

REVERSIBLE AND IRREVERSIBLE LINE BROADENING OF PHOTOCHEMICAL HOLES IN AMORPHOUS SOLIDS

J. FRIEDRICH, D. HAARER

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

and

R. SILBEY

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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We discuss the temperature dependence of photochemical hole line shapes in experiments where the burning and the measuring temperature are either identical or different. We show that this temperature dependence will be different for two cases. Analysis of the line shape of photochemical holes yields information on irreversible processes in organic glasses.

Photochemical hole burning (PHB) has emerged as a powerful technique to study T_1 and T_2 dephasing processes in organic and inorganic [1–5] solids. In crystalline systems the technique of PHB has been used to investigate the temperature dependence of the optical relaxation parameters according to the relation

$$\Gamma_h(T) = 2\gamma(T) . \quad (1)$$

Γ_h is the measured width of the photochemical hole, γ is the homogeneous linewidth characterized by the longitudinal and transverse relaxation times T_1 and T_2^* : $\gamma/2 = 1/2T_1 + 1/T_2^*$ (rad/s).

The above relation holds for short burning times and low laser powers [6,7]. The temperature dependence of the hole width is solely determined by the temperature dependence of the relaxation parameters. Hence, the width is reversible if the temperature is cycled from low to high values and vice versa. Recently, photon echo techniques [8] have been applied to non-photochemical hole burning, opening the possibility of using this powerful technique for PHB measurements also.

A completely different situation holds if PHB experiments are performed in amorphous host materials. Since glasses are, by definition, characterized by a non-equilibrium state of their microscopic parameters, one has to discuss the validity of eq. (1) under the various experimental conditions.

The temperature dependence of Γ_h can be measured in two ways: First (case A), the temperature T can be chosen such that the hole burning photochemistry and the line shape analysis are performed at the same temperature. This experiment requires a virgin sample, i.e. a sample without photochemical hole, for each experimental data point of the $\Gamma_h(T)$ dependence. Various experiments have been performed using this method [9]. In crystalline systems eq. (1) would hold for this experiment. In amorphous systems the situation is not quite as clear [10]. Even though the validity of eq. (1) is generally assumed, its experimental verification has not been fully established yet.

The second way (case B) to perform the temperature dependent PHB experiments is different [10]: One burns the photochemical hole at the lowest accessible temperature T_0 . Then one raises the temperature in well-defined steps and measures the linewidth $\Gamma_h(T)$. Note that in this case the burning temperature and the measuring tem-

perature are not the same (except for the data point with the lowest temperature T_0). Even for crystalline systems, eq. (1) would have to be modified. In amorphous systems for which irreversible spectral diffusion processes occur due to the TLS (two level systems) degree of freedom, eq. (1) has to be further modified to include the above spectral diffusion processes. In the following we present a model calculation of the line shape function for an experiment of type B. The model will include both reversible and irreversible contributions to the linewidth. We assume that these spectral diffusion processes are too slow to affect the homogeneous line shape.

For the line shape function of a photochemical hole one has to calculate the site distribution function of centers which are converted to a photoproduct which absorbs at a wavelength far removed from the original absorption band. Hence the site distribution function after burning is given by

$$N_0(\omega') = N_{\text{inh}}(\omega') - a(t)\pi^{-1}\gamma(T_0)/[(\omega' - \omega_L)^2 + \gamma^2(T_0)] \quad (2)$$

For simplicity it was assumed that the burning process reproduces the natural line shape function. $\gamma(T_0)$ is the homogeneous width of the photoreactive species at the temperature T_0 , ω_L the laser frequency and $a(t)$ the fraction of molecules burnt during an irradiation time t .

So far the system was considered as an ensemble of "frozen in" optical centers absorbing at the various frequencies ω' .

Now one has to consider how tunneling or thermal activated hopping processes between TLS levels can modify the above equation by modifying the site distribution function $N_0(\omega')$. $N_{\text{inh}}(\omega')$ will, before photochemistry is performed, represent a stationary distribution, i.e. it is unchanging in time. This distribution is gaussian and can, with good approximation, be considered as being independent of temperature. Hole burning will produce a narrow dip in $N_{\text{inh}}(\omega')$ [eq. (2)], and this represents a potentially non-stationary distribution, for one may assume that, if the system has any degrees of freedom given by TLS tunneling or hopping processes, these processes will tend to restore the original stationary distribution $N_{\text{inh}}(\omega')$. This will occur because the number of molecules which can fill the hole by these processes will be larger than those to deepen the hole. This could be called a population gradient in frequency space quite in analogy to the concentration gradient governing chemical diffusion processes. The number of centers which are able to redistribute after the population gradient has been produced by hole burning is a function of temperature. We assume that at the burn temperature, T_0 , the probability of a center tunneling is zero, but as we raise the temperature, the probability of a center tunneling from ω' to $\omega + \Delta\omega$ is given by $P(\omega \rightarrow \omega' + \Delta\omega; T)$. The final site distribution $N_f(\omega', T)$ after tunneling is related to the initial site distribution $N_0(\omega')$ by

$$N_f(\omega', T) = N_0(\omega') - N_0(\omega') \sum_{\Delta\omega} P(\omega' \rightarrow \omega' + \Delta\omega; T) + \sum_{\Delta\omega} P(\omega' + \Delta\omega \rightarrow \omega'; T) N_0(\omega' + \Delta\omega) \quad (3a)$$

In this the second term represents tunneling away from ω' and the third term tunneling into ω' . We now introduce three assumptions: (a) the inhomogeneous distribution, $N_{\text{inh}}(\omega')$ is stationary, i.e. independent of the tunneling processes; (b) $P(\omega' \rightarrow \omega' + \Delta\omega; T) = K(T, T_0) \exp[-(\Delta\omega)^2/\sigma^2] (\pi^{1/2}/\sigma)$, where $K(T, T_0)$ is the fraction of centers which can tunnel at T (all of which were frozen at T_0)[†] and the gaussian distribution is the range of new frequencies which can be reached from ω' by tunneling processes[‡]; (c) $K(T, T_0)$ and σ are independent of ω' . Assumption (a) means that if $N_{\text{inh}}(\omega')$ is substituted for $N_0(\omega')$, $N_f(\omega', T) = N_{\text{inh}}(\omega')$. Therefore

$$0 = -N_{\text{inh}}(\omega') \sum_{\Delta\omega} P(\omega' \rightarrow \omega' + \Delta\omega; T) + \sum_{\Delta\omega} P(\omega' + \Delta\omega \rightarrow \omega'; T) N_{\text{inh}}(\omega' + \Delta\omega) \quad (3b)$$

Subtracting (3b) from (3a) gives,

[†] Recently, Jackson [11] has reformulated the present theory taking into account the possibility of tunneling at T_0 .

[‡] In some systems, a lorentzian diffusion kernel may be preferable to a gaussian. In this case, the hole line shape will be lorentzian at all temperatures.

$$N_f(\omega', T) = N_0(\omega') - K(T, T_0)[N_0(\omega') - N_{\text{inh}}(\omega')] \sum_{\Delta\omega} \exp(-\Delta\omega^2/\sigma^2)(\pi^{1/2}/\sigma) \\ + K(T, T_0) \sum_{\Delta\omega} [N_0(\omega' + \Delta\omega) - N_{\text{inh}}(\omega' + \Delta\omega)] \exp(-\Delta\omega^2/\sigma^2)(\pi^{1/2}/\sigma). \quad (3c)$$

σ is directly related to the width of the TLS asymmetry distributions in the ground and in the excited state. This width has lately been estimated for a specific PHB system [10].

If one is only interested in the spectral line shape function of the hole rather than in the line shape function of the entire absorption profile, one can define $\delta N_0(\omega')$ and $\delta N_f(\omega')$ as

$$\delta N_0(\omega') = N_{\text{inh}}(\omega') - N_0(\omega'), \quad \delta N_f(\omega') = N_{\text{inh}}(\omega') - N_f(\omega'), \quad (4)$$

where δN_f is the number of molecules determining the hole after the above described frequency redistribution. With eq. (4), we can rewrite eq. (3) as follows

$$\delta N_f(\omega') = [1 - K(T, T_0)]\delta N_0(\omega') + K(T, T_0) \int \delta N_0(\omega' + \Delta\omega) \exp(-\Delta\omega^2/\sigma^2)(\pi^{1/2}/\sigma) d\Delta\omega \quad (5)$$

changing the sum in (3) to an integral. The line shape $L_f(\omega)$ of a hole burnt at T_0 and measured at a temperature T is given by the convolution of δN_f with the natural line shape function $g_T(\omega - \omega')$ (whose temperature dependence represents reversible line broadening of the hole)

$$g_T(\omega - \omega') = \pi^{-1} \gamma(T) / [(\omega - \omega')^2 + \gamma^2(T)] \quad (6)$$

and

$$L_f(\omega, T) = \int d\omega' \delta N_f(\omega') g_T(\omega - \omega') = [1 - K(T, T_0)] L_0(\omega, T) \\ + K(T, T_0) \int d\omega' d\Delta\omega \frac{\gamma(T_0) \exp(-\Delta\omega^2/\sigma^2)(\pi^{1/2}/\sigma)^{-1}}{(\omega' + \Delta\omega - \omega_L)^2 + \gamma^2(T_0)} \frac{\gamma(T_0)}{(\omega - \omega')^2 + \gamma^2(T)}. \quad (7)$$

$L_0(\omega, T)$ is a convolution of two lorentzians and, hence, is also a lorentzian

$$L_0(\omega, T) = \pi^{-1} [\gamma(T_0) + \gamma(T)] / \{(\omega - \omega_L)^2 + [\gamma(T_0) + \gamma(T)]^2\}. \quad (8)$$

The width of this line shape function is the sum of the low-temperature width stemming from the burning process and the high-temperature width stemming from the measuring process. If $T_0 = T$ the well-known factor of $2\gamma(T)$ of eq. (1) is obtained. The integral over ω' in eq. (7) can be carried out and yields a Voigt profile, namely

$$L_f(\omega, T) = [1 - K(T, T_0)] L_0(\omega, T) \\ + K(T, T_0) \int d\Delta\omega \exp(-\Delta\omega^2/\sigma^2)(\pi^{1/2}/\sigma)^{-1} [\gamma(T_0) + \gamma(T)] / \{(\omega + \Delta\omega - \omega_L)^2 + [\gamma(T_0) + \gamma(T)]^2\}. \quad (9)$$

The above result shows that type B hole burning experiments, as carried out in ref. [10], will yield a superposition of a lorentzian with a Voigt profile. The factor $K(T, T_0)$ determines how large the fraction of centers will be which participates in the spectral diffusion due to TLS thermally assisted tunnelling or hopping processes. It is interesting to discuss some limiting cases of eq. (9):

(A) Burning and measuring at T_0 : In this case we assume that $K(T, T_0)$ is zero and, hence, the hole line shape is lorentzian with a width of twice the homogeneous width [$\Gamma_h(T) = 2\gamma(T)$].

(B) Burning at T_0 and measuring at T : In this case one has to distinguish two further cases. Case B₁ in which no irreversible spectral diffusion processes occur, i.e. $K(T, T_0) = 0$. The hole is again lorentzian with a width given by

$$\Gamma_h(T) = \gamma(T_0) + \gamma(T). \quad (10)$$

The homogeneous width follows from a deconvolution of eq. (9). Also, one can check quite easily whether the condition of $K(T, T_0) = 0$ is fulfilled, by performing a complete temperature cycle experiment. If the hole recovers its original width at T_0 , spectral diffusion processes play a negligible role. Fig. 1A shows a PHB system, namely quinizarin in an alcoholic glass, where this condition is not fulfilled. Fig. 1B shows quinizarin in boric acid glass. In this system the condition $K(T, T_0) = 0$ is fulfilled up to temperatures of 20 K. Here, the two experiments of type A (triangles) and type B (full circles) can be reduced to the same master curve (crosses and open circles) for the homogeneous linewidth $\gamma(T)$ by using eq. (1) for type A experiments and eq. (10) for type B. The insert of fig. 1 (right-hand side) shows that a lorentzian line shape characterizes the hole under this condition.

The second, more general case B_2 is experimentally verified in the system quinizarin in alcoholic glasses (fig. 1A). If $K(T, T_0)$ approaches 1, the shape of the hole is given by a Vöigt profile

$$L_T(\omega, T) = \int d\Delta\omega \exp(-\Delta\omega^2/\sigma^2) (\pi^{1/2}\sigma)^{-1} [\gamma(T_0) + \gamma(T)] / \{(\omega + \Delta\omega - \omega_L)^2 + [\gamma(T_0) + \gamma(T)]^2\}. \quad (11)$$

It is characterized by a gaussian width σ and a lorentzian width $\gamma(T_0) + \gamma(T)$. This yields a lorentzian line for $\sigma \ll \gamma(T_0) + \gamma(T)$ and a gaussian line for $\sigma \gg \gamma(T_0) + \gamma(T)$. The two line shapes shown, represent the hole before and after a complete temperature cycle from $T_0 = 5$ K to 21 K and back again to T_0 . The linewidth before the temperature cycle is given by $2\gamma(T_0)$. The linewidth and shape after the cycle reflects the distribution $\exp(-\Delta\omega^2/\sigma^2)\pi^{1/2}/\sigma$. The difference between the lorentzian and gaussian fits is almost negligible for the cycled hole while it is very pronounced for the hole before cycling. The gaussian component in the line shape results from the TLS induced frequency changes, which, in turn, can provide microscopic information on the energy surfaces of the TLS [10].

Finally a comment should be made on the case A experiment. The above model was based on the assumption

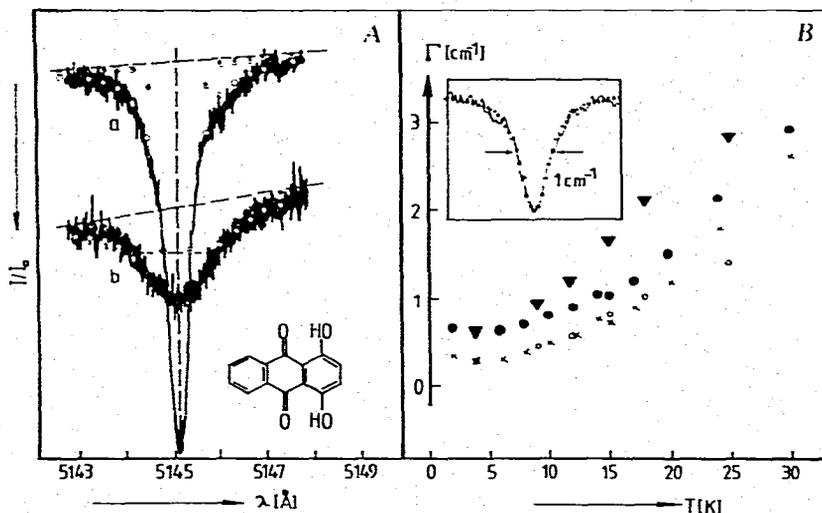


Fig. 1. (A) Quinizarin in EtOH. (a) The hole burnt and measured at $T_0 = 5$ K. Note the marked difference between the lorentzian (open circles) and the gaussian fit. (b) The hole measured at T_0 , but after a complete temperature cycle. Note the small difference between the lorentzian and the gaussian fit. (B) Quinizarin in boric acid. The triangles and circles represent type A and B experiments, respectively. Both experiments can be reduced to the same values of $\gamma(T)$ for $T \leq 20$ K. Open circles correspond to the calculation of $\gamma(T)$ using the triangles, crosses to the calculation of $\gamma(T)$ using the filled circles. The insert shows a line burnt at 3.9 K and measured at 14 K. Note the lorentzian shape. Experimental data from ref. [10].

that the hole shape at the burning temperature is determined by the natural line shape function. But this assumption may not always hold, since, at the burning temperature, a certain fraction of the TLS systems may already be in thermal equilibrium. This fraction may be negligible at very low temperatures but may be substantial at higher temperatures. The PHB photochemistry leads to a reduction of photochemical systems and thus to a deviation from the thermal equilibrium distribution. This is subsequently restored only in a fraction of the photochemical systems, namely the fraction which can perform ground-state tunneling or hopping processes at the burning temperature. These processes change the site energy and, thus, lead to an inhomogeneous line broadening [10]. In this case the line shape can be expressed (similar to eq. (9)) as a superposition of a lorentzian (originating from those TLS which are not equilibrated) and a thermally weighted Vöigt profile (originating from the equilibrated TLS). The relative weight of both contributions depends on the temperature. At higher temperatures the thermally weighted Vöigt profile is expected to predominate [11].

According to the above model [eq. (9)], spectral diffusion processes are of minor importance, if type A and type B experiments reduce to the same master curve. Hence, in this case the hole shape is expected to be determined by the true homogeneous line shape. Fig. 1b shows that in the case of a boric acid matrix this situation holds up to 20 K. This explains the excellent fit of the hole shape to a lorentzian (insert). Above that temperature the onset of spectral diffusion processes is observed. This onset allows one to estimate the lowest barrier height. In boric acid glass this barrier height is on the order of $10\text{--}20\text{ cm}^{-1}$. For $T > 20\text{ K}$, the line shape is expected to deviate from a lorentzian in both types of experiments.

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