

Transient features of optical bleaching as studied by photochemical hole burning and fluorescence line narrowing

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This paper presents various laser excitation experiments on matrix-isolated 1,4-dihydroxyanthraquinone (DAQ). The molecular spectra are studied in two different organic glasses, namely a hydrogen-bonding matrix of 3:1 EtOH/MeOH and a nonhydrogen-bonding matrix of 3-Me-pentane. The experimental techniques are photochemical hole burning (PHB) and fluorescence line narrowing (FLN). The main difference between the two organic glass matrices is the host-induced photoreactivity of DAQ in the alcohol matrix and the photostability of DAQ in the pentane matrix. This difference leads to "anomalous" spectral features in the photoreactive alcohol-DAQ system. In this system, the zero-phonon transition appears to be more intense at higher temperatures, contrary to the well-proven theories on electron-phonon coupling. The unusual spectral line shapes are explained as transient features due to the efficient photochemistry of DAQ in hydrogen-bonding matrices.

INTRODUCTION

Two processes are known which lead to persistent spectral hole burning in inhomogeneously broadened optical bands of dye molecules embedded in organic crystals or glasses at low temperatures: one process is based on photochemistry and was first discovered by Gorokhovskii *et al.*¹ in a frozen solution of H₂-phthalocyanine in a Shpol'skii crystal. The dye molecules were excited by a narrow bandwidth laser at a specific frequency within the low energy absorption band. The laser-selected molecules were photochemically transformed to a different species with a different absorption spectrum. Hence, molecules absorbing at the laser frequency were bleached and a spectral hole was formed. The other process, commonly referred to as nonphotochemical or photophysical hole burning, was discovered by Kharlamov and co-workers.² Its characteristic feature is the observation of spectral hole burning with photochemically inactive molecules, like perylene and others, embedded in organic glasses. Since it could be shown that this process is based on a one photon excitation, ruling out multiphoton ionization, it was interpreted as being due to tunneling processes in amorphous materials.³⁻⁵ This model was introduced by Anderson *et al.*⁶ to explain the anomalous low temperature specific heat, the heat conduction and the ultrasonic attenuation in disordered solids.⁷ The photophysical hole burning process could be explained⁴ by assuming that the potential of the tunnel states is deformed upon excitation of the dye molecules in such a way, that tunneling can occur in the excited state but is forbidden or very slow in the ground state. Hence, the excitation energy of the dye molecule is different before and after tunneling and a hole is burnt at the laser frequency without inducing any molecular photochemical change of the dissolved guest molecule.

Although the basic processes of photochemical and photophysical hole burning are quite different, it may

sometimes be difficult to distinguish between the two processes. As a rule, photophysical hole burning exhibits a low quantum yield and shows different saturation behavior⁸: the phototransformation process reaches a dynamical equilibrium after a fraction of the molecules is transferred to a different state. The depth of the hole remains constant and amounts to only a small fraction of the entire absorption intensity.

The pioneering papers by Gorokhovskii and Kharlamov stimulated the scientific activity in this field.³ The main effort was concentrated on extracting the pertinent spectral parameters of the optical line profile, such as the homogeneous width and the electron-phonon coupling. Those parameters are usually masked by the large inhomogeneous width. It was possible to determine the homogeneous linewidth and the associated dephasing time for several guest molecules in various host materials.¹⁰⁻¹²

In a recent paper on photochemical hole burning in organic glasses,¹³ we investigated the growth of the hole as a function of the laser burning time in order to get information on the electron-phonon coupling in amorphous materials. By using a simple site model, we have shown that the growth of the hole is nonlinear for long burning times. This is due to the fact that the photochemistry in the zero-phonon line saturates much earlier than the photochemistry initiated in the phonon side bands of molecules which have their zero-phonon origin at frequencies lower than the laser frequency. The following paper is based on a mathematical model which had been developed earlier.¹³ It predicts the transient features of optical saturation which occur during the PHB process. These saturation phenomena also determine the line shapes of the measured FLN spectra as will be shown below.

The main idea, whose quantitative mathematical description will be given, is the following: a narrow line shape feature, such as a narrow zero-phonon transition overlaps with only a few site energies of the inhomogeneous line profile and hence will bleach photochemically after a short irradiation time. A broader line shape

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feature, such as a phonon sideband,¹³ or a temperature-broadened zero-phonon line will bleach slower because it overlaps with a larger number of sites within the inhomogeneous line profile. The different saturation behavior can be checked by measuring the different FLN spectra after various stages of photochemical bleaching. As we have shown before, the profile of a hole can be described by a superposition of four terms: the zero-phonon hole, the direct phonon side hole, the pseudo-phonon side hole, and the phonon-phonon term. We show that this superposition holds for all burning times, and that the various terms are characterized by different bleaching times, which are calculated within the framework of our model. We will document that the different bleaching times and their temperature dependence lead to peculiarities in the FLN spectra of photoactive molecules.

To support our model, we compare the FLN spectra of the same probe molecule, namely 1,4-dihydroxy-anthraquinone (DAQ) in two different types of organic glasses. This comparison also supports the earlier proposed photochemical nature of the hole burning process involved.

EXPERIMENTAL

Zone refined DAQ was dissolved in a 3:1 (v/v) mixture of EtOH/MeOH and in 3-Me-pentane. The samples were degassed and sealed under vacuum. The concentrations were chosen in such a way that both samples had an optical density of about 0.2 at the maximum of the first absorption band (5145 Å). The excitation was carried out either with the green line (5145 Å) of an argon ion laser with a power density of approximately 7 mW/cm² or with a high pressure Xe lamp in conjunction with an appropriate interference filter. The resolution of the spectrometer was 0.15 Å for the hole burning experiments while it was 1.5 Å for the fluorescence experi-

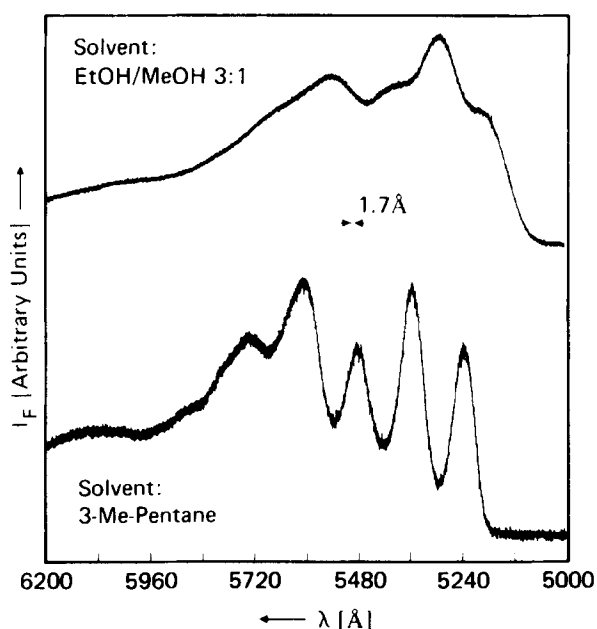


FIG. 1. Broadband fluorescence spectra of 1,4-dihydroxy-anthraquinone in EtOH/MeOH and in 3-Me-pentane at 1.8 K.

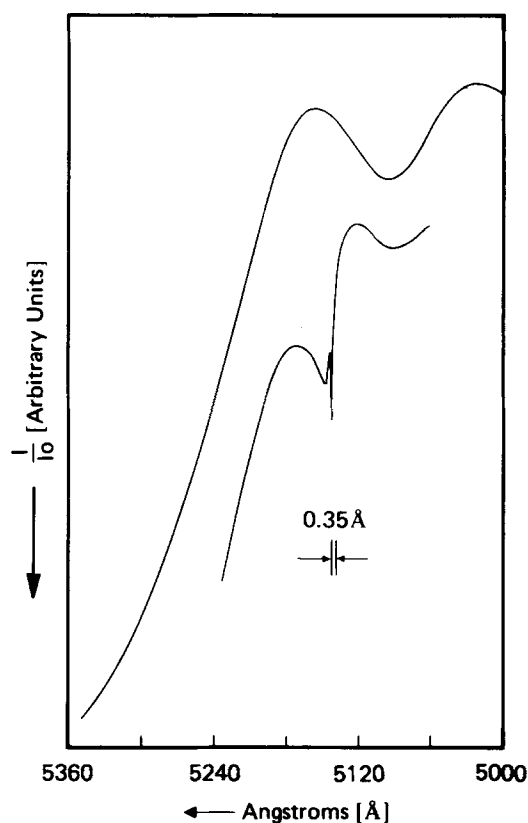


FIG. 2. A photochemical hole burnt in the absorption spectrum of 1,4-dihydroxyanthraquinone in a mixture of EtOH/MeOH. Temperature: 1.8 K; irradiation time: 15 min; laser power: 7 mW/cm². The sharp zero-phonon hole at 5145 Å, and the broad pseudo phonon hole at lower energies are clearly discernible.

ments. The samples were immersed in superfluid He at temperatures between 1.8 and 2 K.

RESULTS

Figure 1 shows the inhomogeneously broadened low temperature fluorescence spectra of DAQ in an EtOH/MeOH glass and in 3-Me-pentane. DAQ was excited into the first vibrational band around 5000 Å with a broadband Xe high-pressure lamp. Even though both spectra show the same structure, the inhomogeneous bandwidth in the alcoholic glass is by far larger than in 3-Me-pentane. This result indicates that the molecule matrix interaction is very different in the two samples. This is most likely a consequence of the hydrogen bonds between the host and guest molecules. Figure 2 displays a hole burning experiment in the alcoholic glass. The sample was irradiated with the 5145 Å line of an argon ion laser for approximately 15 min. Subsequently, the absorption spectrum was scanned with a high resolution monochromator (0.15 Å). The measured spectrum shows a very sharp (0.25 Å) zero-phonon hole resonant with the laser frequency and a broad, less deep side hole at lower frequencies, the "pseudophonon hole" (see Ref. 13).

If we compare the hole burning spectrum with the laser excited FLN spectrum (Fig. 3), we see that no

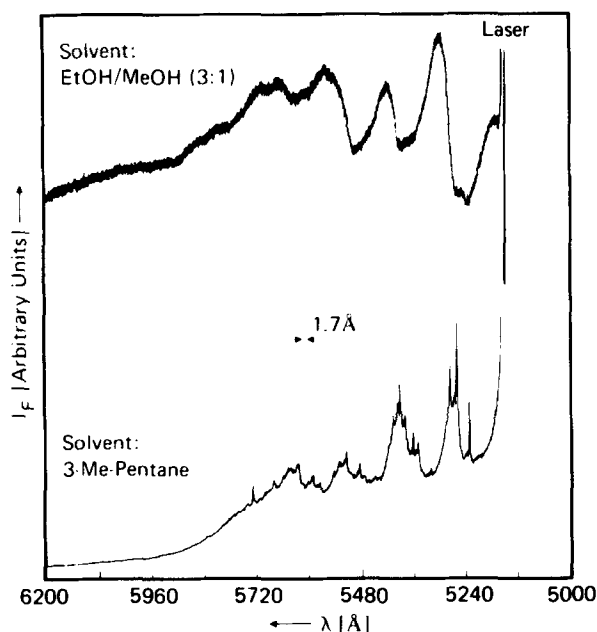


FIG. 3. Laser excited (5145 Å, argon ion laser) emission spectra of 1,4-dihydroxyanthraquinone in two different types of organic glasses. Temperature: 1.8 K; irradiation time before scanning: 15 min; power level: 7 mW/cm².

zero-phonon lines are detectable. The spectrum shows only broad bands with a width on the order of a phonon side band (80 Å). Quite in contrast to the experiments in the alcohol glass, the FLN spectrum of DAQ in 3-Me-pentane exhibits pronounced quasiline structure.

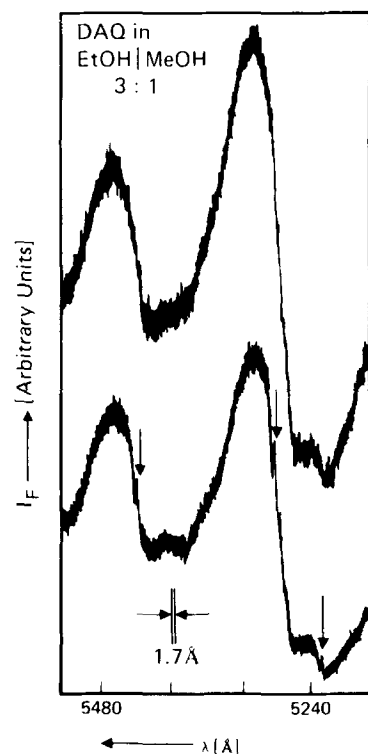


FIG. 4. Comparison of two different scans of the emission spectrum of 1,4-dihydroxyanthraquinone in EtOH/MeOH. Irradiation time before scanning: upper trace 15 min; lower trace 5 min; power level: 7 mW/cm²; temperature: 1.8 K.

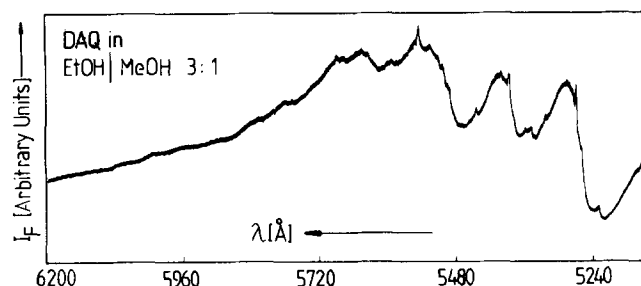


FIG. 5. Laser excited emission spectrum of 1,4-dihydroxyanthraquinone in EtOH/MeOH. The sample was photochemically saturated at 1.8 K. Then, the temperature was abruptly increased to about 20 K and the spectrum scanned. Note the well resolved zero-phonon structure.

Both spectra were obtained under identical experimental conditions. Before scanning, the two samples were irradiated for 15 min with the 5145 Å line (7 mW/cm²) of the argon ion laser, which was also used as excitation source.

We can summarize our results at this point as follows:

- DAQ exhibits narrow zero-phonon type lines in the 3-Me-pentane matrix under FLN conditions. DAQ *does not* show zero-phonon type structures in the alcohol mixture.
- DAQ *does not* exhibit hole burning in the nonhydrogen-bonded 3-Me-pentane matrix (negative results not shown as figure). DAQ *does*, however, show efficient PHB in the hydrogen-bonded alcohol host.

From the above observations, it is quite obvious that FLN and PHB are mutually exclusive phenomena. If PHB photochemistry occurs, the resonant zero-phonon transitions at the laser frequency are bleached and hence, a broadband fluorescence spectrum appears under FLN conditions.

To test the validity of the above conclusion, two fluorescence spectra of DAQ in EtOH/MeOH are compared. One after prolonged laser irradiation, where one can expect complete bleaching of the zero-phonon structure and the other after short laser irradiation during which only partial bleaching is expected. The upper trace of Fig. 4 corresponds to the spectrum in which the zero-phonon transitions are bleached (15 min irradiation, as in Fig. 3). The lower trace of Fig. 4 was obtained from a sample which was only shortly irradiated with the exciting laser before scanning. Obviously, in the latter case, the resonantly absorbing molecules are not totally bleached and the zero-phonon lines do show up. They are marked with arrows.

The photochemically saturated samples show a quite interesting dependence on sudden temperature changes. In Fig. 5, the fluorescence spectrum of a sample is displayed, which was driven into saturation at 1.8 K and which was then subjected to a sudden temperature change up to approximately 20 K. As a result, the broadened bands exhibit well resolved zero-phonon origins whose intensity is only weakly changing with irradiation time. Therefore, the complete spectrum can be easily scanned.

It will be shown below that this thermal behavior has nothing to do with an unusual change in the electron-phonon coupling with temperature. It depends instead on the different rate with which the low-temperature and the high-temperature spectra bleach under identical laser excitation conditions.

DISCUSSION

The interpretation of the presented data is based on a site model, which was presented in an earlier paper.¹³

The model

The spectrum of a photochemical (or photophysical) hole after burning for a time τ is given by a convolution of the ground-state population $N^\tau(\omega)/N$ and the true molecular line shape function $g(\omega - \omega')$:

$$L^\tau(\omega) = A_0 - \sigma \int_{-\infty}^{+\infty} \frac{N^\tau(\omega')}{N} g(\omega - \omega') d\omega' . \quad (1)$$

A_0 is the unburnt absorption spectrum, σ the integrated absorption cross section, and N the total number of molecules in the sample volume.

The molecular line shape function $g(\omega - \omega')$ is characterized by a zero-phonon line $z(\omega - \omega')$ and a phonon side band $p(\omega - \omega' - \Delta)$.

$$g(\omega - \omega') = \alpha z(\omega - \omega') + (1 - \alpha) p(\omega - \omega' - \Delta) . \quad (2)$$

α is the Debye-Waller-factor representing the relative intensity in the zero-phonon line. Δ is the phonon relaxation energy. z and p are chosen as normalized functions. Using a simple two-state model and utilizing the steady-state approximation, we can calculate the number $N_\tau(\omega')$ of molecules which are left at the frequency ω' after initiating laser photochemistry at frequency ω_L for a time τ , as

$$N^\tau = N_0(\omega') \exp \left\{ -\sigma \frac{I}{\hbar\omega_L} \phi \tau [\alpha z(\omega_L - \omega') + (1 - \alpha) p(\omega_L - \omega' - \Delta)] \right\} . \quad (3)$$

I is the laser intensity and ϕ the phototransformation yield. $N_0(\omega')/N$ is the inhomogeneous distribution and represents the relative number of molecules which absorb at ω' into their zero-phonon origin.

In the preceding paper,¹³ we have shown that in the so-called short burning time limit, the line shape $L^\tau(\omega)$ of the hole is well described by a superposition of four terms: the zero-phonon hole, the direct- and the pseudophonon hole, and the phonon-phonon term. Here, we want to show that these four contributions describe the experiments for all burning times, and that it is possible to evaluate the various terms in an analytical fashion.

To this purpose, we expand the exponential in Eqs. (3) and (1), realizing that the term with $n=0$ is compensated by A_0 . We have

$$L^\tau(\omega) = -\sigma \int_{-\infty}^{+\infty} \frac{N_0(\omega')}{N} \sum_{n=1}^{\infty} \frac{1}{n!} \left[-\sigma \frac{I}{\hbar\omega_L} \phi \tau \{ \alpha z(\omega_L - \omega') \right.$$

$$\left. + (1 - \alpha) p(\omega_L - \omega' - \Delta) \right]^n [\alpha z(\omega - \omega') + (1 - \alpha) p(\omega - \omega' - \Delta)] d\omega' . \quad (4)$$

In order to further simplify this integral expression, we make use of the fact that z is a very sharp function compared to both the phonon spectrum p and to the inhomogeneous distribution. Hence, we expect only contributions from the integral in a small range around ω_L . As a consequence, all mixed terms of type $z^{n-k} p^k$ ($k=1, 2, \dots, n-1$) in the expansion above vanish, because $p(\omega_L - \omega' - \Delta)$ is vanishing at $\omega' = \omega_L$. (There are no phonons with energy zero.) Therefore, we can write

$$L^\tau(\omega) = -\sigma \int_{-\infty}^{+\infty} \frac{N_0(\omega')}{N} \left(\sum_{n=1}^{\infty} \frac{\{ -\sigma [I/(\hbar\omega_L)] \phi \tau \alpha \}^n}{n!} z^n(\omega_L - \omega') + \sum_{n=1}^{\infty} \frac{\{ -\sigma [I/(\hbar\omega_L)] \phi \tau (1 - \alpha) \}^n}{n!} p^n(\omega_L - \omega' - \Delta) \right) \times [\alpha z(\omega - \omega') + (1 - \alpha) p(\omega - \omega' - \Delta)] d\omega' .$$

Adding a term for $n=0$ in the two sums, we can carry out the summation and arrive at

$$L^\tau(\omega) = -\sigma \int_{-\infty}^{+\infty} \frac{N_0(\omega')}{N} \left\{ \exp \left[-\sigma \frac{I}{\hbar\omega_L} \phi \tau \alpha z(\omega_L - \omega') \right] - 1 \right\} + \left\{ \exp \left[-\sigma \frac{I}{\hbar\omega_L} \phi \tau (1 - \alpha) p(\omega_L - \omega' - \Delta) \right] - 1 \right\} \times [\alpha z(\omega - \omega') + (1 - \alpha) p(\omega - \omega' - \Delta)] d\omega' . \quad (5)$$

Thus, we have reduced the line shape function of the hole to four terms. The *first* one is a convolution of the function

$$n_z(\omega_L - \omega') = -\exp \left[-\sigma \frac{I}{\hbar\omega_L} \phi \tau \alpha z(\omega_L - \omega') \right] + 1 , \quad (6)$$

with the zero-phonon line shape $z(\omega - \omega')$. n_z is a sharply peaked function at $\omega' = \omega_L$ and represents the relative number of molecules bleached at the zero-phonon frequency during a burning time τ . We can put the slowly varying inhomogeneous distribution in front of the integral and take advantage of the fact that z is normalized. Then we get

$$zz(\omega) = \sigma \alpha \frac{N_0(\omega_L)}{N} \times \left\{ 1 - \int_{-\infty}^{+\infty} \exp \left[-\alpha \sigma \frac{I}{\hbar\omega_L} \phi \tau z(\omega_L - \omega') \right] z(\omega - \omega') d\omega' \right\} . \quad (7)$$

zz is the zero-phonon hole. This expression is identical to the one derived by Voelker *et al.*¹⁴ We note that the shape of the hole is different from the true molecular zero-phonon line shape function z depending on the burning time τ . Only for short burning times, where the exponential function is well described by a linear expansion, the hole shape is given by a correlation function of the true molecular line shape z (see Ref. 13). Thus, in this case, the homogeneous width can be determined by evaluating a hole burning experiment. This situation was called the short burning time limit.

The *second term* is a convolution of n_z with the phonon spectrum $p(\omega - \omega' - \Delta)$. Since p is slowly varying with respect to n_z , we can put it (together with the inhomogeneous distribution) in front of the integral and get

$$zp(\omega) = \sigma(1 - \alpha) \frac{N_0(\omega_L)}{N} p(\omega - \omega_L - \Delta) \times \int_{-\infty}^{+\infty} \left\{ 1 - \exp\left[-\sigma \frac{I}{\hbar\omega_L} \phi \tau \alpha z(\omega_L - \omega')\right] \right\} d\omega' .$$

We note that, for all burning times, zp is proportional to the phonon spectrum whose zero-phonon origin is at the laser frequency. The above contribution corresponds to phonon excitations of those molecules which were bleached by zero-phonon photochemistry. Hence, we call zp the direct-phonon hole. The integral factor above represents the burning time dependence of the direct hole. For an approximate evaluation we represent $z(\omega_L - \omega')$ by a rectangular line shape with the homogeneous width Γ_z .

Then, we can easily carry out the integration and get

$$zp(\omega) = \sigma(1 - \alpha) \frac{N_0(\omega_L)}{N} p(\omega - \omega_L - \Delta) \times \left(1 - \exp\left\{ \frac{-\sigma[I/(\hbar\omega_L)] \phi \tau \alpha}{\Gamma_z} \right\} \right) \Gamma_z . \quad (8)$$

The *third term* is a convolution of the function

$$n_p(\omega_L - \omega' - \Delta) = -\exp\left[-\sigma(1 - \alpha) \frac{I}{\hbar\omega_L} \phi \tau p(\omega_L - \omega' - \Delta)\right] + 1 , \quad (9)$$

with the zero-phonon profile $z(\omega - \omega')$. n_p represents the relative number of molecules with their origin at ω' which were bleached by absorption into their phonon states. Since z is normalized and sharp compared to n_p , we can directly replace it by a δ function. Hence, we have

$$pz(\omega) = \sigma\alpha \frac{N_0(\omega)}{N} \left\{ 1 - \exp\left[-\sigma(1 - \alpha) \frac{I}{\hbar\omega_L} \phi \tau p(\omega_L - \omega - \Delta)\right] \right\} . \quad (10)$$

This term accounts for the zero-phonon contributions to the hole from molecules which were bleached via absorption into a phonon level. It is zero at the laser frequency and extends (in contrary to the direct phonon hole) to lower frequencies. Hence, we called this term pseudophonon hole. It is not related to photochemistry in the zero-phonon line. We also note that it is, to some extent, dependent on the inhomogeneous width. In case that this width is large compared to the characteristic features of the true molecular line shape profile, we have shown that, in the short burning time limit, the direct- and the pseudophonon hole are identical in shape and depth. Since this situation was never met by our experiments, we concluded that the electron-phonon coupling characterized by the Debye-Waller factor is not uniform in a glass.¹³

Finally, the *fourth term* is given by the convolution of n_p with the phonon spectrum

$$pp(\omega) = \sigma(1 - \alpha) \int_{-\infty}^{+\infty} \frac{N_0(\omega')}{N} \times \left\{ 1 - \exp\left[-\sigma \frac{I}{\hbar\omega_L} \phi(1 - \alpha) \tau p(\omega_L - \omega' - \Delta)\right] \right\} \times p(\omega - \omega' - \Delta) d\omega' . \quad (11)$$

This term accounts for the phonon contribution of those molecules which were phototransformed via absorption into phonon states.

We call it the phonon-phonon hole. It has contributions on both sides of the zero-phonon line. In the short burning time limit, it is a symmetric function on both sides of the laser frequency, regardless of the symmetry of the phonon spectrum. In the limit of weak electron-phonon coupling ($\alpha \rightarrow 1$), this term is small as compared to the direct- and the pseudophonon hole since not only the factor in front of the integral but also the integrand itself tends to zero. In case of strong electron-phonon coupling, the pp term is the leading one, since zp as well as pz vanish as α tends to zero. In this case, a broad hole on both sides of the laser frequency is expected. Comparing the results of the model with the hole burning experiment, we see that not all four terms can be clearly assigned. The sharp zero-phonon hole is very prominent. However, the direct-phonon hole is almost invisible. On the other hand, the pseudophonon hole on the long wavelength side of the zero-phonon line is very pronounced. From this asymmetry of the hole profile, we concluded that the pp term is very small in agreement with the observed weak electron-phonon coupling in organic glasses and Shpol'skii matrices.^{13,21}

Bleaching times of a spectral hole in an organic glass

The above model shows that the burning time dependence is totally different for the zero-phonon hole and the direct phonon sideband on the one hand, and the pseudophonon hole and the phonon-phonon term on the other hand. The bleaching time behavior in the zero-phonon hole follows from Eq. (6). For simplicity, we again approximate z by a rectangular line shape function with the width Γ_z corresponding to the homogeneous linewidth. Then, we can calculate the relative number of molecules N_z^T which are photochemically (photophysically) transformed via zero-phonon absorption at ω_L by integrating Eq. (6):

$$N_z^T = \left(\exp\left\{ \frac{-\sigma[I/(\hbar\omega_L)] \phi \alpha \pi}{\Gamma_z} \right\} - 1 \right) \Gamma_z \equiv \left[\exp\left(-\frac{\tau}{\tau_b^*}\right) - 1 \right] \Gamma_z .$$

Here, we have defined a bleaching time τ_b^* for the zero-phonon photochemistry

$$\tau_b^* = (\Gamma_z \hbar\omega_L) / (\sigma I \phi \alpha) . \quad (12)$$

This burning time behavior is reflected in Eq. (7).

For comparison, we calculate in the same way, i. e., assuming a rectangular shape, the bleaching time for the photochemistry initiated in the phonon sideband (pseudophonon hole and phonon-phonon term) from Eq. (9):

$$\tau_b^* = (\Gamma_p \hbar\omega_L) / [\sigma I \phi (1 - \alpha)] . \quad (13)$$

Γ_p is the width of the phonon sideband. Even though the

actual bleaching times are somewhat dependent on the true line shape functions, Eqs. (12) and (13) reflect several important features: first, we note that the bleaching times are proportional to the width of the associated part of the line shape function. This proportionality accounts for the fact that the number of molecules in a certain spectral range is roughly proportional to its width. While this width is very small for the zero-phonon line ($\approx 1 \text{ cm}^{-1}$), it is large for the phonon sideband ($\approx 30\text{--}40 \text{ cm}^{-1}$). Thus, we have the result that the photochemistry in the zero-phonon hole saturates on a short time scale compared to the photochemistry in the phonon sideband. This behavior is accurately reflected by the emission spectra of Figs. 3 and 4. The zero-phonon lines are only observed for laser irradiation times less than the bleaching time τ_b^z . If the irradiation time exceeds the zero-phonon bleaching time, emission is only observed from the nonresonantly excited molecules resulting in broadband fluorescence (Figs. 3 and 4).

We further note that, apart from the widths, the bleaching times depend on the Debye–Waller factor and on the phototransformation yield. Within the framework of the simple model used here, α is a constant. However, from the asymmetry of the hole shape in the short burning time limit,¹³ we argued earlier that the Debye–Waller factor is not uniform, and that the strongly coupled centers dominate the spectrum in the phonon side band (pseudophonon hole), whereas the opposite holds for the zero-phonon line. A similar argument may arise concerning the phototransformation yield. However, in our case, we can assume that the quantum yield is not influenced by the phonons, because the first step in the photoreaction is a relaxation to the lowest triplet state,¹⁵ which is not dependent on phonon excitations.

On the other hand, there might be situations in which the yield in the phonon sideband is different from the one in the zero-phonon line. It is known, for instance, that in photophysical hole burning,⁸ the tunneling processes induced in the phonon sideband may be more efficient (by the assistance of phonons) than in the zero-phonon line. Hence, to be general, we write for the ratio of the bleaching factors

$$\frac{\tau_b^z}{\tau_b^p} = \frac{\Gamma_z \phi_p (1 - \alpha_p)}{\Gamma_p \phi_z \alpha_z} \quad (14)$$

We are now in a position where we can precisely define the limiting cases introduced in a recent paper.¹³ If the following condition is fulfilled

$$\tau \ll \tau_b^z, \quad (15)$$

we say that the system is in the short burning time limit. In this case, we observe zero-phonon emission. The width of the zero-phonon hole is roughly twice the homogeneous width. If, however,

$$\tau \gg \tau_b^z, \quad (16)$$

we say that the system is in the photochemical saturation limit. In this case, there is no zero-phonon emission. The width of the zero-phonon hole is no longer related to the homogeneous width, but shows saturation broadening. We should point out that these limits are

strongly dependent on temperature, since τ_b^z is strongly dependent on temperature (via Γ_z and α). The next paragraph will deal with this aspect.

Influence of temperature changes on the emission spectra of photoreactive impurity centers

The spectral line shape of the fluorescence emission of impurity molecules in solid amorphous or crystalline materials is mainly governed by the temperature dependence of the Debye–Waller factor, which is given by the well known relation¹⁶

$$\alpha(T) = \exp \left\{ -S \left[1 + \frac{2\pi^2}{3} \left(\frac{T}{\theta} \right)^2 \right] \right\} \quad (17)$$

Equation (17) holds in case that the temperature of the system is small compared to the Debye temperature θ , and its validity was demonstrated for a variety of crystalline organic materials.^{17,18} According to this relation, the integrated intensity of the zero-phonon line decreases with increasing temperature. The situation is, however, completely different in case of photoreactive impurity centers. Because of the short bleaching time of the zero-phonon line due to photochemical processes [Eq. (12)], the system approaches the photochemical saturation fast, so that zero-phonon emission is absent. If the system, which was bleached at 2 K, is subjected to a sudden change in temperature (2–20 K, as is the case in our experiment), then, the number of molecules within the homogeneous width shows also a sudden increase. This is due to the fact that the number of resonantly absorbing molecules is roughly proportional to the width of the zero-phonon line. This width, however, increases rapidly with temperature.⁸ For example, we found that for 1,4-dihydroxyanthraquinone in EtOH, at 20 K, the width is about a factor of 5 larger than at 2 K. Hence, the number of molecules which can undergo zero-phonon emission increases approximately by the same factor. That means, at higher temperatures, the system is no longer saturated and zero-phonon emission is observed at higher temperatures, as clearly shown by our results (Fig. 4).

From Eq. (12) we can conclude that, at higher temperatures, it takes a much longer time to drive the system into photochemical saturation. Hence, at the laser power level of the experiment, the spectrum can be easily scanned before all the resonant molecules are bleached. Apart from the temperature dependence due to the homogeneous width, there are some additional effects on the zero-phonon bleaching time. From Eq. (12), it is obvious that the change of the Debye–Waller factor with temperature [Eq. (17)] leads to an additional increase of the bleaching time. However, in most organic materials, the Debye temperature is about 100 K, and, hence, in the temperature range of our experiment, this influence is negligible.

Another complication arises from tunneling processes in the ground state. The zero-phonon emission lines of a photobleached sample, which show up at higher temperatures, should exhibit small dips at their maxima due to the hole burning process at low temperatures. However, at 20 K, holes burnt at 1.8 K are very shallow

because phonon assisted tunneling processes in the groundstate become progressively important with increasing temperature. As discussed by Anderson *et al.*,⁶ there is, at a given temperature, only one subset of the entire distribution of two level systems in thermal equilibrium, namely those systems which allow for tunneling processes on the time scale of the experiment. With increasing temperature, a new subset of two-level systems is thermally equilibrated by phonon induced tunneling processes. Since the photoreactive impurity molecules interact with the two level systems of the amorphous matrix, these processes may lead to a change in site energy of the impurity centers, thereby restoring part of the groundstate population at the laser frequency. At the optical resolution of the experiments presented in this paper, this influence on the line shape of the zero-phonon emission is negligible. It is discussed in detail in a forthcoming publication where we present higher resolution experiments.¹⁹

Finally, we point out that the phototransformation yield may be sensitive to the temperature. Though this problem seems to be of minor importance in case of photochemical hole burning for the temperature range considered, it might be important in case of photophysical hole burning even at very low temperatures.

Summarizing this section, we can say that the laser excited fluorescence spectra of photoactive centers dissolved in organic glasses show an "anomalous" temperature dependence. The relative intensity of the zero-phonon line is small at low temperatures and is larger at higher temperatures. Our simple model, however, shows that this temperature dependence is not related to an anomalous electron-phonon coupling, but can be explained by taking into account the influence of temperature on the bleaching times through the strong increase of the homogeneous linewidth.

The nature of the hole burning process

Even though the main features of our model are rather insensitive to the detailed nature of the hole burning process, i. e., photochemical or photophysical, the discussion of the influence of temperature on the bleaching rates has shown that there are situations in which it is quite important to know whether the phototransformation is photochemical or photophysical in nature.

On the basis of several experiments,^{9,20,21} the hole burning process of 1,4-dihydroxyanthraquinone was interpreted as being due to an excited-state proton transfer reaction which leads to a breakage of an internal hydrogen bond and subsequently to a new formation of an external hydrogen bond with the solvent. The direct consequence of this model is that photochemical hole burning is only possible in solvents capable of hydrogen bond formation with the impurity molecule. All alcoholic glasses fulfill this criterion and, indeed, efficient hole burning occurs in all investigated glasses of this kind.

The experiments in 3-Me-pentane strongly corroborate this model. 3-Me-pentane is not capable of forming hydrogen bonds with 1,4-dihydroxyanthraquinone. Hence, according to the model, no photochemical transformation should occur. This is nicely demonstrated by the

laser excited fluorescence spectra of Fig. 3: the absence of any efficient photoreaction in 3-Me-pentane leads to the appearance of intense zero-phonon emission. It is possible, however, that there is photophysical hole burning, in 3-Me-pentane as well as in EtOH/MeOH. However, the corresponding photophysical yield must be very low,⁸ so that this process can be neglected at the laser power level used in our experiment.

SUMMARY

In this paper, we have shown that the laser excited fluorescence spectra of photoreactive centers in amorphous materials have very special features: the broad phonon sidebands dominate at low temperatures while sharp zero-phonon lines show up at higher temperatures as a transient phenomenon. This behavior was explained by employing a simple two-level site model which leads to the conclusion that the bleaching times for the zero-phonon photochemistry and for the photochemistry initiated in the phonon sideband differ roughly in the same way as the associated linewidths (i. e., a factor of about 40). Furthermore, the model led to a precise definition of the so-called photochemical saturation and the short burning time limit. It was shown, that these limits are strongly temperature dependent.

Finally, the combined investigation of hole burning and fluorescence line narrowing in two different types of organic glasses supported the notion that the phototransformation process is photochemical in nature and is due to an excited state proton transfer reaction.

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