ELSEVIER

Journal of Luminescence 64 (1995) 131–134

JOURNAL OF LUMINESCENCE

Thermally activated barrier crossing and hole-filling in donor–acceptor electron transfer systems

Mingzhen Tian[a], Tiejun Chang[b,*], Jiahua Zhang[a], Haiyu Wang[a], Kai Dou[a], Baozhu Luo[a], Shihua Huang[a], Jiaqi Yu[a]

[a] *Changchun Institute of Physics, Chinese Academy of Sciences, 1 Yanan Road, Changchun 130021, China*

[b] *Department of Physics, Jilin University, 83. Jiefang Road, Changchun 130023, China*

Received 29 August 1994; revised 18 November 1994; accepted 13 December 1994

Abstract

An electron donor–acceptor-doped polymer for photon-gated spectral hole burning (PHB) was described as a two-level system (TLS). Thermal hole-filling was studied by the temperature cycling experiment. A thermally activated barrier crossing model in a TLS is used to explain the hole-filling process was verified by numerically fitting between the theoretical and the experimental results. The maximum barrier heights in several PHB materials were obtained.

1. Introduction

Photon-gated spectral hole burning in the organic donor–acceptor electron transfer system has attracted extensively interests because of its application background in frequency-domain optical storage. Several materials have been investigated from the aspects in hole-burning process, such as the photon-gating effect, temperature dependence of hole width and hole-burning efficiency. The electron transfer process and the coupling reactions between dopant molecules and polymer hosts have been discussed [1–5]. A few works on hole-filling processes have been done [6], however, the filling mechanisms are not clear now.

The organic molecule-doped crystals and glasses for photophysical or photochemical hole burning which resulted from environmental rearrangements or chemical reactions have been studied as two level systems (TLS) successfully [8–12]. With this model, the phase space of this kind of systems consisted of an ensemble of double-well potentials with different energies and barriers shown as in Fig. 1. The two lowest potential wells at the ground state correspond to the burnt and unburnt states, respectively. The hole-burning process system was excited by lasers and transited from the unburnt state to the burnt one through some higher energy states, while the thermally induced tunneling at the ground state caused hole filling.

Although works on the TLS model to describe donor–acceptor electron transfer systems for PHB have not been presented till now, we may make a reasonable assumption that the model may be suitable to these systems, because it has been successfully applied to study the relaxation processes in the photochemical materials, such as photoionization in rare earth ion-doped mixed crystals [13]

* Corresponding author.

SSDI 0022-2313(95)00021-6

and photon-induced proton transfer in organic molecule-doped polymers [9, 11, 12]. In this paper, studies on thermally induced hole-filling with TLS model are reported. The hole areas decreasing with temperature were measured with a temperature cycling experiment and the results fitted very well with the thermally activated barrier crossing model in the TLS.

2. Experimental

An electron donor, Zinc-tetraphenylbenzoporphyrin(ZnTPBP) and an acceptor, p-hydroxybenzaldehyde (PHBA) or p-aminoacetophenone (PAAP), were doped in polymer matrix polymethacrylate (PMMA) or polyvinylbutyral (PVB). Four organic films, ZnTPBP/PHBA/PMMA, ZnTPBP/PAAP/PMMA, ZnTPBP/PHBA/PVB and ZnTPBP/PAAP/PVB, were prepared with the method we reported previously [3]. The concentration of electron donor molecules is on the order of 10^{-6} mol/g and that of the acceptor 2×10^{-3} mol/g.

A He–Ne laser provided frequency-selecting beam with a wavelength $\lambda_1 = 632.8$ nm and power $P_1 = 0.64$ mW. A Nd:YAG(SHG) laser provided the gating beam, with $\lambda_2 = 532$ nm and $P_2 = 1.4$ mW. The diameter of the radiation spot was 1 mm and the burning time was 100 s. The hole was detected by probing the transmitted light with a high-resolution spectrometer (SPEX 1403) and the hole area was calculated by a microcomputer. Temperature cycling was performed as the following way in the helium gas closed-cycling cryostate system. A hole was burnt at a low temperature (T_b) and the area was measured. Then, the temperature of the system was raised to T, called the annealing temperature, and cycled back to T_b where the hole area was measured again. The annealing temperature dependence of hole area was obtained by a series of cycling process with different T.

3. Results and discussion

The mechanism of the donor–acceptor electron transfer system have been studied in our previous works [3]. Fig. 2 depicts the two-photon hole in curve (a) burnt by frequency-selecting laser simultaneously with the gating laser described in Section 2 and the one-photon hole in curve (b) burnt by frequency-selecting laser only with the same power and time as that in curve (a). Comparing the facts in Figs. 2(a) and (b), one can get a gating ratio on the order of 40–50 which means the two-photon-excited reaction is the main process in these systems.

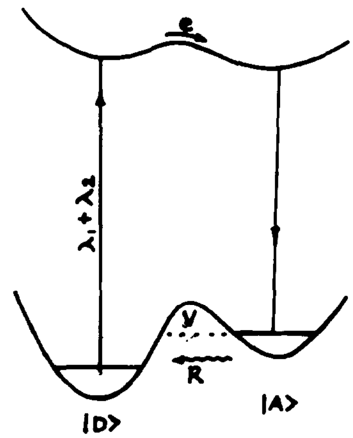

Fig. 1. The diagram of a TLS for PHB consists of the educt state |D⟩ and product state |A⟩ separated by a barrier V.

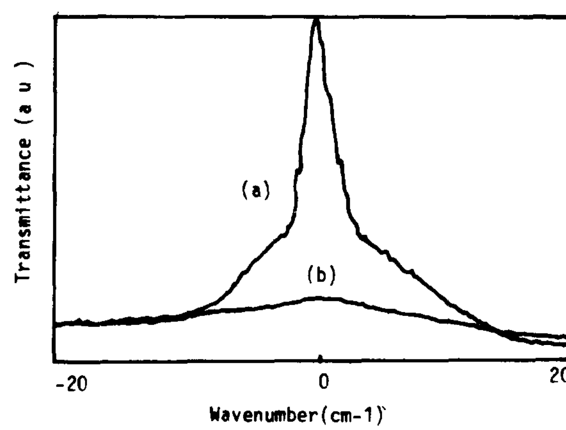

Fig. 2. The gating effect of the gating laser in sample ZNTPBP/PAAP/PMMA at 26 K. (a) A hole was burnt by selecting the laser at 632.8 nm and the gating laser at 532 nm simultaneously; (b) a hole was burnt by selecting the laser only.

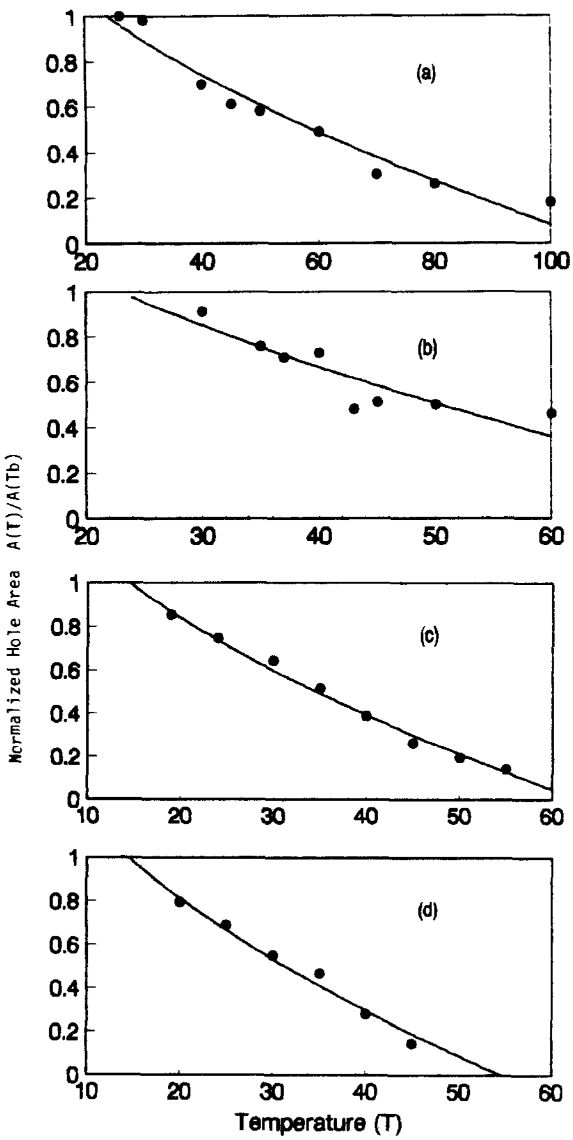

Fig. 3. Temperature dependence of the relative hole area in (a) ZnTPBP/PHBA/PMMA, (b) ZnTPBP/PAAP/PMMA, (c) ZnTPBP/PHBA/PVB and (d) ZnTPBP/PAAP/PVB; points: experimental data, lines: calculated curves.

Fig. 3 (points) gives the experimental results of normalized hole areas $A(T)/A(T_b)$ dependent on the annealing temperature in ZnTPBP/PHBA/PMMA (a), ZnTPBP/PAAP/PMMA (b), ZnTPBP/PHBA/PVB(c) and ZnTPBP/PAAP/PVB (d), respectively, which show the hole areas decreasing with that temperature. For the cases of (a) and (b) the initial burning temperature $T_b = 26$ K, for (c) and (d) $T_b = 14$ K. An additional cycling to the same temperature had no influence on the hole area.

The donor–acceptor-doped polymers we studied for photon-gated spectral hole burning were considered a TLS as shown in Fig. 1. The two lowest stable potential wells correspond to the educt and product states of the photochemical process in hole burning, respectively. In the hole-burning process, a donor molecule of the donor–acceptor pair was excited by two photons from its ground state corresponding to unburnt potential well we called donor state to the high triplet state through a series of singlet and triplet states. At the high triplet state the barrier height was relatively low and the system easily converted from one well to another through electron transfer from the donor molecule to the acceptor, then relaxed to the product well at the ground state we called acceptor state. Thus a hole was formed. To the contrary, thermally hole-filling was assumed as a thermally activated barrier crossing process from the acceptor state to the donor state. The change of the hole area in temperature cycling between T_b and T is a measure of the number of burnt donor–acceptor pairs which returned from the acceptor state to the donor state.

From well-known tunneling model [7], we accepted the distribution of barrier height separating acceptor and donor state as follows [8]

$$G(V) = g_0 V^{-1/2}, \tag{1}$$

which can be normalized by introducing cut-off values V_{max} and V_{min}, respectively. To an annealing temperature T there is a barrier height $V_T = \alpha kT$. Systems with barrier heights $V < V_T$ can convert from the $|A\rangle$ to the $|D\rangle$ through barrier crossing with the crossing rate

$$R = R_0 \exp(-V/kT), \tag{2}$$

where R_0 is the attempt frequency on the order of $10^{12}\ s^{-1}$ [10]. Systems with barrier heights $V > V_T$ will remain at the $|A\rangle$ state.

The normalized hole area as a function of the annealing temperature can be interpreted by the relative number of donor–acceptor pairs remains at $|A\rangle$. For a given temperature, this number can be calculated by integrating the barrier distribution Eq. (1) from V_T to V_{max}. The result is

$$A(T)/T_b = [1 - (\alpha kT/V_{max})^{1/2}]/ \times [1 - (\alpha kT_b/V_{max})^{1/2}]. \quad (3)$$

In a donor–acceptor-doped polymer so-called persistent spectral hole was formed through two-photon-induced electron transfer. So the decay of the hole area in the experimental time scale of thousands of seconds can be neglected and we can assume $R = 1/t$ from which we estimated $\alpha = \ln(R_0 t)$ is of the order of 30. It is important to notice that the factor α cannot be affected significantly by changing $R_0 t$ at the order of 10^2–10^4 because of its logarithmic form. In Eq. (3), we have a regularity of the normalized hole area dependent on the annealing temperature T in the form of square root. The curves in Fig. 3 denote the normalized hole area calculated with Eq. (3). By fitting the calculated curve and experimental results, we can conclude the following:

(1) The thermal hole filling process was verified to be explained very well by the thermally induced barrier crossing model in a TLS with a distribution of barrier height given in Eq. (1).

A symmetric distribution of the barrier height described by a Gaussian function around a central barrier height have been successfully applied to protein-doped glassy matrix and rare earth ion-doped mixed crystals [11, 13]. However, it was unsuitable for the cases we studied, because it resulted in the hole area decreasing with annealing temperature in a stepped fashion which is not the fact in our cases.

(2) The maximum barrier heights in four materials was obtained to be (a) 2300 cm, (b) 1720 cm, (c) 1270 cm and (d) 1150 cm.

In these materials, the electron acceptor, PHBA, and the polymer matrix, PMMA, correspond to the higher barriers which is advantageous to the hole stability. The V_{max} in the donor–acceptor-doped polymer is larger than in organic photophysical hole-burning systems [8–12] and smaller than in the inorganic mixed crystal system [13], which agrees with the photochemical nature of the hole-burning reaction in the organic donor–acceptor electron transfer system.

References

[1] W.P. Ambrose, W.E. Moerner, Chem. Phys. 144 (1990) 71.
[2] H. Suzuki, T. Shimada, Appl. Phys. Lett. 59 (1991) 1814.
[3] B. Luo, M. Tian, W. Li, S. Huang, J. Yu, J. Lumin. 53 (1992) 259.
[4] H. Suzuki, T. Shimada, Jpn. J. Appl. Phys. 31 (1992) 706
[5] H. Suzuki, T. Nishi, T. Shimada, H. Hiratsuka, J. Appl. Phys. 73 (1993) 374.
[6] M. Tian, B. Luo, W. Li, S. Huang, J. Yu, J. Lumin. 58 (1994) 191.
[7] P.W. Anderson, B.I. Halperin, C.M. Varma, Philos. Mag. 25 (1972) 1
[8] W. Kohler, J. Friedrich, H. Scheer, Phys. Rev. A 37 (1988) 660.
[9] W. Beinl, J. Friedrich, D. Haarer, J. Chem. Phys. 81 (1984) 3915.
[10] W. Kohler, J. Meler, J. Friedrich, Phys. Rev. B 35 (1986) 4031.
[11] Kohler, J. Friedrich, Phys. Rev. Lett. 59 (1987) 2199.
[12] W. Kohler, J. Zollfrank, J. Friedrich, Phys. Rev. B. 39 (1988) 5414.
[13] J. Zhang, S. Huang, J. Yu, Opt. Lett. 17 (1992) 1146.