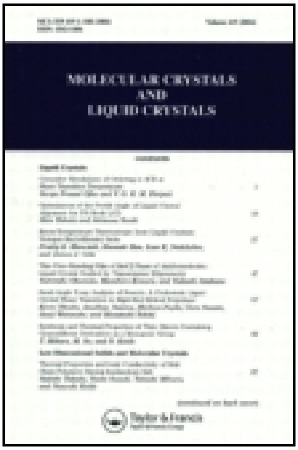

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Non-Site-Selective Excitation of a Doped Dye and Laser-Induced Hole Filling in Photochemical Hole-Burning

Norio Murase [a] & Kazuyuki Horie [b]

[a] Central Research Laboratory, Hitachi Ltd., Tokyo, Japan

[b] Dept. of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, Japan

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NON-SITE-SELECTIVE EXCITATION OF A DOPED DYE AND LASER-INDUCED HOLE FILLING IN PHOTOCHEMICAL HOLE-BURNING

NORIO MURASE
Central Research Laboratory, Hitachi Ltd., Tokyo, Japan

KAZUYUKI HORIE
Dept. of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, Japan

Abstract The mechanism of laser-induced hole filling (LIHF) in photochemical hole-burning is discussed qualitatively and quantitatively based on non-site-selective excitation of a doped dye. The dye molecules used were sulfonated tetraphenylporphine and disodium mesoporphyrin, both embedded in poly(vinyl alcohol). Experimental temperatures were in the range 4-20 K. The extent of LIHF at wavelengths shorter than the wavelength of a newly irradiating laser has a monotonically decreasing dependence on the increase in wavelength difference and reflects the degree of thermal excitation in the S_0 state. On the other hand, the wavelength dependence of the extent of LIHF at wavelengths longer than the wavelength of a newly irradiating laser exhibits two peaks, reflecting the energy levels in the S_1 state. It also depends on the experimental temperature. Besides these dependences, the extent of LIHF also depends on the molecular structure of the doped dye.

Keywords: hole-burning, hole-filling, site-selective, tetraphenylporphyrine, mesoporphyrin

INTRODUCTION

Since the invention of photochemical hole-burning (PHB) memory,[#1] it has been studied extensively because it is a promising approach for high density storage devises.[#2-#4] PHB has been assumed to be a site-selective spectroscopy, and PHB memory devices take advantage of this site-selectivity to store information in the wavelength domain.

However, our recent works have revealed important new findings as follows:
(1) Although the concept of a PHB memory using multiple holes (~1000 multiplicity) has been proposed, we showed that, to achieve an ultrahigh recording density (>10 Gbit/cm^2),

the holes must be formed with sufficient depth (~0.2 of relative depth) in the wavelength domain.[#5]

(2) However, this is prevented[#6] by laser-induced hole filling (LIHF), which decreases the depths of previously burnt holes, without changing their widths, by the irradiation of another wavelength.

(3) In PHB in dye-doped polymer systems, the site-selective excitations are usually accompanied by non-site-selective excitations due to the occurrence of other types of transitions than the purely electronic transition.[#7]

(4) These non-site-selective excitations are the origin of LIHF, so it is important to understand them in order to be able to reduce them.[#8]

The mechanism of LIHF has been studied only by a few researchers.[#9-#13] They have interpreted the phenomenon qualitatively in various ways. However, their theories do not explain observations such as the wavelength dependence of LIHF below 20 K. Here we report experimental observations of the dependence of the extent of LIHF on the wavelengths of the holes being filled, temperatures (4.2, 15, and 20 K), and the molecular structure of the doped dye. Based on these observations, the mechanism of LIHF is then discussed qualitatively and quantitatively from the viewpoint of the extent of non-site-selective excitation of the doped dye.

EXPERIMENTAL

A sample composed of sulfonated tetraphenylporphine (TPPS, Figure 1(a)) doped into poly(vinyl alcohol) (PVA) was used for the measurements of the hole wavelength and temperature dependence of LIHF. To determine the dependence of LIHF on molecular structure, we also used disodium mesoporphyrin (MPS, Figure 1(b)) doped into PVA. TPPS has four phenyl groups bonded to meso-positions, whereas MPS has no phenyl groups. The experimental apparatus has been explained previously.[#14] Experimental temperatures were 4.2, 15, and 20 K.

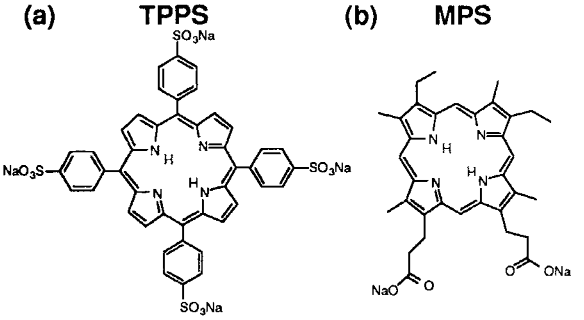

FIGURE 1 Molecular structure of (a) sulfonated tetraphenylporphine (TPPS or tetrasodium 5,10,15,20-tetra(4-sulfonatophenyl)porphine) and (b) disodium mesoporphyrin (MPS or disodium 7,12-diethyl-3,8,13,17-tetramethyl-21H,23H-porphine-2,18-dipropionate).

The experimental procedure for obtaining the extent of LIHF, γ, in TPPS/PVA was as follows.

Multiple holes were at first formed at wavelength λ in the lowest-energy absorption band in the region from 635 nm to 660 nm except for 642.0 nm (Figure 2(a)). Next a burning at 642.0 nm (λ_f) was performed to fill the earlier holes with a pre-determined burning energy, E_f. (For example, E_f is 257 mJ/cm^2 in Figure 2(b)) Other hole depths $\Delta A_{E_f}(\lambda)$ after the burning at 642.0 nm were measured as a function of E_f and λ. For the sake of quantitative analysis, we define the hole filling extent $\gamma(\lambda)$ as

$$\gamma(\lambda) \equiv \lim_{E_f \to 0} \left[1 - \Delta A_{E_f}(\lambda) / \Delta A_0(\lambda) \right] / E_f, \tag{1}$$

where $\Delta A_0(\lambda)$ is an original hole depth, namely, the hole depth at λ before the burning for the filling experiment. In the case of Figure 2(c), the γ value of the hole at 645.0 nm [indicated by * in Figures 2(a), (b)] is 2.00 x 10^{-3} cm^2/mJ. We estimated the experimental error in γ to be <10%.

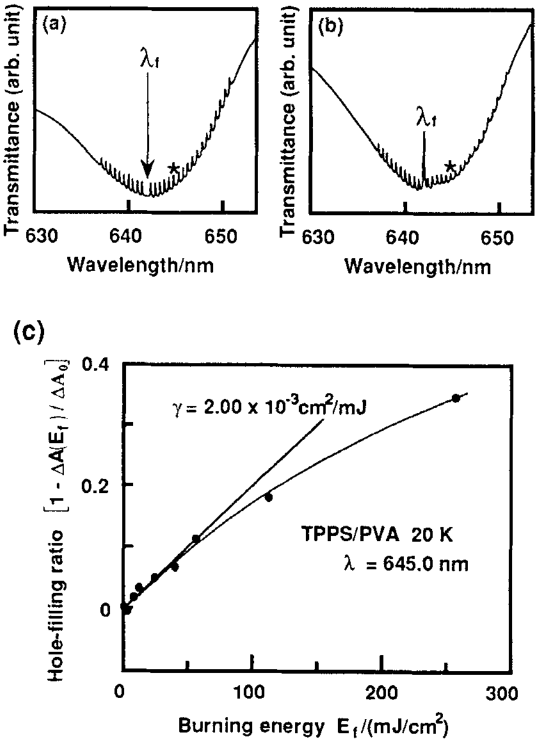

FIGURE 2 Quantitative experiment for laser-induced hole filling (LIHF) at 20 K for TPPS/PVA.

(a) Multiple hole formation before the filling measurement burn.

(b) Hole profiles after the burning of 257 mJ/cm^2 at 642.0 nm (λ_f). The originally burned holes are filled to some extent without changing their widths. For example, the hole at 645.0 nm (indicated by *) is filled ≈35%.

(c) Hole-filling ratio $[1-\Delta A_{E_f}(\lambda)/\Delta A_0(\lambda)]$ at 645.0 nm as a function of burning energy E_f at 642.0 nm (λ_f). Filled circles represent observed data. The drawn curve is a guide for the eye. The corresponding $\gamma(\lambda)$ is 2.00 x 10^{-3} cm^2/mJ, which is obtained by the extrapolation method of Eq. (1).

OBSERVED EXTENTS OF LIHF

Wavelength dependence for TPPS/PVA system at 20 K

The black circles in Figure 3 are experimental measurement of hole filling extent $\gamma(\lambda)$ for TPPS/PVA system at 20 K. The curve is drawn as a guide for the eye.

At wavelengths shorter than λ_f, $\gamma(\lambda)$ monotonically decreases with the decrease in λ and gradually approaches a constant value γ_0 of ~ 5×10^{-4} cm^2/mJ.

At wavelengths longer than λ_f, $\gamma(\lambda)$ exhibit two peaks. First $\gamma(\lambda)$ increases to reach the first maximum at ~643 nm. This energy difference from λ_f corresponds to the energy of the low-energy excitation mode E_S (23.5 cm^{-1} or 0.96 nm) of PVA[#15] as given in Figure 3. Next $\gamma(\lambda)$ decreases slightly and then increases again to reach the second higher maximum at ~652 nm. This energy difference from λ_f is slightly greater than the first vibronic energy V_1 (169 cm^{-1} or 6.94 nm) of TPPS,[#7,#16] which we consider to be the major contribution.

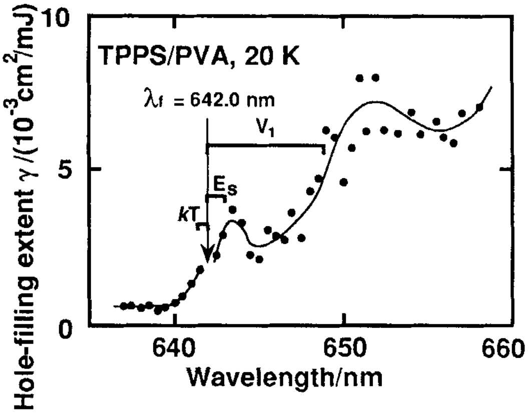

FIGURE 3 Wavelength dependence of the hole filling experiment on TPPS/PVA at 20 K. The *burning* wavelength λ_f is 642.0 nm. This figure also shows the energy of the low-energy excitation mode E_S (23.5 cm^{-1} or 0.96 nm),[#15] energy difference between the first main satellite hole and the resonant hole V_1 (169 cm^{-1} or 6.94 nm),[#7,#16] and kT at 20 K (13.9 cm^{-1} or 0.57 nm).

Temperature dependence for TPPS/PVA system

The black circles in Figure 4 show the temperature dependence of the hole filling extent $\gamma(\lambda)$ for TPPS/PVA system in the wavelength region shorter than λ_f at 4.2, 15, and 20 K. Figure 4(c) is the same data as those in the

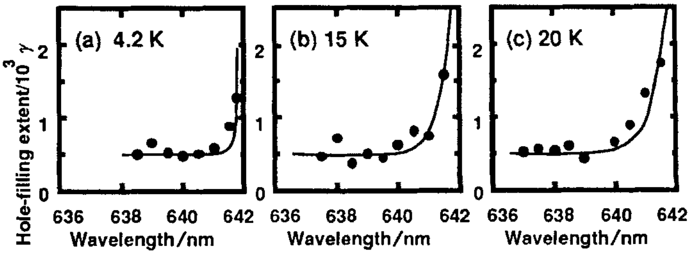

FIGURE 4 Hole-filling extent $\gamma(\lambda)$ in the wavelength region shorter than λ_f of 642.0 nm at (a) 4.2 K, (b) 15 K, and (c) 20 K for TPPS/PVA. Black circles show the observed data. The solid curve represents the optimized results for the cage model.

wavelength region shorter than λ_f in Figure 3. At all these three temperatures, as λ decreases, $\gamma(\lambda)$ monotonically decreases and eventually approaches a constant value γ_0. However, at lower temperatures (Figures 4(a), (b)), the slope of the curve close to λ_f is steeper.

Figure 5 shows the temperature dependence of hole filling extent $\gamma(\lambda)$ for TPPS/PVA system in the wavelength region longer than λ_f at 4.2 and 20 K. White circles in the figure are the same data as those in the wavelength region longer than λ_f in Figure 3. At lower temperatures, the structure of the wavelength dependence is even more prominent. The important point is that the position of the first peak at ~643 nm is unchanged, although the position of the second peak does change.

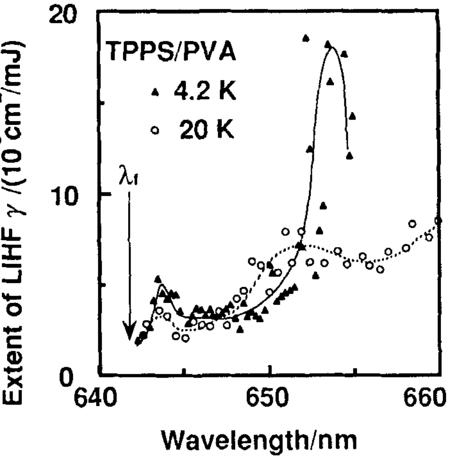

FIGURE 5 Dependence of hole-filling extent $\gamma(\lambda)$ on temperature for TPPS/PVA. White circles, which indicate the filling extent $\gamma(\lambda)$ at 20 K, are the same data as in the wavelength region longer than λ_f in Figure 3. Black triangles indicate the filling extent $\gamma(\lambda)$ at 4.2 K.

Molecular structure dependence at 20 K

Figure 6 shows the hole-filling extent γ plotted against the difference between the wavelengths of the hole-forming burns and the hole-filling burn for two different systems at 20 K, TPPS/PVA (○) and MPS/PVA (▲). The origin of the abscissa (λ_f) corresponds to 642.0 nm for TPPS/PVA and 620.0 nm for MPS/PVA. In the wavelength region shorter than λ_f, γ for MPS/PVA decreases more steeply than that for TPPS/PVA, and eventually they approach the same value γ_0.

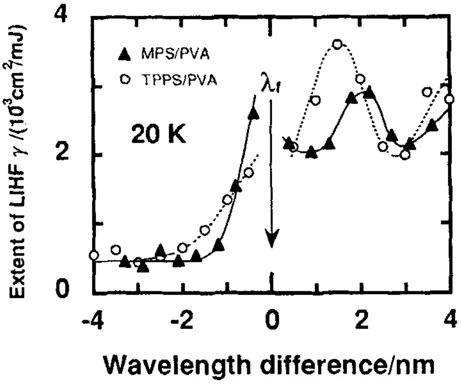

FIGURE 6 Hole-filling extent γ plotted against the difference between the wavelengths of the hole-forming burns and the hole-filling burn for TPPS/PVA (○) and MPS/PVA (▲) at 20 K. The zero value on the abscissa corresponds to 642.0 nm for TPPS/PVA and 620.0 nm for MPS/PVA.

DISCUSSION

Qualitative understanding of the mechanism of LIHF[#8]

We have already qualitatively proposed the mechanism of LIHF as follows: dyes doped into amorphous material have many energy levels such as lattice vibrational levels and vibronic levels. Therefore, these dyes can be excited non-site-selectively through other types of transitions than the purely electronic zero-phonon transition as shown in Figure 7(b). These transitions decrease the absorbance in a previously burned wavelength region relative to an unburned region .

The observed wavelength dependence of LIHF (Figure 3) can be explained at least qualitatively very well by the non-site-selective excitation profile of Figure 7(a).

Wavelength and temperature dependence of LIHF

We followed up on the above theory by making a quantitative analysis of LIHF.

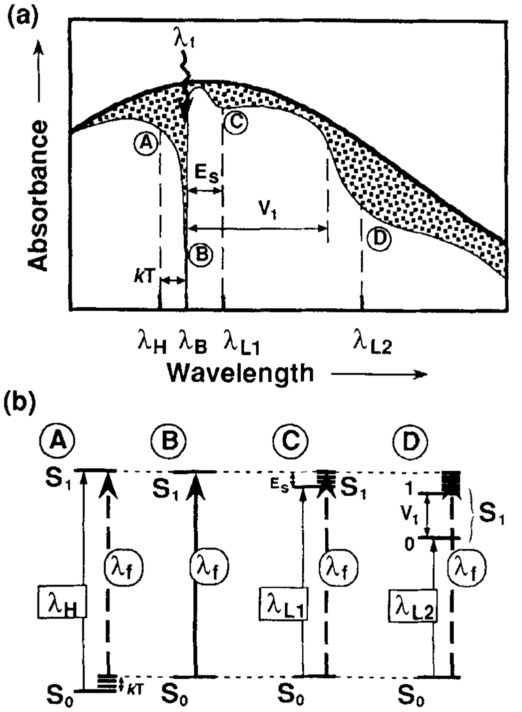

FIGURE 7 Schematic diagram of site-selective (Ⓑ) and non-site-selective excitations (Ⓐ, Ⓒ, and Ⓓ) in (a) absorption profile and (b) energy level diagrams. Non-site-selective excitations are of three types: excitations from thermally excited S_0 states (Ⓐ), excitations to lattice vibronic states in S_1 (Ⓒ), and to vibrationally excited states of dye molecules in S_1 with lattice vibrations (Ⓓ).

To explain LIHF in the wavelength region shorter than λ_f, we introduce the following model[#17] (cage model): doped-dye molecules are confined to a certain length of a cage in amorphous material. The energy of a doped-dye molecule in the S_0 state is thermally distributed in the cage. Setting the cage length to 0.40 Å results in a fairly good quantitative explanation of the measured wavelength and temperature dependence of LIHF for TPPS/PVA. These successful results are shown by the solid curves in Figures 4(a) - (c).

To interpret LIHF in the wavelength region longer than λ_f, the measured wavelength dependence of LIHF at 20 K for TPPS/PVA was analyzed to estimate system parameters governing non-site-selective excitations: the Debye-Waller factor (DWF), the energy of lattice vibrational excitation accompanying the purely electronic excitation, and other parameters related to two kinds of vibronic excitations.#7 The value of DWF agreed well with the value estimated by the method of photon-echo.#18 Other parameters estimated by the present method were larger than the values estimated by the method of satellite hole formation.#7 This suggests that some other processes than the optical non-site-selective excitation through the S_1 state could play a role in LIHF in the longer wavelength region. Furthermore, Figure 5 shows that non-site-selective excitation caused by the λ_f irradiation tends to be concentrated at specific wavelengths at lower temperatures.

Molecular structure dependence of LIHF at 20 K

As shown in Figure 6, γ for MPS/PVA decreases more steeply in the wavelength region shorter than λ_f than γ for TPPS/PVA does. This wavelength dependence was analyzed based on the same cage model. The resultant cage length was estimated to be 0.29 Å for MPS/PVA compared to 0.40 Å for TPPS/PVA. The shorter value for MPS/PVA is reasonable because the MPS molecule is lighter, flatter and more rigid than TPPS molecule, since the four phenyl groups bonded to meso-positions in TPPS are not located in the porphine-ring plane#19 and easily vibrated in optical transitions.#20 These features in the molecular structure of MPS are probably the cause of the steep decrease of γ in the wavelength region shorter than λ_f, because they lead to a shorter cage length and smaller number density of energy levels in the S_0 state, and thus increase the site-selectivity in PHB.

For the viewpoint of practical application, another important requirement in addition to greater site-selectivity is to retain the width of inhomogeneous broadening $\Delta\omega_i$. However the $\Delta\omega_i$ of the MPS/PVA system (9.7 nm) is smaller than that of the TPPS/PVA system (13.6 nm). We think this is due to the lower randomness around the MPS molecules because of its simple molecular structure. It is therefore quite likely that high site-selectivity and wide inhomogeneous broadening are mutually opposing features.

CONCLUSIONS

Non-site-selectivity in photochemical hole-burning (PHB) was discussed on the basis of the extent of laser-induced hole filling (LIHF). Experimental observations showed that it depends on wavelength, temperature, and molecular structure of the doped dye. Our samples were sulfonated tetraphenylporphine (TPPS) doped into poly(vinyl alcohol) (PVA) and disodium mesoporphyrin (MPS) doped into PVA.

The LIHF at wavelengths shorter than the newly irradiated wavelength λ_f reflects the energy levels in the S_0 state and its wavelength and temperature dependences are quantitatively explained fairly well by a cage model in which a dye doped into amorphous material is confined to a certain length of cage. This cage length can be reduced by choosing a flat, rigid dye molecule, in order to obtain greater site-selectivity in PHB.

The wavelength dependence at wavelengths longer than λ_f reflects the energy levels in the S_1 state. Quantitative analysis shows that the system parameters governing non-site-selectivity, such as the parameters related to vibronic transitions, are larger than previously estimated values by another method.[#7] This suggests that some processes other than the optical non-site-selective excitation through the S_1 state could play a role in LIHF in the longer wavelength region. At lower temperatures, non-site-selective excitation caused by the λ_f irradiation tends to be concentrated at specific wavelengths.

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REFERENCES

1. G. Castro, D. Haarer, R. M. Macfarlane, and H. P. Trommsdorff, U.S. Patent 4,101,976 (July 18, 1978).
2. A. R. Gutierrez, J. Friedrich, D. Haarer, H. Wolfrum, IBM J. Res. Develop., **26,** 198(1982).
3. M. Yoshimura, M. Maeda and T. Nakayama, Chem. Phys. Lett., **143,** 342(1988).
4. H. Suzuki, T. Shimada, T. Nishi and H. Hiratsuka, Jpn. J. Appl. Phys., **28,** Suppl. 28-3, 251(1989).
5. N. Murase, K. Horie, M. Terao, and M. Ojima, J. Opt. Soc. Am. B **9,** 998(1992).
6. N. Murase, K. Horie, M. Terao, and M. Ojima, Nippon Kagaku Kaishi, **1992,** 1117(1992).
7. K. Horie, N. Murase, and M. Ikemoto, Technical Digest on Spectral Hole-Burning and Luminescence Line Narrowing: Science and Applications, 1992 (Optical Society of America, Washington D. C., 1992) Vol. 22, pp. 252-255. ; N. Murase, and K. Horie, J. Chem. Phys. in press.
8. N. Murase, and K. Horie, Chem. Phys. Lett. in press.
9. B. L. Fearey, T. P. Carter, and G. J. Small, Chem. Phys., **101,** 279(1986).
10. R. van den Berg and S. Völker, Chem. Phys., **128,** 257(1988).
11. A. Furusawa, and K. Horie, J. Chem. Phys., **94,** 80(1991).
12. L. Shu, and G. J. Small, J. Opt. Soc. Am. B, **9,** 738(1992).
13. W. -H. Kim, M. McPhillen, J. M. Hayes, and G. J. Small, Chem. Rev. in press.
14. T. Suzuki, K. Horie, A. Furusawa, and T. Yamashita, Chem. Materials, **5,** 366(1993).
15. A. Furusawa, K. Horie, and I. Mita, Chem. Phys. Lett., **161,** 227(1989).

16. K. Horie, M. Ikemoto, T. Suzuki, S. Machida, T. Yamashita and N. Murase, Chem. Phys. Lett., **195,** 563(1992).
17. N. Murase, and K. Horie, submitted to J. Mol. Spectrosc.
18. S. Saikan, A. Imaoka, Y. Kanematsu, K. Sakoda, K. Kominami, and M. Iwamoto, Phys. Rev. B, **41,** 3185(1990).

19. The Porphyrines, Volume III, Physical Chemistry, Part A, edited by D. Dolphin (Academic Press, New York, 1978).
20. R. Tamkivi, I. Renge, and R. Avarmaa, Chem. Phys. Lett., **103,** 103(1983).