, and, hence, have filled the hole to some extent. Taking this into account by multiplying eq. (5) with p^{-1} , we see, that the slope of the logarithmic decay law is now given by the ratio $(4R_{\max}/R_{\min})^p$. This ratio is determined by the fastest and the slowest rates which can be observed *experimentally*. Since the fastest rate which can be measured by our experiment is $R_1 = 1/t_1$, we have

$$(4R_{\max}/R_{\min})^p = R_1/R_{\min} = 1/t_1 R_{\min}. \quad (6)$$

Inserting eq. (6) into eq. (5) we arrive at

$$A/A_1 = 1 - [\ln(R_1/R_{\min})]^{-1} \ln(t/t_1). \quad (7)$$

Eq. (7) is appropriate for evaluating our experimental data. From fig. 2, one gets the following slopes: for the proton: 12.14%/decade \pm 8% and for the deuteron: 5.26%/decade \pm 8%.

The corresponding ratios of the rates are:

$$(R_1/R_{\min})_H \approx 1.2 \times 10^8.$$

$$(R_1/R_{\min})_D \approx 2.4 \times 10^{19}.$$

The above numerical values should be taken as rough estimates due to the simplicity of the underlying model.

It is rather interesting to discuss the very large isotope effect in some more detail. We know that the tunneling matrix element can be written as:

$$\Delta_0 = h\Omega \exp(-\lambda) = h\Omega \exp(-m^{1/2}\lambda'), \quad (8)$$

with λ' being determined by the TLS barrier heights. Assuming that deuteration does not change the potential distribution of the glass [20] one can conclude from eq. (8) that the deuteration effect is small for fast rates and large for slow rates. If one were to explain the deuteration effect on the basis of eq. (8) and the following relation,

$$\lambda = (2mV_0/\hbar^2)^{1/2} d/2, \quad (9)$$

one would have to assume maximum barrier heights on the order of several 1000 cm^{-1} (for $d = 5 \text{ \AA}$). These maximum barrier heights are well above the glass temperature, indicating that the glass transition is certainly *not* determined by the highest barriers but by low barriers which allow segments of the glassy matrix to move thus leading to a "decay" of barriers which are high in the frozen state and which are lowered during the melting process by a collective motion.

In conclusion, we have shown, that the statistical properties of the amorphous state govern the decay of photochemical states. The range of the decay rates is immense and extends over many orders of magnitudes. The experimentally determined isotope effect allows one to reach conclusions about maximum barrier heights, which are well above energies corresponding to the glass temperature.

The authors acknowledge the support of the Stiftung Volkswagenwerk.

References

- [1] G.J. Small, in: Spectroscopy and excitation dynamics of condensed molecular systems, eds. V.M. Agranovich and R.M. Hochstrasser (North-Holland, Amsterdam, 1983).
- [2] R.C. Zeller and R.O. Pohl, Phys. Rev. B4 (1971) 2029.
- [3] P.W. Anderson, B.I. Halperin and C.M. Varma, Phil. Mag. 25 (1972) 1.
- [4] W.A. Philips, J. Low Temp. Phys. 7 (1972) 351.
- [5] S. Hunklinger, in: Festkörperprobleme XVII, ed. J. Treusch (Vchweg, Braunschweig, 1977).
- [6] W.A. Philips, ed., Amorphous solids (Springer, Berlin, 1981).
- [7] J.M. Hayes, R.P. Stout and G.J. Small, J. Chem. Phys. 74 (1981) 4266.
- [8] J. Friedrich, H. Wolfrum and D. Haarer, J. Chem. Phys. 77 (1982) 2309.
- [9] H.P.H. Thijssen, A.F.M. Dicker and S. Völker, Chem. Phys. Letters 92 (1982) 7.
- [10] H.P.H. Thijssen, S. Völker, M. Schmidt and H. Port. Chem. Phys. Letters 94 (1983) 537.
- [11] E. Cuellar and G. Castro, Chem. Phys. 54 (1981) 217.
- [12] S.K. Lyo and R. Orbach, Phys. Rev. 84 (1981) 2029.
- [13] S.K. Lyo, Phys. Rev. Letters 48 (1982) 688.
- [14] P. Reineker and H. Morawitz, Chem. Phys. Letters 86 (1982) 359; H. Morawitz and P. Reineker, Solid State Commun. 42 (1982) 609.
- [15] J. Friedrich and D. Haarer, Chem. Phys. Letters 74 (1980) 503.
- [16] J.L. Black and B.I. Halperin, Phys. Rev. B16 (1977) 2879.
- [17] J. Friedrich, D. Haarer and R. Silbey, Chem. Phys. Letters 95 (1983) 119.
- [18] D.L. Fox, B. Golding and W.H. Haemmerle, Phys. Rev. Letters 49 (1982) 1356.
- [19] J. Jäckle, Z. Physik 257 (1972) 212.
- [20] R.P. Bell, The tunnel effect in chemistry (Chapman and Hall, London, 1980) ch. 4.