EFFECT OF HYDROGEN BOND STRENGTH
ON RESORUFIN NON-PHOTOCHEMICAL HOLE BURNING
IN ETHANOL–2,2,2-TRIFLUOROETHANOL GLASSES

Hiroshi TANAKA [1], Fumio KOKAI [2], John I. BRAUMAN and M.D. FAYER
Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Relative hole burning efficiencies of resorufin in ethanol–2,2,2-trifluoroethanol (TFE) and TFE–hydroxyl deuterated ethanol (EtOD) mixed glasses as a function of the mole fraction of TFE are reported. The hole burning efficiency is found to increase in both mixed glass systems, with a greater increase occurring in EtOD/TFE glasses. In all cases the hole width was found to be independent of the glass composition. The relationship between the hole burning efficiency and hydrogen bond strengths is discussed.

1. Introduction

Hole formation in non-photochemical hole burning (NPHB) of chromophore–glass systems has been the subject of many recent studies [1]. The two-level system (TLS) structure of glasses [2,3] which is coupled to solute chromophores' electronic states has been invoked to explain NPHB [4] and has been successfully applied to describe other characteristics of the holes produced by NPHB [5–7]. However, to a great extent the details of the mechanism of hole formation on a molecular level remain unknown.

Based on hydroxyl deuteration effects on hole burning efficiencies of tetracene in ethanol (EtOH) and methanol mixed glasses [6] as well as for resorufin in EtOH [7] it has been demonstrated that hydrogen bonds are intimately involved in NPHB in hydrogen bonding systems. Recently we have investigated the dependence on EtOH concentration of the hole burning efficiency of resorufin in EtOH and EtOD (hydroxyl deuterated ethanol) mixed glasses. An essentially quadratic increase in the hole burning efficiency with increasing EtOH concentration was

observed [8]. This quadratic behavior indicates that NPHB involves a concerted double hydrogen bond rearrangement. A simple kinetic model based on a concerted double hydrogen bond rearrangement was able to reproduce the experimental data without adjustable parameters. Two specific molecular rearrangements were proposed; one involving a rotation of two EtOH hydrogen bonds about a single resorufin outer ring β oxygen and the other involving the elongation of a hydrogen bond to one of the outer ring β oxygens and the shortening of a hydrogen bond to the other outer ring β oxygen. Although the deuteration of hydroxyl hydrogen was found to cause a dramatic decrease in the efficiency of hole burning, the deuteration had no detectable effect on either photon echo dephasing times or the hole widths [7]. This clearly demonstrates that optical dephasing and NPHB involve distinct mechanical degrees of freedom of the glass in these systems.

The deuteration effect briefly discussed above can be interpreted in terms of a TLS model as a mass effect on the tunneling rate between two energy minima on the excited chromophore-TLS potential curve. The two energy minima correspond to two distinct hydrogen bonding situations between the resorufin and the EtOH glass. A transition from one hydrogen bond arrangement to another will change the resorufin's optical transition energy, and therefore cause hole burning. Deuteration does not change the hy-

drogen bond strengths, but through the mass effect has a dramatic impact on the rate of the concerted double hydrogen bond rearrangement. It is therefore interesting to study the effect of hydrogen bond strength on hole burning efficiency (quantum yield for hole burning). In addition to mass, hydrogen bond strength would be expected to play a role in the photoinduced concerted double hydrogen bond rearrangement responsible for hole burning in resorufin–EtOH glasses. 2,2,2-trifluoroethanol (TFE) is known to be an exceptionally strong hydrogen bonding solvent [9–13] with very similar polarity to EtOH [9,12]. In the present work, we report the dependence of hole burning efficiencies in systems of resorufin in TFE/EtOH and TFE/EtOD mixed glasses. We find that the addition of TFE increases the hole burning efficiency but does not change the hole width (dephasing time). The relationship between hydrogen bond strength and hole burning efficiency is discussed.

2. Experimental procedures

A Coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to burn and detect holes as described in ref. [14]. To avoid excitation of vibronic transitions and to ensure observation of the 0–0 transition hole, hole burning experiments were performed on the red sides of the absorption spectra. Therefore, the hole burning wavelengths were changed to track the spectral shifts of the mixed samples. Wavelengths from 584 nm for EtOH (or EtOD) 100% samples to 582.5 nm for TFE 50% samples were used to maintain the same relative position in each spectrum.

Holes were burned with fluences ranging between 0.5 $\mu J/cm^2$ and 1200 $\mu J/cm^2$ and detected with less than 0.2 $\mu W/cm^2$. Laser spot sizes of 1 mm in diameter were employed. All experiments were performed at 1.87±0.01 K. The concentration of resorufin (Aldrich) was 2×10^{-4} mol/ℓ in all samples. This concentration is sufficiently low that there are no resorufin–resorufin interactions. The samples were prepared by cooling the solutions in 1 mm spectroscopic cuvettes rapidly (>1 K/s) [14,15].

The relative hole burning efficiencies were determined by comparing the hole areas per photon ab-

sorbed. 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

Absorption spectra for the solutions of resorufin in EtOH and in TFE at room temperature are shown in fig. 1. The latter shows a blue-shift. A blue-shift of the resorufin spectrum in hydrogen bonding solvents has been observed previously [10]. TFE is a much stronger hydrogen bonding solvent than EtOH because TFE is a far better H donor than EtOH [9–13]. The blue-shift displayed in fig. 1 can arise because of a decrease in the ground state energy of resorufin caused by the stronger hydrogen bonding between TFE and resorufin compared to EtOH. The excited state is less strongly stabilized because the solvation geometry is not optimal. In addition, the broadening of the structural features of the resorufin–TFE spectrum can come from stronger electron–phonon coupling (stronger coupling of the electronic excitation to the environment) also caused by stronger hydrogen bonding in TFE than in EtOH.

Figs. 2 and 3 show the dependences of the hole burning efficiencies (quantum yield for hole burn-
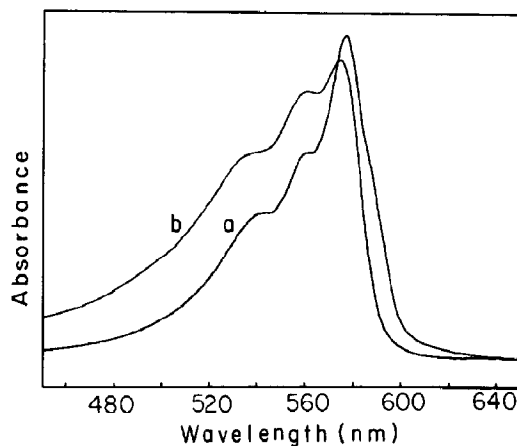

Fig. 1. Absorption spectra of resorufin in EtOH (a) and TFE (b) at room temperature. The blue-shift of the spectrum in TFE is indicative of increased hydrogen bond strength between the resorufin and the solvent.
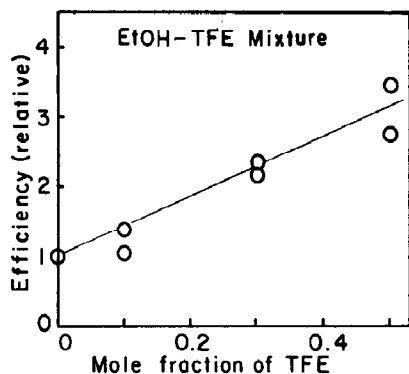
Fig. 2. Dependence of relative hole burning efficiency of resorufin in EtOH/TFE mixed glasses on mole fraction of TFE. The relative hole burning efficiency in pure EtOH is taken to be unity.

ing) on TFE mole fraction for resorufin in TFE/EtOH and TFE/EtOD mixed glasses. The efficiencies are normalized to the efficiency in 0% TFE glasses of EtOH and EtOD, respectively. (The efficiency in 100% EtOH is 66 times greater than in 100% EtOD [8].) In both TFE mixed glass systems, the efficiency increases with increasing TFE mole fraction. This behavior is more prominent for the case of EtOD, reflecting not only the deuteration effect mentioned above but also the effect of the TFE. In a mixture of TFE and EtOD there are four species, i.e. EtOH, EtOD, TFEH and TFED, since the hydroxyl hydrogens are sufficiently acidic for random-
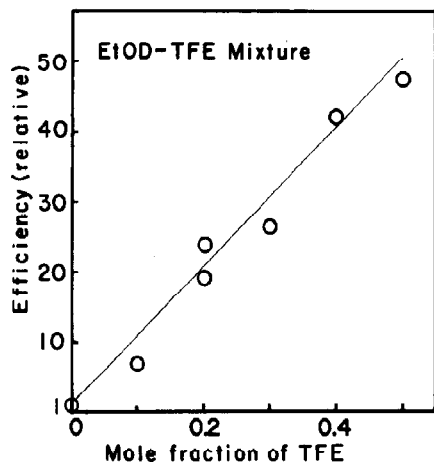

Fig. 3. Dependence of relative hole burning efficiency of resorufin in EtOD/TFE mixed glasses on mole fraction of TFE. The relative hole burning efficiency in pure EtOD is taken to be unity. The hole burning efficiency in pure EtOH is 66 times greater than in pure EtOD.

ization of hydroxyl H and D atoms to occur. Nonetheless, the TFE has a significant effect. For example, at 0.2 mole fration TFE in EtOD, the hole burning efficiency increased a factor of approximately 20, while for a 0.2 mole fraction of EtOH in EtOD the efficiency increased a factor of 5 [8].

In previous experiments on EtOH/EtOD mixed glasses, it was possible to cover the full range of concentrations from 0.0 to 1.0 mole fraction of EtOH. For TFE/EtOH (or EtOD) mixed glasses, above 0.7 mole fraction of TFE the samples always formed a polycrystalline white powder even though the samples were plunged directly into liquid helium. There also appear to be some microcrystals formed in the glasses even at lower concentrations. This was evidenced by increased light scattering from the samples compared to identically prepared samples of EtOH/EtOD mixed glasses. In some spatial locations in some samples, anomalously low efficiencies were observed. These low efficiency spots always displayed an extremely large amount of light scattering. To confirm that the measurement on such a spot was actually characteristic of the position in the sample, the hole burning measurements were repeated at different wavelengths. In all cases, identical efficiencies were recorded. We postulate that these locations have a large concentration of microcrystals. The light scattering by the microcrystals produces an erroneously large number for the optical density and reduces the true fluence of the hole burning laser beam. These two factors result in the calculation of an inaccurate very low efficiency. In figs. 2 and 3, data from points which exhibited the very intense light scattering were not included. The problems associated with light scattering prevent the acquisition of the very high quality data necessary for a quantitative analysis of the concentration trends which was possible in the EtOH/EtOD system [8]. However, the qualitative trends and a semiquantitative analysis can provide insights into the role of hydrogen bonding in these hole burning systems.

There have been extensive studies on strong hydrogen bonding systems [16]. It is generally established for potential energy curves for H atom motion along a hydrogen bond, that, as the hydrogen bond becomes stronger, the potential becomes a more energetically symmetrical double well. For a weak hydrogen bond, the two minima of the double well are

quite different energetically. As the hydrogen bond becomes stronger, not only do the double well minima become energetically similar, but the potential barrier and the distance between the two potential minima become lower and shorter, respectively [16-18]. Hydrogen bonds of the type $O^-...H-O'$ and the type $=O...H-O'$ (where $=O$ represents a carbonyl oxygen) have average $O---O'$ bond lengths of approximately 2.7 Å and belong to a class of hydrogen bonds that have essentially symmetrical double well potentials [18]. Furthermore, it is well recognized in hydrogen bonding solutions, that an H atom in a hydrogen bond becomes more mobile as the acidity of proton donor and basicity of proton acceptor increase [17]. Therefore, the potential barrier and the distance between two potential minima for H atom motion in a hydrogen bond to resorufin are expected to be lower and shorter for TFE than for EtOH. TFE is also a much better hydrogen donor than EtOH. The net result should be a higher tunneling rate for an H in a TFE-resorufin hydrogen bond than in an EtOH-resorufin hydrogen bond.

In our work on the deuteration effect briefly described above, two possible hydrogen bond rearrangements were proposed to explain NPHB in the resorufin-ethanol system [8]. One is associated with two hydrogen bonds at the alkoxide anion site of resorufin and the other is associated with two hydrogen bonds, one at the carboxyl oxygen and the other at the alkoxide anion. (In an isolated ion, the two exocyclic oxygen atoms of the resorufin ion would be equivalent. Each oxygen could be considered to be partially ionic and to have a partial double bond. Alternatively, two resonance structures can be described. In one structure, one oxygen is an alkoxide anion and the other is a carbonyl oxygen. In the second structure the identities of the alkoxide oxygen and the carbonyl oxygen are interchanged. In an ethanol glass, for any particular resorufin ion, the symmetry and thus the equivalence of the exocyclic oxygens will be destroyed. The location of the Na counter ion and the configuration of the ethanol solvent will, in general, not be symmetrical. This will lead to one of the oxygens being more ion like and the other being more carbonyl like. Clearly there will be a distribution in the degree of this asymmetry. When an alkoxide or carbonyl oxygen is referred to, it is 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.)

According to Renn et al., the S_0-S_1 excitation of resorufin causes a charge transfer of about 0.3 electrons towards the pyridinic nitrogen [19]. Motions of the intermolecular hydrogen bonding hydrogens can be induced by the change in the charge distribution in resorufin upon excitation. These motions can lead to a new stable structure, and therefore NPHB. The higher tunneling rate for hydrogens in hydrogen bonds involving TFE versus EtOH is then responsible for the increased NPHB efficiency in the EtOH-TFE mixed glasses as the concentration of TFE is increased.

In the study of NPHB of resorufin in EtOH-EtOD mixed glasses, a simple reaction rate model for a concerted double hydrogen bond rearrangement was able to describe quantitatively the concentration dependence of the NPHB efficiency [8]. It was found that the rate constant for the concerted double hydrogen bond rearrangement (hole burning efficiency) was 66 times greater in EtOH than in EtOD. However, it was not possible to form a pure TFE glass, and the quality of the data in the TFE/EtOH (EtOD) systems was reduced because of the light scattering problems mentioned above. These experimental factors prevent a similar quantitative analysis of the data. However, using an approach identical to the model employed to analyze the EtOH/EtOD experiments, it is possible to make reasonable estimates of the relative NPHB efficiencies (relative concerted double hydrogen bond rearrangement rate constants) resorufin would have in pure TFE and in pure TFED (hydroxyl hydrogen deuterated). Taking the relative efficiency in EtOD as 1, the efficiency in TFE is between 400 and 500, and the efficiency in TFED is between 75 and 150. The efficiency in TFE is approximately 7 times greater than in EtOH. The efficiency in TFED is approximately 100 times greater than in EtOD. This dramatic increase suggests that deuterium tunneling is more important for the stronger, shorter hydrogen bonded TFED system.

While the substitution of TFE or TFED for EtOH or EtOD has a dramatic effect on NPHB efficiencies, this study gives a preliminary indication that the substitution has little effect on the optical dephasing of resorufin. Fig. 4 displays hole burning data for re-
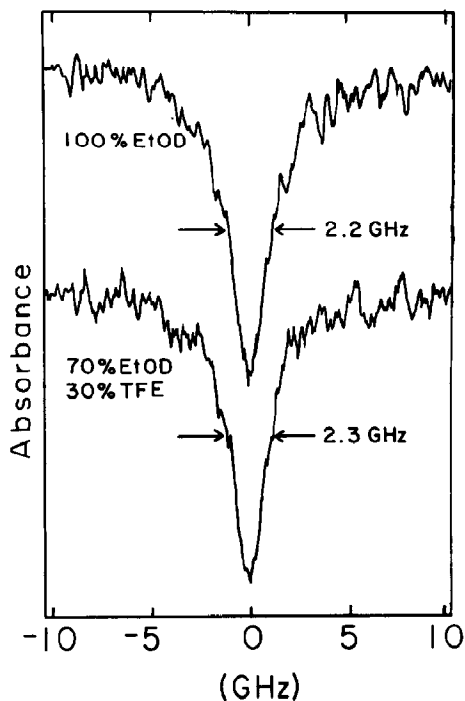
Fig. 4. Experimental hole lineshapes for resorufin in pure EtOD and in a mixed glass of 70% EtOD and 30% TFE. The hole depths are 5%. Within experimental error the hole widths are identical, and they are identical to hole widths previously reported for EtOH [7,22] and EtOD [7] at the experimental temperature of 1.9 K.

sorufin in pure EtOD and in a mixed glass of 70% EtOD and 30% TFE. The hole depths are 5%. Within experimental error the hole widths are identical, and they are identical to hole widths previously reported for EtOH [7,20] and EtOD [7] at the experimental temperature of 1.9 K. The hole widths were found to be independent of TFE concentration for all the mixed glasses with EtOH and EtOD studied. As in the deuteration experiments [7,8] this demonstrates that the mechanical degrees of freedom responsible for hole burning are not the same as the TLS responsible for optical dephasing.

The lack of sensitivity of the optical dephasing to the concentration of TFE is rather remarkable. EtOH forms extended hydrogen bonded chains. TFE is a much better hydrogen donor than EtOH and is thus a poor hydrogen acceptor from EtOH. Therefore TFE acts as a chain terminator in mixtures with EtOH [9], and less extended hydrogen bonded structures are expected. The lack of sensitivity of the resorufin optical dephasing to the extent of the hydrogen bonded solvent network supports the idea that changes in hy-

drogen bonded structures are not involved in the TLS responsible for optical dephasing.

Acknowledgement

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