

# Correlation effects in vibrational hole burning

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This paper presents a theoretical model which describes correlation effects in nonresonant photochemical holes. The model calculations are compared with experiments of photochemical hole burning (PHB) in electronically excited vibrational states of 1,4-dihydroxyanthraquinone (DAQ) in alcohol glass matrices. Vibrational hole burning shows some specific features such as the occurrence of several nonresonant holes in the electronic origin which differ considerably in their widths and integrated optical density from the resonant hole. The difference in linewidth is related to a vibrational inhomogeneity which is superimposed on the observed relaxation broadening. The experiments show that the vibrational inhomogeneity is not uniform but varies with the vibrational state.

## INTRODUCTION

This study deals with photochemical hole burning (PHB)<sup>1,2</sup> in electronically excited vibrational states of dye molecules in organic glasses. 1,4-dihydroxyanthraquinone (DAQ) was used as a probe molecule; alcohol glass was used as a matrix. As shown in several recent papers,<sup>3-6</sup> DAQ exhibits rather efficient hole burning in alcoholic glasses, which was attributed to light induced proton rearrangement reactions. PHB in vibrationally excited electronic states shows several new features compared to PHB in the electronic origin.

These features are: (1) the fast relaxation processes in higher excited states and (2) an inhomogeneous broadening mechanism, which is due to vibrational inhomogeneity.

Vibrational inhomogeneity was first discussed by Abram *et al.*<sup>7</sup> Later Gorokhovskii and Kikas<sup>8</sup> employed the concept of vibrational inhomogeneity to explain the broadening of nonresonant photochemical holes in polycrystalline samples. Here, we present a (phenomenological) line shape theory of nonresonant photochemical holes in organic glasses.

## EXPERIMENTAL DETAILS AND RESULTS

Hole burning was performed in dilute solutions of 1,4-dihydroxyanthraquinone (DAQ) in an EtOH/MeOH mixture (3:1, *v/v*) at 1.8 K. The photochemistry was achieved with a pulsed dye laser, tuned to 5032 Å near the maximum of the first vibrational band. The bandwidth was about 0.1 cm<sup>-1</sup>. After a burning time of about 30 min a rather shallow hole was detected at the laser frequency. The resolution of the spectrometer was 1 cm<sup>-1</sup>. Figure 1 shows the absorption spectrum of DAQ before and after hole burning. We see that, besides the resonant hole at the laser frequency, a series of nonresonant holes appears in the electronic origin. We note that the area of each of the nonresonant holes is at least as large as that of the resonant hole [Figs. 2(a) and 2(b)]. It is also obvious that the nonresonant holes are considerably broader than the parent hole.

## DISCUSSION

### Nonresonant holes and correlation effects in the line shape

The appearance of multiple nonresonant holes in the electronic origin after laser irradiation into a vibrational band was first explained by Kharlamov *et al.*<sup>9</sup> These authors have shown that, in cases in which the inhomogeneous linewidth is comparable to vibrational frequencies, PHB through laser irradiation at one frequency can lead to a multitude of photochemical holes. The number of holes is roughly given by the number of vibrations overlapping with their inhomogeneous width at the laser frequency. Those vibrational states which have their band maximum above the laser frequency are burnt in low energy sites; states with their band maximum be-

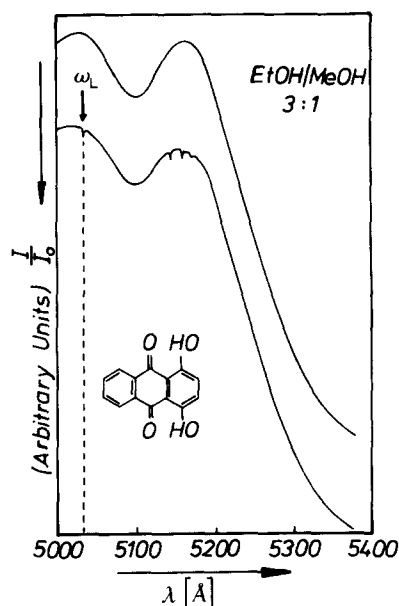


FIG. 1. Absorption spectrum of 1,4-dihydroxyanthraquinone in an EtOH/MeOH mixture at 1.8 K. Lower trace: Absorption after hole burning at 5032 Å (30 min, 1 mW/cm<sup>2</sup>). Several nonresonant holes show up in the electronic origin.

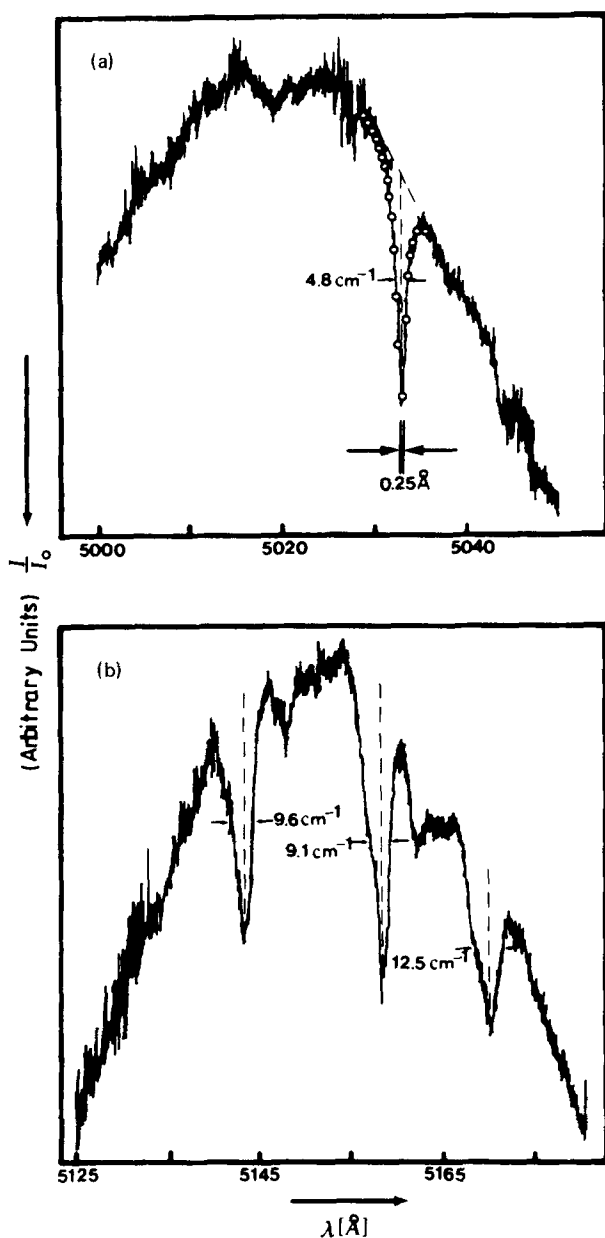


FIG. 2. Enlarged scale of Fig. 1. (a) The resonant hole, fitted to a Lorentzian. (b) The nonresonant holes.

low the laser frequency are burnt in high energy sites. This site pattern shows up in the inhomogeneous envelope of the electronic origin (see Fig. 1). The energy splitting between the resonant hole and the nonresonant holes is given by the corresponding vibrational frequencies in the excited state. For DAQ, doped in EtOH/MeOH mixtures, laser irradiation at 5032 Å leads to PHB in at least three vibrational states (Fig. 1). In the high resolution scan (Fig. 2) three prominent holes and two peaks with lower intensity appear.

In order to understand the line shapes and the intensity ratios of the resonant and the relaxed photochemical holes, one has to express the resonant hole in terms of the pertinent photochemical parameters.<sup>6,10</sup> In the short burning time limit, the line shape of the resonant zero phonon hole  $Z_n Z_n$  is given by

$$Z_n Z_n(\omega) = \sigma_n^2 \alpha_n^2 \frac{I}{\hbar \omega_L} \phi_n \tau p(\omega_L - \omega_n) \times \int_{-\infty}^{+\infty} Z_n(\omega_L - \omega' + \omega_n) Z_n(\omega - \omega' + \omega_n) d\omega', \quad (1)$$

with the integrated absorption cross-section  $\sigma$ , the Debye-Waller factor  $\alpha$ , the photochemical yield  $\phi$ , the laser intensity  $I$ , and the laser frequency  $\omega_L$ .  $\tau$  is the burning time and  $p(\omega - \omega_n)$  is the inhomogeneous distribution of the  $n$ th (vibrational) transition with a width  $\Gamma_n$ :

$$p(\omega - \omega_n) = \frac{1}{\sqrt{2\pi} \Gamma_n} \exp\left\{-\frac{1}{2} \frac{(\omega - \omega_n)^2}{\Gamma_n^2}\right\}. \quad (2)$$

The index  $n$  labels the molecular parameters in the  $n$ th excited state.  $Z_n$  represents the normalized line shape function of the zero phonon line. The line shape of the nonresonant hole is calculated in a similar way, but, instead of Eq. (2), one has to use a two-dimensional Gaussian distribution (e.g., see Ref. 11):

$$p(\omega_1 - \omega_n, \omega_2 - \omega_0) = \frac{1}{2\pi} \frac{1}{\sqrt{\det \hat{C}}} \exp\left\{-\frac{1}{2} \omega^T \hat{C}^{-1} \omega\right\}, \quad (3)$$

where  $\hat{C}$  represents the correlation matrix

$$\begin{aligned} \{\hat{C}\}_{12} &= \langle (\omega_1 - \omega_n)(\omega_2 - \omega_0) \rangle \\ &= \iint (\omega_1 - \omega_n)(\omega_2 - \omega_0) p(\omega_1 - \omega_n, \omega_2 - \omega_0) d\omega_1 d\omega_2. \end{aligned} \quad (4)$$

The use of a two-dimensional Gaussian distribution accounts for the fact that the inhomogeneous distribution in the resonant state  $|n\rangle$  and in the off resonant state  $|0\rangle$  may be correlated to some extent. The diagonal elements  $\langle (\omega_1 - \omega_n)^2 \rangle \equiv \Gamma_n$ ,  $\langle (\omega_2 - \omega_0)^2 \rangle \equiv \Gamma_0$  represent the widths of the inhomogeneous distributions. The non-diagonal elements  $\langle (\omega_1 - \omega_n)(\omega_2 - \omega_0) \rangle$  represent the amount of correlation between the distributions of the two states. This amount of correlation is characterized by the degree of correlation  $\rho$ ,

$$\rho \equiv \frac{\langle (\omega_1 - \omega_n)(\omega_2 - \omega_0) \rangle}{\Gamma_n \Gamma_0}. \quad (5)$$

If  $\rho = 1$ , we have complete correlation. If  $\rho = 0$ , we have vanishing correlation.

In our hole burning experiment  $p(\omega_1 - \omega_n, \omega_2 - \omega_0)$  represents the probability that a photochemical change in the spectrum initiated with laser light at  $\omega_1$  in the state  $|n\rangle$  shows up at a frequency  $\omega_2$  in the state  $|0\rangle$ . Thus, similar to Eq. (1), the line shape of a nonresonant hole is then given by

$$\begin{aligned} Z_n Z_0(\omega) &= \sigma_n \sigma_0 \alpha_n \alpha_0 \phi_n \cdot \tau \cdot \frac{I}{\hbar \omega_L} \\ &\times \iint p(\omega_1 - \omega_n, \omega_2 - \omega_0) Z_n(\omega_2 - \omega' + \omega_0) \\ &\times Z_0(\omega - \omega' + \omega_0) d\omega_2 d\omega'. \end{aligned} \quad (6)$$

Let us consider the two limiting cases of vanishing and complete correlation, which can be compared with experimental spectroscopic data.

(i) Vanishing correlation between state  $|n\rangle$  and  $|0\rangle$ :

In this case  $p(\omega_1 - \omega_n, \omega_2 - \omega_0)$  reduces to a product of two independent Gaussians

$$p(\omega_1 - \omega_n, \omega_2 - \omega_0) = \frac{1}{2\pi\Gamma_n\Gamma_0} \times \exp\left\{-\frac{1}{2}\frac{(\omega_1 - \omega_n)^2}{\Gamma_n^2}\right\} \exp\left\{-\frac{1}{2}\frac{(\omega_2 - \omega_0)^2}{\Gamma_0^2}\right\}.$$

Inserting this distribution in the above line shape Eq. (6) and identifying the excitation frequency  $\omega_1$  with the laser frequency  $\omega_L$ , we get

$$Z_n Z_0(\omega) = \sigma_n \sigma_0 \alpha_n \alpha_0 \phi_n \frac{I}{\hbar\omega_L} \cdot \tau \cdot \frac{1}{2\pi\Gamma_n\Gamma_0} \times \exp\left\{-\frac{1}{2}\frac{(\omega_L - \omega_n)^2}{\Gamma_n^2}\right\} \iint \exp\left\{-\frac{1}{2}\frac{(\omega_2 - \omega_0)^2}{\Gamma_0^2}\right\} \times Z_n(\omega_2 - \omega' + \omega_0) Z_0(\omega - \omega' + \omega_0) d\omega_2 d\omega'.$$

The integration over  $\omega_2$  and  $\omega'$  is easily carried out by taking advantage of the fact that in organic glasses  $Z_n$  and  $Z_0$  can be considered as  $\delta$  functions compared to the inhomogeneous distribution. The result is

$$Z_n Z_0(\omega) = \sigma_n \sigma_0 \alpha_n \alpha_0 \phi_n \frac{I}{\hbar\omega_L} \cdot \tau \frac{1}{2\pi\Gamma_n\Gamma_0} \times \exp\left\{-\frac{1}{2}\frac{(\omega_L - \omega_n)^2}{\Gamma_n^2}\right\} \exp\left\{-\frac{1}{2}\frac{(\omega - \omega_0)^2}{\Gamma_0^2}\right\}. \quad (7)$$

That is, in case of no correlation we get a broad line shape for the nonresonant "hole," determined by the inhomogeneous distribution of the nonresonant state. Note, that, for the latter case, no fluorescence line narrowing is possible. Experimentally this is true for a variety of molecular systems.<sup>12</sup> For dye molecules in organic glasses, it holds, as a rule, if  $n$  is an electronic state.

(ii) Complete correlation between states  $|n\rangle$  and  $|0\rangle$ : In this case the two-dimensional Gaussian distribution (3) can be reduced to a product of a Gaussian and a  $\delta$  function

$$p(\omega_1 - \omega_n, \omega_2 - \omega_0) = \frac{1}{\sqrt{2\pi}\Gamma_n} \exp\left\{-\frac{1}{2}\frac{(\omega_1 - \omega_n)^2}{\Gamma_n^2}\right\} \times \delta\{(\omega_2 - \omega_0) - (\omega_1 - \omega_n)S\}. \quad (8)$$

$S$  is a scaling factor defined by

$$S = \frac{\langle(\omega_1 - \omega_n)(\omega_2 - \omega_0)\rangle}{\Gamma_n^2} = \frac{\Gamma_0}{\Gamma_n} \cdot \rho. \quad (9)$$

Putting  $\omega_1 = \omega_L$  we calculate the line shape from Eq. (6) as

$$Z_n Z_0 = \sigma_n \sigma_0 \alpha_n \alpha_0 \phi_n \tau \frac{1}{\sqrt{2\pi}\Gamma_n} \times \exp\left\{-\frac{1}{2}\frac{(\omega_L - \omega_n)^2}{\Gamma_n^2}\right\} \frac{I}{\hbar\omega_L} \times \int Z_n\{(\omega_L - \omega_n)S - \omega' + 2\omega_0\} Z_0(\omega - \omega' + \omega_0) d\omega'. \quad (10)$$

In this case we get a sharp side hole given by a convolution of the resonant with the nonresonant zero phonon line. This side hole is centered at

$$(\omega_L - \omega_n) \frac{\Gamma_0}{\Gamma_n}$$

within the inhomogeneous distribution of the state  $|0\rangle$ . The scaling factor  $S$  accounts for the fact that the inhomogeneous distributions of the two states might be very different. In case they are equal, this factor becomes 1 for complete correlation, according to Eq. (9).

If the zero phonon lines are Lorentzians with widths  $\gamma_n$  and  $\gamma_0$  (HWHM), respectively, the convolution can be carried out

$$\int_{-\infty}^{+\infty} Z_n\{[(\omega_L - \omega_n)S - \omega' + 2\omega_0]\} Z_0(\omega - \omega' + \omega_0) d\omega' = \frac{1}{\pi} \frac{\gamma_n + \gamma_0}{[\omega - (\omega_L - \omega_n)S - \omega_0]^2 + (\gamma_n + \gamma_0)^2}. \quad (11)$$

The homogeneous width of the relaxed hole  $\gamma$  is a sum of the homogeneous width of the resonant zero phonon transition  $\gamma_n$ , and the nonresonant zero phonon transition  $\gamma_0$ , hence, it is expected to be narrower than the width of the resonant hole which is  $2\gamma_n$ . This condition is not met by our experimental findings, which show larger linewidths for the nonresonant holes. Hence, we have to consider the general case where correlation exists between  $|n\rangle$  and  $|0\rangle$ , but it not complete.

The two-dimensional Gaussian distribution can be calculated as

$$p(\omega_1 - \omega_n, \omega_2 - \omega_0) = \frac{1}{2\pi\Gamma_n\Gamma_0\sqrt{(1-\rho)^2}} \exp\left\{-\frac{1}{2}\frac{(\omega_1 - \omega_n)^2}{\Gamma_n^2}\right\} \times \exp\left\{-\frac{1}{2}\frac{[(\omega_2 - \omega_0) - (\omega_1 - \omega_n)S]^2}{\Gamma_0^2(1-\rho^2)}\right\}. \quad (12)$$

Inserting this distribution in the line shape Eq. (6) we see that the shape of the nonresonant hole is given by a Voigt profile:

$$Z_n Z_0(\omega) = \sigma_n \sigma_0 \alpha_n \alpha_0 \phi_n \tau \frac{I}{\hbar\omega_L} \frac{1}{2\pi\Gamma_n\Gamma_0(1-\rho^2)^{1/2}} \times \exp\left\{-\frac{1}{2}\frac{(\omega_L - \omega_n)^2}{\Gamma_n^2}\right\} \iint \exp\left\{-\frac{1}{2}\frac{[(\omega_2 - \omega_0) - (\omega_L - \omega_n)S]^2}{\Gamma_0^2(1-\rho^2)}\right\} \cdot Z_n(\omega_2 - \omega' + \omega_0) \times Z_0(\omega - \omega' + \omega_0) d\omega_2 d\omega'. \quad (13)$$

For very narrow zero phonon lines  $Z_n$  and  $Z_0$  this shape turns into a Gaussian, with a width of

$$\Gamma = \Gamma_0(1-\rho^2)^{1/2} \quad (14)$$

depending on the amount of correlation.

In our experiment, where the molecules are excited into an electronic vibrational transition, the correlation between the resonant and the relaxed state is fairly high. As a consequence the side holes in Figs. 1 and 2 are quite sharp. With Eq. (14) we can estimate the order of magnitude of the correlation loss, as

$$1 - \rho \approx 10^{-5}.$$

The experiment shows that this loss of correlation is not uniform but changes within the three nonresonant holes

TABLE I. Ground and excited state vibrational frequencies of dihydroxyanthraquinone. Frequency shifts and correlation loss factors.

Vibration	$B_1, \delta(C-O)$	$A_1, \delta(C-O)$	$A_1, \delta(C=O)$
Ground state frequency ( $\text{cm}^{-1}$ ) (Shpol'skii matrix)	311	417	455
Ground state frequency ( $\text{cm}^{-1}$ ) EtOH/MeOH (6)	308	420	452
Excited state frequency ( $\text{cm}^{-1}$ ) EtOH/MeOH	429	486	537
Shift to higher energies in the excited state ( $\text{cm}^{-1}$ )	121	66	85
Correlation loss factor $1 - \rho$	$1.5 \times 10^{-5}$	$1.5 \times 10^{-5}$	$3 \times 10^{-5}$

up to a factor of 2. This small loss of correlation can only be measured, because the resonant hole is so sharp, i. e., a considerable loss of correlation would suppress the appearance of vibrational holes.

#### Comparison with experiments

As we have pointed out the degree of correlation is different for the various vibronic transitions. The widths of the holes at 5143 and 5159 Å are about a factor of 2 larger, whereas the width of the hole at 5170 Å is almost a factor of 3 larger than the width of the parent hole. This broadening is mainly attributed to a loss in correlation between the various vibrational states and the electronic origin.

Following Gorokhovskii and Kikas,<sup>8</sup> we explain the loss of correlation by assuming that the vibrational frequencies of the probe molecules vary within the site distribution (vibrational inhomogeneity), i. e., the molecules in the individual sites differ both in their electronic energies as well as in their vibrational frequencies.

Hole burning in the first vibrational band of DAQ yields three nonresonant holes in the origin of the absorption spectrum (Fig. 1). The measured vibrational frequencies can be assigned to in-plane CO vibrations<sup>13</sup> as listed in Table I. The vibrational energies correspond to excited state frequencies which differ from the ground state frequencies by unusually large amounts as is listed in Table I. Both, the large frequency shift and the high intensity of these three low frequency modes which are all localized at the CO groups reflect an excited state charge transfer, characterizing the first singlet level of DAQ. This charge transfer is due to the charge redistribution between the electron-donating COH group and the electron-accepting carbonyl group. A charge transfer model of the lowest excited

state had been suggested earlier,<sup>4,13,14</sup> however, the first experimental evidence for this charge redistribution are the large shifts of the CO vibrations indicative of higher force constants in the excited state. (Straight forward absorption experiments do not yield the CO frequencies due to inhomogeneous broadening.)

In spite of correlation losses, the vibrational bands are quite narrow. After deconvoluting the homogeneous widths, whose magnitude was experimentally obtained from Fig. 2(a) and from hole burning data in the band origin, we get correlation losses on the order of  $(1 - \rho) \approx 10^{-5}$ . The data are listed in Table I.

Even though the correlation factors of the three CO vibrations do not differ by large amounts, they might show trends which are characteristic of different coupling strengths of the constituents of the chelate ring to the polar environment. It could, for instance, be significant that the C=O vibration shows the largest correlation loss. One would expect, in a simple chemical picture, that this group is most exposed to the polar groups of the alcohol matrix and, hence, shows the largest correlation loss. Our spectroscopic findings should not be overinterpreted at the present time, they might, however, point into an interesting direction, namely the possibility of measuring the various degrees of molecule solvent-cage interaction by evaluating correlation effects.

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