

AN INVESTIGATION OF THE MECHANISM OF NON-PHOTOCHEMICAL HOLE BURNING OF RESORUFIN IN ETHANOL GLASS

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Non-photochemical hole burning (NPHB) studies of resorufin in glasses composed of mixtures of ethanol/ethanol-*d* (hydroxyl hydrogen deuterated) are reported. The relative hole burning efficiencies, determined from hole area per photon absorbed, are found to show an essentially quadratic dependence on the concentration of ethanol. The mechanism of NPHB is discussed in terms of a model of photoinduced concerted rearrangement of intermolecular hydrogen bonds between two ethanol molecules and a resorufin molecule.

1. Introduction

Non-photochemical hole burning (NPHB) has been observed in systems of various photochemical stable chromophores embedded in disordered solid matrices (for recent reviews, see refs. [1,2]). Structural rearrangement of a chromophore's local environment, induced by electronic excitation of the chromophore, is responsible for NPHB. Since the two-level system (TLS) [3] model for the interpretation of the mechanism of NPHB was applied by Hayes and Small [4], several interesting results concerned with the relationship between NPHB and the TLS have been reported. The NPHB experiments on tetracene showed that hole burning was more facile in hydrogen-bonding glasses, suggesting that the TLS responsible for hole burning involved the hydroxyl group [5]. Indeed, a decrease in the efficiency of hole production with deuteration of hydroxyl hydrogens of the glass was observed in the tetracene system [6]. Further, a few ionic dyes in hydrogen-bonding polymers exhibited very efficient hole burning [7].

Recently photon echo and hole burning experi-

ments on the ionic dye resorufin in ethanol and ethanol-*d* (hydroxyl hydrogen deuterated) glasses have been reported [8]. The deuteration of hydroxyl hydrogen was found to cause a dramatic decrease in the efficiency of hole burning, although the deuteration had no detectable effect on either the photon echo dephasing times or the hole widths. This clearly demonstrated that optical dephasing and NPHB involve distinct mechanical degrees of freedom of the glass. It was concluded that the photoinduced rearrangement in the ethanol glass responsible for NPHB involves a motion of the hydrogen-bonding hydrogens. Although these results indicate that the hydroxyl group is involved in NPHB, the details of the photoinduced molecular rearrangements are still unknown.

In this Letter, hole burning experiments on resorufin in glasses which are mixtures of ethanol and ethanol-*d* are reported. Based on measurements of the hole area per photon absorbed, the relative hole burning efficiencies (relative quantum yield for hole burning) are evaluated. A plot of efficiencies as a function of the glass composition is interpreted in terms of a model of photoinduced rearrangements of intermolecular hydrogen bonds formed by two ethanol molecules and a resorufin molecule.

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2. Experimental procedures

Hole burning experiments were performed on glasses composed of ethanol/ethanol-*d* ($\text{CH}_3\text{CH}_2\text{-OD}$) mixtures with resorufin (Aldrich) as the chromophore. The resorufin concentration was 2×10^{-4} mol/l, and the sample solutions were contained in 1 mm spectroscopic cuvettes. Each sample was placed in a liquid helium immersion dewar. The glass was formed by cooling the sample rapidly (≥ 1 K/s) through the glass transition in a manner which has been previously described [8,9]. The hole burning experiments were carried out at 1.87 ± 0.01 K. A Coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to burn and detect the holes as described in ref. [9]. All holes were burned at 584 nm with a spot size of 1 mm. The burn fluences varied from 2 to 1200 $\mu\text{J}/\text{cm}^2$, and holes were detected with 0.1–0.2 $\mu\text{W}/\text{cm}^2$. The relative hole burning efficiencies were determined by comparing the hole area per photon absorbed for various fluences. The range of hole depths used for the measurements of hole areas was from 1 to 10%. The values of hole area per photon absorbed were confirmed to be independent of the hole depth and fluence for this range of depths.

3. Results and discussion

Chromophores in organic glasses exhibit very wide inhomogeneously broadened absorption spectra. We ascribe the inhomogeneous broadening in the spectrum of resorufin in ethanol glass to the different configurations of resorufin molecule, sodium counter ion, and ethanol molecules. Optical excitation of resorufin molecules with a narrow band dye laser selects a set of chromophores with a variety of solvent configurations which have nearly identical electronic transition energies. Subsequent rearrangement of the local environments about the chromophores depletes this set while producing a range of new environments. This results in a narrow spectral hole whose corresponding intensity is spread over the rest of the band.

In these experiments, the decrease in the hole burning efficiency of resorufin due to the deuteration of the hydroxyl hydrogen of ethanol was ob-

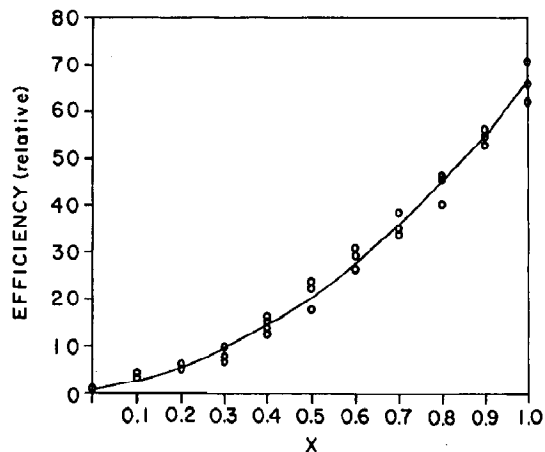


Fig. 1. Observed (circles) and calculated (solid line) hole burning efficiencies of resorufin in ethanol/ethanol-*d* mixed glasses as a function of mole fraction of ethanol, X . The solid line is calculated using eqs. (3)–(5) without adjustable parameters. The agreement between experiment and the calculated curve supports the model of a concerted double hydrogen bond rearrangement being responsible for the non-photochemical holeburning.

served in various ethanol/ethanol-*d* mixed glasses. This decrease may be attributed to the reduction in the mobility of a deuterium compared to a hydrogen. The reduction in mobility has been observed in low temperature solids in various processes such as hydrogen abstraction [10], proton transfer [11,12], and photoisomerization [13].

In fig. 1 the hole burning efficiencies of the various mixed glasses, relative to that of a sample of resorufin in pure ethanol-*d*, are plotted versus the mole fraction of ethanol. The change in the hole burning efficiency can be described as an essentially quadratic function of ethanol concentration. This quadratic dependence immediately suggests that the NPHB mechanism involves a concerted double hydrogen bond rearrangement.

In the isolated ion, the two oxygen atoms attached at the β positions of the outer rings of the resorufin ion would be equivalent (see fig. 2 for structure). Each oxygen atom would be partially ionic with a partial double bond. Alternatively, a pair of resonance structures can be described in which one oxygen is a singly bonded alkoxide anion and the other is a carbonyl oxygen. In the ethanol glass, the symmetry will be destroyed. The location of the Na counter ion and the configuration of the ethanol sol-

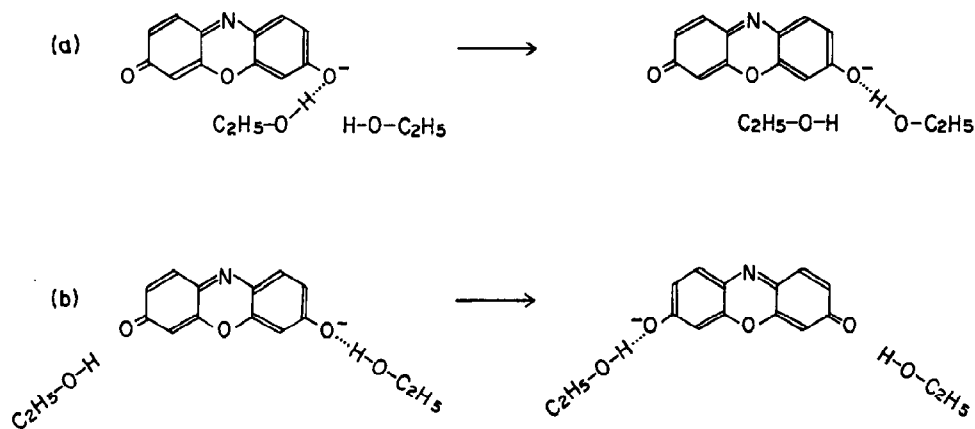


Fig. 2. Two possible photoinduced rearrangements of intermolecular hydrogen bonds between two ethanol molecules and a resorufin molecule. The sodium counter ion is not depicted. The rearrangement in (a) involves rotations of the two hydrogen bonds about the alkoxide anion (see text for a discussion of the inequivalence of the two oxygens in the solid solution). The rearrangement in (b) involves a shift of the charge in the resorufin and a change in the strengths of the hydrogen bonds. The dotted line between the H and the alkoxide anion represents a strong hydrogen bond. There is also a hydrogen bond between the H and the carbonyl oxygen, but it is weaker.

vent will, in general, not be symmetrical. This will lead to one of the β oxygens being more ion like and the other being more carbonyl like. Clearly there will be a distribution in the degree of this asymmetry. In the following, alkoxide ion or carbonyl oxygen are referred to in the sense of the asymmetry in the bonding and charge distribution, rather than a statement that one oxygen is a pure ion and the other forms a pure double bond.

The formation of an intermolecular hydrogen bond between the alkoxide ion of resorufin and the hydroxyl hydrogen of an ethanol is expected in a low temperature ethanol glass based on work on alcoholic solutions [14]. In addition, a significant change in the charge distribution occurs in resorufin upon excitation to the lowest excited singlet state as has been demonstrated by Stark effect measurements [15,16]. Therefore, motions of intermolecular hydrogen-bonding hydrogens caused by the change in the charge distribution in resorufin upon excitation are likely to play a role in the NPHB process.

To interpret the experimental data on hole burning efficiencies as a function of glass composition, we suggest a model of photoinduced rearrangements of intermolecular hydrogen bonds between two ethanol molecules and a resorufin. Consider the following rearrangement reaction scheme:



where EtOH and EtOH* are two ethanol molecules located next to a resorufin molecule in different configurations, and R is a resorufin molecule. The rate of the rearrangement reaction (γ) in terms of the rate constant for two ethanol molecules (k_{HH}) and the concentration of ethanol molecules associated with the rearrangement reaction ($[\text{EtOH}]$) is expressed as

$$\gamma = k_{\text{HH}} [\text{EtOH}]^2, \quad (2)$$

Four different kinds of rearrangements can occur in the ethanol/ethanol-*d* mixed glasses, i.e. H-H, H-D, D-H, and D-D rearrangements. The rate of rearrangement in the mixture (γ_{M}) is

$$\gamma_{\text{M}} = k_{\text{HH}} [\text{EtOH}]^2 + (k_{\text{HD}} + k_{\text{DH}}) [\text{EtOH}] [\text{EtOD}] + k_{\text{DD}} [\text{EtOD}]^2, \quad (3)$$

where $[\text{EtOD}]$ is the concentration of ethanol-*d* molecules associated with the rearrangement reactions, k_{HD} and k_{DH} are rate constants for rearrangement reactions with an ethanol and an ethanol-*d* molecule, and k_{DD} is the rate constant for rearrangement reactions with two ethanol-*d* molecules.

To evaluate the rate for the mixture (eq. (3)), we assume a homogeneous distribution of ethanol and ethanol-*d* molecules. The probability of finding an ethanol or ethanol-*d* involved in the reaction is only dependent on the concentrations of ethanol and

ethanol-*d* in the mixture. Furthermore, we assume equal probabilities for the formation of an intermolecular hydrogen bond with a hydroxyl proton or with a hydroxyl deuteron. Finally, the following equation for the rate constants is assumed,

$$k_{\text{HD}} = k_{\text{DH}} = (k_{\text{HH}}k_{\text{DD}})^{1/2}. \quad (4)$$

The ratio of the rate constants obtained from the experimental values of hole areas per photon absorbed for samples of resorufin in pure ethanol and in pure ethanol-*d* glasses is

$$k_{\text{HH}}/k_{\text{DD}} = 66 \pm 6. \quad (5)$$

Assuming eqs. (3), (4) and (5), the relative rearrangement reaction rate (hole burning efficiency) for resorufin in various mixed glasses of ethanol and ethanol-*d* can be calculated. The calculated values are shown in fig. 1 as a solid line, which is in excellent agreement with the experimental data.

The agreement supports the basic model described by the rate equations. The model as outlined above discusses intermolecular hydrogen bond rearrangements. Two possible photoinduced rearrangements are shown in fig. 2. One is a rearrangement (fig. 2a) which occurs around the alkoxide anion of resorufin. This rearrangement involves rotation of hydroxyl groups. Another is the rearrangement (fig. 2b) which involves both the alkoxide anion and the carbonyl oxygen of resorufin. In this rearrangement, there is a hydrogen bond to both oxygens. The dotted line from H to O represents a strong bond at the alkoxide anion. The carbonyl oxygen is more weakly hydrogen bonded. The rearrangement involves a shift of charge and a shift in the location of the weak and strong hydrogen bonds. In both of the suggested rearrangements the driving force is the redistribution of charge in the resorufin upon optical excitation. Stark shift data demonstrate that the resorufin dipole moment vector changes significantly [16], and CNDO calculations support the idea of substantially increased charge on the N atom. The polar solvent environment will react to this change in dipole moment vector and charge distribution. Intermolecular interactions will change magnitude and direction, and the solvent will move into a somewhat altered configuration to accommodate the resorufin excited state. This solvent motion can aid in promoting the rearrangement reactions.

While either of the proposed rearrangements could account for the agreement between the rate equation model and the experimental data, it is important to bring out three points. First, any concerted double hydrogen bond rearrangement will be consistent with the rate equations. While the two written are plausible, others can exist. For example, a double hydrogen bond rearrangement could involve bonds only among ethanol molecules near the resorufin, and not bonds to the resorufin. Ethanol forms hydrogen bonding networks. In accommodating the change in intermolecular interactions brought on by the creation of the resorufin excited state, the H-bonding network could shift a pair of H-bond partners, altering the structure around the resorufin. However, it is not clear that such a rearrangement could shift the resorufin transition energy sufficiently to be responsible for hole burning.

Second, while we have presented data on relative rate constants for structural rearrangements associated with hole burning, there may actually be a distribution of rate constants because of the distribution of local environments. Then the observed relative rate constants would be average values. However, the results are independent of hole depth for the range of hole depths (1% to 10%) examined in this study, and there is no evidence of dispersive kinetics [2] in the experiments described here.

Finally, any rearrangement that occurs must be essentially permanent, since the holes persist as long as the sample is kept at low temperature. Thus the double hydrogen bond rearrangement must not revert to the original structure when the chromophore returns to the ground state. This suggests that the solvent structure modifications which would accompany the rearrangements depicted in fig. 2 stabilize the new structure.

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