Site-selective fluorescence spectroscopy in dye-doped polymers. I. Determination of the site-energy distribution and the single-site fluorescence spectrum

Jeung Sun Ahn,* Yasuo Kanematsu, and Takashi Kushida
Department of Physics, Osaka University, Toyonaka, Osaka 560, Japan
(Received 9 September 1992; revised manuscript received 23 April 1993)

Laser-induced fluorescence spectra have been measured, including narrow resonance fluorescence lines appearing at the same energy as the exciting light, for dye molecules doped in polymer films at low temperatures. This has been made possible by the combination of short light pulses from a cw mode-locked laser for the excitation and a time-correlated single-photon counting method for the detection. The distribution of the number of the molecules as a function of the energy of the zero-phonon line in the sample has been obtained from the excitation profile of the resonance fluorescence line. The fluorescence spectra of dye molecules in a single site have also been determined by making use of the saturation effect of the laser-induced fluorescence. The procedures of the experiment and analysis are reported in detail.

I. INTRODUCTION

In the localized centers in disordered materials such as glasses and polymers, the optical spectra are often dominated by inhomogeneous broadening that reflects the nonuniformity of the microscopic environment of the individual center. In such cases, it is important to discriminate between the site-energy distribution which causes the inhomogeneous broadening, and the spectrum without the effect of the inhomogeneous broadening. Generally, optical-absorption and fluorescence spectra of a localized center in a solid consist of a narrow zero-phonon line and a broad phonon sideband. The widths and shapes of these lines and bands without inhomogeneous broadening give valuable information on the dephasing relaxation, electron-phonon interaction, vibrational energy distribution of the host material, and so on. On the other hand, the site-energy distribution gives other important information on the static interaction between the individual center and the host lattice.

The spectral profile of a localized center without the effect of the inhomogeneous broadening is considered to be obtainable from luminescence-line-narrowing, spectral-hole-burning, and photon-echo experiments.[1–11] Among these techniques, the site-selective fluorescence method is considered to be more advantageous than the spectral hole burning and photon echo from the viewpoint of the accuracy of the result obtained. This is because the sensitivity of the fluorescence measurement is very high, and also because undistorted spectra can be obtained by this linear method. The fluorescence process is rather simple, so that the interpretation and analysis contain less ambiguity. In the case of spectral hole burning, the shape of the hole changes with burning time on account of the dispersion of the burning rate among the centers in various sites.[8] Furthermore, the hole shape is modified by the generation of photoproducts. In the photon echo, on the other hand, though it is possible to obtain the phonon-sideband profile by the use of Fourier analysis,[9] it is difficult to achieve the high accuracy and very high time resolution needed for the determination of the broadband shape, especially under the condition of weak exciting light required to avoid the spectral-hole-burning effect. We have attempted an accurate determination of the fluorescence spectrum of the guest molecule in polymer films by eliminating the effect of the inhomogeneous broadening, using a site-selective fluorescence technique.

For our purpose, it is necessary to measure the spectral shapes of both the zero-phonon line and accompanying phonon sideband. As for the zero-phonon line, that due to a purely electronic transition is more suitable than a vibronic line, since it is seldom that we observe an isolated vibronic line and its phonon sideband which are not affected by other vibronic lines. However, a special technique is required to determine the spectral shape of such a zero-phonon line by eliminating the effect of the inhomogeneous broadening by the site-selective fluorescence method. This is because it is necessary to measure the fluorescence spectrum of the resonance line, which appears at the same wavelength as the exciting light and accordingly coexists with a very strong background of the scattered exciting light. When the fluorescence decay time is long, it is not so difficult to separate the fluorescence signal from the scattered excitation light, for example by use of a double chopper.[3] In the case of organic dye molecules, however, the fluorescence decay time is short (typically several ns). Moreover, the fluorescence signal is weak, because the excitation intensity must be low enough in order to prevent the spectral-hole-burning effect from occurring during the measurement. To overcome this difficulty, we have combined a time-correlated single-photon-counting technique having high sensitivity and high time resolution with repetitive short light pulses from a cw mode-locked laser. It has been found to be possible to obtain resonance fluorescence spectra by rejecting the scattered laser light with a time-gate set long after the termination of the exciting pulse.

In this paper, measurements of the laser-induced fluorescence spectra in dye-doped polymers are reported.

0163-1829/93/48(12)/9058(8)/$06.00

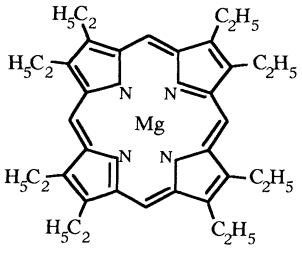
The study has focused on the energy region of the lowest optical transition of the dye molecule. The experimental determination of the site-energy distribution will be discussed. The procedures of the experiment and analysis to determine the fluorescence spectrum accurately by eliminating inhomogeneous broadening will be also discussed in detail. A part of the present work has already been reported briefly.[12] We have also determined the density of states of vibrational modes of polymers weighted by the coupling strength between the guest molecule and the host polymer from the analysis of the laser-induced fluorescence spectra. This will be reported in the following paper.[13]

II. EXPERIMENTAL PROCEDURES

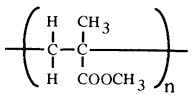
A. Samples

Thin films of polystyrene (PS) and polymethylmethacrylate (PMMA) doped with Mg-octaethylporphyrin (MgOEP) were chosen as samples, because intense fluorescence and relatively large Debye-Waller factors are expected at low temperatures, and also because the persistent spectral-hole-burning effect is rather weak in these materials. The structural formulas of these host polymers and MgOEP are shown in Fig. 1. Since the MgOEP molecule has relatively high symmetry (D_{4h}), its absorption spectrum is rather simple, with a single band in the energy region of the lowest $Q(0,0)$ absorption band as seen in Fig. 2.

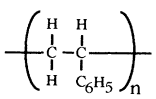
MgOEP was produced by the method of Fuhrhop and Mauzerall.[14] First, octaethylporphyrin (Aldrich, 450 mg) was dissolved in 100 ml of pyridine, 3 g of anhydrous $Mg(ClO_4)_2$ was added, and the solution was gently refluxed for 18 h in the dark. Then the solution was diluted with 200 ml of peroxide-free ether and washed five times with 30 ml of one-tenth saturated sodium acetate solution. This ether solution was evaporated under vacuum to 40 ml and cooled to 0 °C. The resulting crystals,



Mg OEP



PMMA



Polystyrene

FIG. 1. Structural formula of Mg-octaethylporphyrin and polymers used in the experiment.

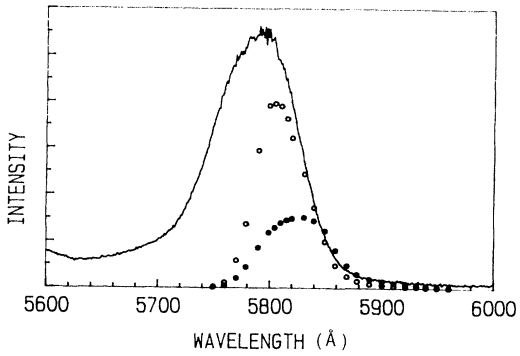


FIG. 2. The absorption spectrum of MgOEP-doped PS at 4 K (solid line). The closed and open circles are the measured and corrected excitation profiles of the resonance fluorescence line at 4 K.

which contain a considerable amount of pyridine, were filtered off. In order to obtain a pyridine-free compound, we dissolved 60 mg of the above pyridine complex in 300 ml of peroxide-free ether and washed it six times with about 200 ml of 0.1-N HCl, then with 100 ml of saturated $NaHCO_3$ solution and three times with 200 ml of water. The ether was then evaporated and the residue was recrystallized from ether/*n*-hexane.

Samples were prepared by mixing the dye solution with the polymer solution. Benzene was used as solvent for the MgOEP/PS solution, whereas tetrahydrofuran was used for the MgOEP/PMMA solution. PS was purchased from Aldrich, and PMMA from Nacalai Tesque. In the preparation of the MgOEP/PMMA solution, several drops of triethylamine were added to the solution of PMMA before mixing the two solutions in order to avoid decomposition of the MgOEP. After casting the mixed solutions onto glass plates and drying them in the dark for several days, transparent films with a thickness of several hundred microns were obtained. Sections of uniform color were cut from the dried film and mounted in a continuous-flow cryostat of liquid helium (Oxford CF1204). The optical density of the samples at 4 K was between 0.5 and 1.2 at the peak of the $Q(0,0)$ absorption band.

B. Experimental setup

Figure 3 shows the experimental configuration employed. The excitation source was a cw mode-locked rhodamine 6G laser, which produced frequency tunable pulses of about 10-ps duration at ~80 MHz in the 570–630-nm wavelength range. The laser beam was split into two parts; the transmitted part was used for the excitation of the sample, and the reflected part as a reference. Fluorescence from the sample was analyzed by a 1-m grating monochromator (Chromatix CT 103) and detected, as a single-photon event, by a cooled photomultiplier (Hamamatsu TV model R928) with a fast rise time (≤ 1 ns) and a high gain ($\sim 10^7$ at 1 kV). Then the output pulse of the photomultiplier was amplified (Hewlett Packard model 8447F), discriminated (ORTEC model

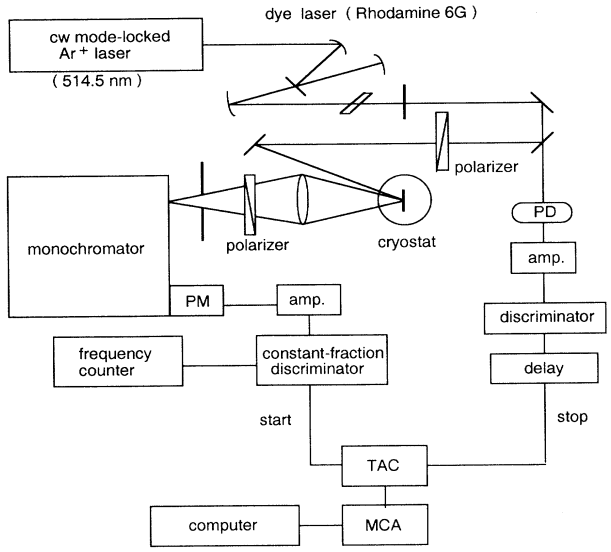


FIG. 3. Experimental arrangement for measuring the laser-induced fluorescence spectrum, including the resonance fluorescence line. PM: photomultiplier; PD: photodiode; TAC: time-to-amplitude converter; and MCA: multichannel analyzer.

583), and then fed into a time-to-amplitude converter (TAC; ORTEC model 467) as a start pulse. The reflected part of the laser beam was detected by a *p-i-n* photodiode (NEC model LSD-39B), amplified (Hewlett Packard model 8447D), discriminated (ORTEC model T105/N), delayed (ORTEC model 425A), and then used as a stop pulse of TAC. The output of TAC, which is proportional to the time difference between the single-photon detection and the next exciting pulse, was analyzed and accumulated in a multichannel analyzer (Canberra model series 30), and the obtained data were transmitted to a personal computer. Thus the time profile of the sum of the fluorescence and the scattered exciting light at each wavelength can be obtained by this method. This time-correlated single-photon counting system with time resolution as high as ≤ 200 ps has already been described in detail.[15,16]

In order to reject the scattered laser light, we accumulated the photon detection signal within a time gate, which was set long after the termination of the exciting laser pulse using a single-channel analyzer equipped in the TAC. Furthermore, we selected samples with good optical quality, and inserted a linear polarizer in the laser beam just before the sample, and a cross-polarized analyzer and an aperture between the sample and the entrance slit of the monochromator. Before and after every measurement of the laser-induced fluorescence spectrum, we recorded the time profile of the signal at the resonance wavelength in order to examine whether or not we can neglect the scattered laser light. When the contamination was not negligible, we subtracted the scattered laser component included in the signal by separating the total time profile into the scattered laser light and fluorescence from the sample.

We measured the spectrum under excitation intensities which were so weak that the effect of the spectral hole burning did not play an essential role. This was checked by observing that the resonance fluorescence intensity did not decrease during the measurement. It was also confirmed that the absorption spectrum did not change appreciably after the measurement. The excitation intensity was varied with variable neutral density filters.

For the determination of the laser-induced fluorescence spectrum in dye-doped PMMA, it was necessary to take into account the nonlinear response of the single-photon counting system due to the dead time of the TAC. We corrected the measured spectra by using the predetermined factor, which was obtained from a comparison between the total photon-counting rate of our system and the rate of the output of the constant-fraction discriminator measured by a frequency counter.

In the case of dye-doped PS, on the other hand, we employed a laser power controller (Cambridge Research and Instrumentation model LPC-VIS) and stabilized the laser intensity. Then it was possible to make measurements under much weaker excitation intensities, so that it was not necessary to correct the measured spectra.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Site-selected fluorescence spectrum

Figure 4 shows the laser-induced fluorescence spectra of a MgOEP-doped PS film. The sample was excited at

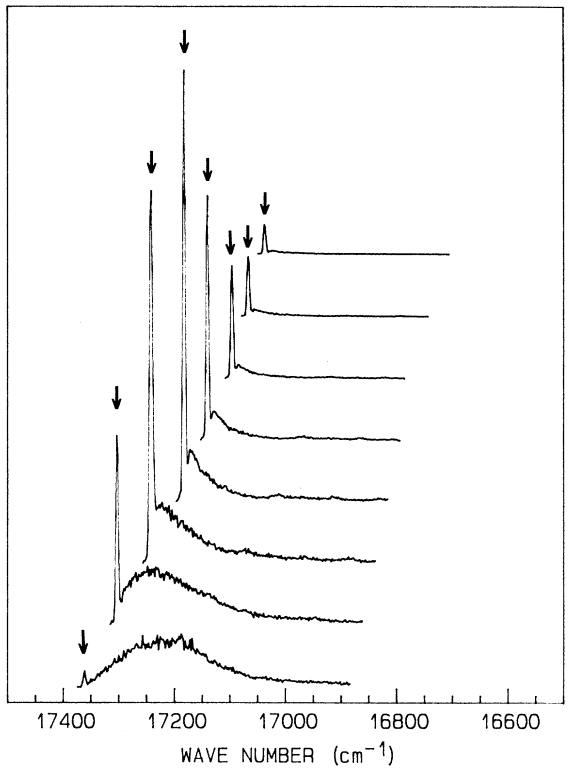


FIG. 4. Fluorescence spectra of MgOEP in a PS film at 4 K excited by laser light of various wave numbers. The arrows denote the energies of the exciting light.

various wave numbers in the $Q(0,0)$ absorption band, and the spectra were normalized by the excitation intensity. Because the optical density of the samples used at 4 K is not small enough, we cannot neglect the effects of the reabsorption of fluorescence and the intensity variation of the laser light in the sample. To compensate for these effects, we corrected the laser-induced fluorescence spectra using the relation

$$F_T(\omega,\omega_L)=\frac{A_T(\omega_L)+A_T(\omega)}{1-10^{-[A_T(\omega_L)+A_T(\omega)]}}F'_T(\omega,\omega_L)\ , \qquad (1)$$

where $A_T(\omega)$ is the optical density of the sample, $F'_T(\omega,\omega_L)$ is the measured fluorescence spectrum, and ω_L is the angular frequency of the exciting light. In Fig. 4, each spectrum consists of two parts; one is a narrow line, whose energy coincides with that of the exciting laser, and the other is a broadband in the low-energy side, whose shape depends on the excitation wave number. This result indicates that the absorption band in this sample is dominated by inhomogeneous broadening.

Let us denote the spectral shape functions of the absorption and fluorescence transitions of a dye molecule in a single site at temperature T as $g_T(\omega;\omega')$ and $f_T(\omega;\omega')$, respectively. Here, ω is the (angular) frequency of light and ω' is the zero-phonon line frequency of molecules in a given site. These shape functions can be expressed in the forms of

$$g_T(\omega;\omega')=\alpha_T z_T(\omega;\omega')+(1-\alpha_T)p_T(\omega;\omega')\ , \qquad (2)$$

$$f_T(\omega;\omega')=\alpha'_T z_T(\omega;\omega')+(1-\alpha'_T)q_T(\omega;\omega')\ , \qquad (3)$$

where the first and the second terms correspond to the narrow zero-phonon lines and the broad phonon sidebands, respectively. The areas of $z_T(\omega;\omega')$, $p_T(\omega;\omega')$, and $q_T(\omega;\omega')$ are normalized to unity, and the fractions of the contribution of the zero-phonon line are given by the Debye-Waller factors α_T and α'_T.

The absorption spectrum of the molecule in a single site is proportional to $\omega g_T(\omega;\omega')$, while the photon-counting fluorescence spectrum is proportional to $\omega^3 f_T(\omega;\omega')$. If we assume that the mirror symmetry relation holds between the absorption and fluorescence shape functions, we have $\alpha_T=\alpha'_T$ and $q_T(\omega;\omega')=p_T(2\omega'-\omega;\omega')$. Further, when the spectral shape functions do not depend on the site, we can write $g_T(\omega;\omega')$ and $f_T(\omega;\omega')$ as $g_T(\omega-\omega')$ and $f_T(\omega-\omega')$.

If the distribution function of the numbers of the guest molecules with the zero-phonon frequency at ω' is given by $G_T(\omega')$, the absorption spectrum of the sample is simply the convolution of the contribution from each site, which is expressed as

$$A_T(\omega)\propto\int d\omega' G_T(\omega')\omega g_T(\omega;\omega')\ , \qquad (4)$$

provided the transition strength is independent of the site. When the sample is excited with monochromatic light at frequency ω_L within the absorption band, the photon-counting fluorescence spectrum will be written as

$$F_T(\omega;\omega_L)\propto\int d\omega' G_T(\omega')\omega_L g_T(\omega_L;\omega')\omega^3 f_T(\omega;\omega')\ , \qquad (5)$$

under the assumption that the saturation effect and the energy migration among the sites are negligible.

At low temperatures, the zero-phonon line is generally very narrow and the spectral shape functions $f(\omega;\omega')$ and $g(\omega;\omega')$ have small values in the frequency regions of $\omega>\omega'$ and $\omega<\omega'$, respectively. Therefore, from Eqs. (2), (3), and (5), we expect that the laser-induced fluorescence spectrum at low temperatures consists of a narrow line at the same energy as the exciting light and a broadband in the low-energy side. The fraction of the resonance line in the laser-induced fluorescence spectrum is given approximately by the product $\alpha_T\alpha'_T$. Thus this fraction gives a rough estimate of the product of the Debye-Waller factors α_T and α'_T.

It is evident from the above discussion that the sharp resonance fluorescence lines in Fig. 4 result from the zero-phonon transitions both in absorption and fluorescence. On the other hand, the broadband is the sum of the phonon sideband of the molecules excited through the zero-phonon absorption line and the fluorescence of molecules excited through the phonon sideband. Because the distribution of the excited molecules is different for different excitation wave numbers, the shape as well as the intensity of the spectrum in Fig. 4 varies with the excitation wave number. Namely, the ratio of the molecules excited through the zero-phonon line to those through the phonon sideband changes with the excitation frequency. This leads to the excitation-frequency dependence of the laser-induced fluorescence spectrum, even when the single-site spectra do not depend on the site.

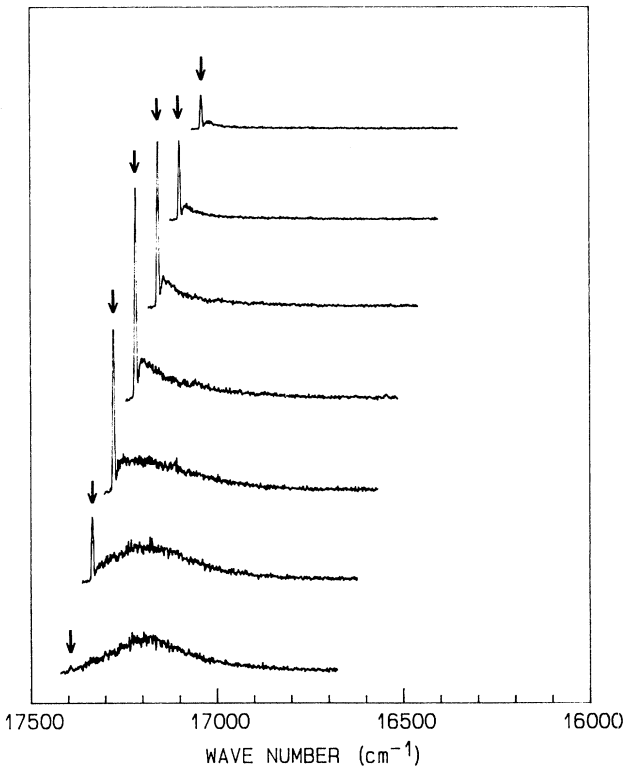


FIG. 5. Laser-induced fluorescence spectra of MgOEP in a PMMA film at 4 K.

As shown in Fig. 5, the laser-induced fluorescence spectra of the MgOEP/PMMA film are similar to those of the MgOEP/PS, except that the fraction of the resonance line is somewhat smaller in the former.

B. Site-energy distribution function

The widths of the resonance fluorescence lines in Figs. 4 and 5 are limited by the resolution of the experimental apparatus. Thus the widths of the zero-phonon lines are very narrow in our samples at 4 K, and we can regard $z_T(\omega;\omega')$ in Eqs. (2) and (3) as a δ function. Then the excitation spectrum of the narrow resonance fluorescence line is expressed as

$$E_T(\omega_L) \propto \omega_L^4 G_T(\omega_L) . \tag{6}$$

Therefore, it is possible to determine the site-energy distribution function $G_T(\omega')$ from the analysis of this excitation spectrum. We obtained the site-energy distribution using the excitation spectrum for the fluorescence intensity corrected by Eq. (1). Thus the corrected excitation spectrum for MgOEP doped in PS is compared with the uncorrected spectrum in Fig. 2. We notice that a more realistic Gaussian-like excitation spectrum is obtained by compensating for the effect of reabsorption, which indicates that our correction is reasonable. The site-energy distributions determined for MgOEP doped in PS and PMMA through Eq. (6) are plotted by closed circles in Fig. 6.

In order to explain the temperature dependence of the absorption spectrum of deoxymyoglobin, a configuration-coordinate model was proposed for the site-energy distribution by Kushida *et al.*[17] In this model, the envelopes of the local minima in the adiabatic potential curves for the electronic ground and excited states are expressed by parabolas as follows:

$$U_g = a(Q-Q_g)^2 , \tag{7}$$

$$U_g = b(Q-Q_e)^2 + U_0 . \tag{8}$$

Here, Q is the configuration coordinate to express the distortion of the dye molecule and/or the surroundings, which is related to the nonuniformity of the microscopic environment around individual dye molecules. The local minima, which are called conformational substates, are assumed to be densely and homogeneously distributed along the Q axis. Then, using the population distribution function in the electronic ground state $\rho_g(Q)$, the site-energy distribution is given by

$$G_T(\omega') = \int dQ\, \rho_g(Q)\delta\left[\frac{U_e-U_g}{\hbar}-\omega'\right] . \tag{9}$$

Let us adopt this model in order to explain the asymmetric spectral shape of the distribution functions of Fig. 6. The dash-dotted lines in the figure are the fitting curves derived from Eqs. (7), (8), and (9) using Gaussian functions for $\rho_g(Q)$. The transition strength was assumed to be independent of Q. We see that the experimentally determined site-energy distribution is well reproduced by this model. Thus the asymmetry of $G_T(\omega')$ with longer tails in the low-energy side is explained by assuming that the curvature of the potential curve is smaller in the electronic excited state compared to the ground state, i.e., $b < a$ in Eqs. (7) and (8).

It is important to make a further investigation of the site-energy distribution on the basis of molecular theory. Several efforts toward such a direction have been made, where interactions and radial distribution functions between molecules are introduced, and an origin of the asymmetric site-energy distribution is discussed.[18–20] What types of interaction and radial distribution functions would give reasonable understanding of real systems is, however, left as an attractive problem. The determination of the site-energy distribution by our method for various guest-host combinations will give valuable information for the study of this problem.

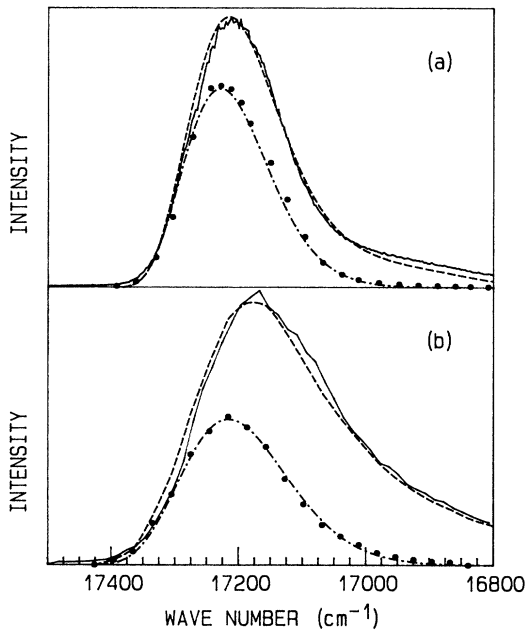


FIG. 6. The fluorescence spectra of MgOEP in (a) PS and (b) PMMA excited by the (a) 472.7-nm and (b) 514.5-nm Ar^+ laser lines at 4 K (solid curves) and site-energy distribution functions (circles). The dash-dotted curves derive from Eqs. (7)–(9), while the dashed curves are from Eq. (10).

C. Single-site fluorescence spectrum

As seen from Eq. (5), the laser-induced fluorescence spectrum is different from the fluorescence spectrum of the guest molecule in a single site. In order to obtain the single-site fluorescence spectrum, we used the saturation effect of the laser-induced fluorescence. That is, we found in our samples that the fluorescence intensity excited by a cw dye laser is not proportional to the exciting laser intensity even under weak excitations (Fig. 7). For these excitation intensities, the persistent spectral-hole-burning effect is considered to be negligible, because the fluorescence intensity was time independent. Nevertheless, the spectral shape of the broad band in the laser-induced

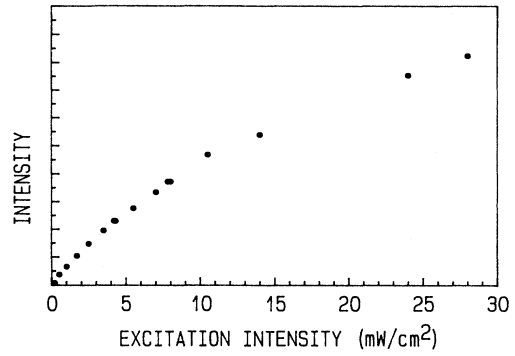


FIG. 7. Excitation-intensity dependence of the fluorescence intensity of MgOEP in PS measured at the peak of the broadband (17 138 cm^{-1}) at 4 K. The excitation source was a cw dye laser at 17 123 cm^{-1}.

fluorescence varied with excitation intensity. These characteristics are considered to arise from the saturation effect. Since the peak absorption cross section is much larger in the zero-phonon line than in the phonon sideband in our samples at 4 K, the saturation effect is expected to be much more significant for the fluorescence excited through the zero-phonon absorption line compared with that through the phonon sideband.

The upper spectrum in Fig. 8(a) was obtained for a MgOEP/PS film under weak excitation where the saturation effect is almost negligible. On the other hand, the lower spectrum was obtained for the case where the saturation effect was considered to occur only in molecules excited through the zero-phonon line. These spectra are corrected using relation (1), and are normalized by the excitation intensity. The difference between these two spectra is shown in Fig. 8(b). This corresponds to the phonon-sideband profile of the fluorescence spectrum of dye molecules in a single site. The phonon sidebands of single-site fluorescence spectra thus determined for the two samples are compared in Fig. 9. We notice that these spectra are very similar to one another, although the peak energy is a little higher in the case of the PMMA matrix.

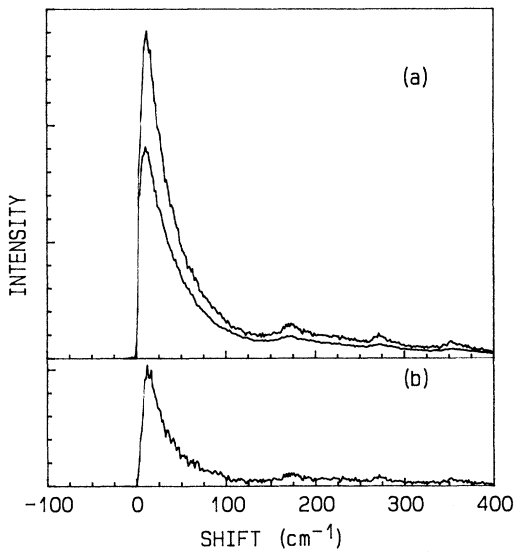


FIG. 8. (a) Broadband profiles of the laser-induced fluorescence spectrum of a MgOEP/PS film at 4 K measured for two excitation intensities (upper: 3.7 mW/cm^2; lower: 28 mW/cm^2). The fluorescence intensity has been divided by the intensity of the exciting cw dye laser at 17 123 cm^{-1}. (b) The difference between the two spectra in (a).

The solid curves in Fig. 6 are the fluorescence spectra of MgOEP doped in PS, and PMMA excited by an Ar^+ laser. These spectra were corrected using relation (1). These spectra did not change essentially when the other lines of the Ar^+ laser were employed for the excitation. Thus the molecules in various sites are considered to be excited rather uniformly, when our sample is illuminated by light within a high-energy broad absorption band. If we assume that the fluorescence shape function does not depend on the site, the fluorescence spectrum under uniform excitation of the molecules in various sites is expressed as

$$F_T(\omega) \propto \int d\omega' G_T(\omega') \omega^3 f_T(\omega - \omega') \ . \tag{10}$$

We fitted the fluorescence spectra in Fig. 6 with that calculated through Eq. (10) using the above-determined site-energy distributions and single-site fluorescence spectra. The Debye-Waller factor used for this fitting was 0.4 for the MgOEP/PMMA film, and 0.62 for the MgOEP/PS. As shown by the dashed curves in Fig. 6, good agreement was obtained between the experiment and calculation, which indicates that the single-site fluorescence spectra in Fig. 9 can be regarded as a homogeneous spectrum that is independent of the site in our samples, and also that the site-energy distribution function has been determined correctly by our experiment.

The solid curve in Fig. 10 shows the laser-induced fluorescence spectrum of MgOEP-doped PS calculated through Eq. (5) from the above-determined site-energy distribution and single-site fluorescence spectrum. It was assumed that the mirror-symmetry relation holds be-

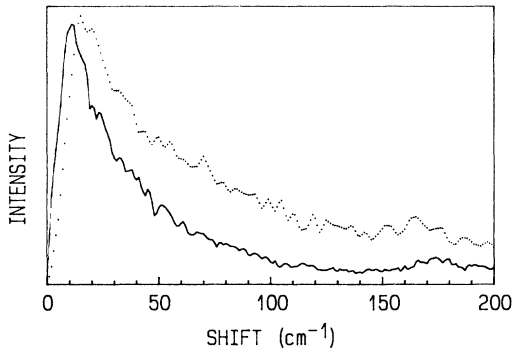


FIG. 9. The phonon-sideband profiles of the single-site fluorescence spectra of MgOEP doped in PS (solid curve) and PMMA (dots).

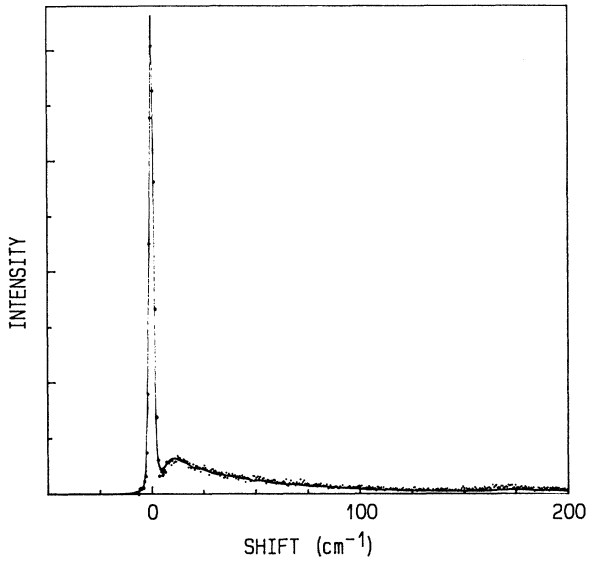


FIG. 10. The laser-induced fluorescence spectrum of MgOEP in PS measured at 4 K under the laser excitation at 17 126 cm^{-1} (dots) and a theoretical curve obtained from Eq. (5) under the assumption that the mirror-symmetry relation holds between the absorption and fluorescence shape functions (solid curve).

tween the absorption and fluorescence spectral shape functions of the guest molecule. We notice that the theoretical fitting curve reproduces the experimental data quite well. This result indicates that the mirror-symmetry relation holds for the molecules in the sites selected at this excitation wavelength.

It was found, however, that except for the case of excitation at the low-energy region of the absorption band, the laser-induced fluorescence spectra were not reproduced well by the calculation through Eq. (5) using the experimentally determined $G_T(\omega')$ and $f_T(\omega;\omega')$, if we assume the mirror-symmetry relation and the site independence of the single-site fluorescence spectrum. It was also found that the absorption spectrum of the sample was not reproduced well by Eq. (4) if we employ the same assumptions. These results indicate that the mirror-symmetry relation does not hold in the high-energy region of the absorption band in our sample. The degeneracy of the excited state corresponding to the Q absorption band may be lifted in our case because of the interaction between the MgOEP molecule and its environment. Therefore, it is probable that the absorption band we examined consists of two components whose energy separation is widely distributed. Part of the excitation into the higher excited state will result in the fluorescence from the lower excited state through the fast intramolecule relaxation. Such fluorescence gives an additional broadband that reflects the wide distribution of the energy separation between the two excited states. This explains the breakdown of the mirror-symmetry relation between the absorption and fluorescence shape functions in the high-energy region of the absorption band. Experimental data to support this interpretation will be reported elsewhere.

IV. CONCLUSION

Site-selective fluorescence spectroscopy has been performed for MgOEP-doped PS and PMMA films at low temperatures. A narrow resonance fluorescence line accompanied by a broadband in the low-energy side has been observed for the laser excitation into the lowest optical-absorption band by rejecting the scattered exciting light using a time gate. To our knowledge, this is the first case in which the spectrum of a narrow resonance fluorescence line has been measured in dye molecules in condensed matter. The laser-induced fluorescence spectrum has been found to depend on the excitation frequency. The phonon-sideband profile of the single-site fluorescence spectrum has been determined from the difference in the fluorescence spectra under cw dye-laser excitations with different intensities. The site-energy distribution that gives inhomogeneous broadening has also been obtained from the excitation profile of the resonance fluorescence line. It has been found that the single-site fluorescence spectrum does not depend on the site, and the mirror-symmetry relation holds between the absorption and fluorescence shape functions in the low-energy region of the absorption band.

ACKNOWLEDGMENTS

The authors are grateful to Ms. Kuniko Hirata for her help in preparing the samples employed for the measurements. This work was supported by the Ministry of Education, Science and Culture of Japan, Grant-in-Aid for General Scientific Research No. 02452039.

*Present address: Institute for Molecular Science, Okazaki 444, Japan.

[1] *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems,* edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983).

[2] M. J. Weber, in *Laser Spectroscopy of Solids,* edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981), p. 189.

[3] T. Kushida and E. Takushi, Phys. Rev. B **12**, 824 (1975).

[4] J. Fünfschilling, I. Zschokke-Gränacher, and D. F. Williams, J. Chem. Phys. **75**, 3669 (1981).

[5] *Persistent Spectral Hole Burning: Science and Applications,* edited by W. E. Moerner (Springer-Verlag, Berlin, 1988).

[6] J. Friedrich, J. D. Swalen, and D. Haarer, J. Chem. Phys. **73**, 705 (1980).

[7] In-Ja Lee, J. M. Hayes, and G. J. Small, J. Chem. Phys. **91**, 3463 (1989).

[8] Y. Kanematsu, R. Shiraishi, A. Imaoka, S. Saikan, and T. Kushida, J. Chem. Phys. **91**, 6579 (1989).

[9]S. Saikan, T. Nakabayashi, Y. Kanematsu, and N. Tato, Phys. Rev. B **38**, 7777 (1988).
[10]S. Saikan, A. Imaoka, Y. Kanematsu, and T. Kishida, Chem. Phys. Lett. **162**, 217 (1989).
[11]S. Saikan, A. Imaoka, Y. Kanematsu, K. Sakoda, K. Kominami, and M. Iwamoto, Phys. Rev. B **41**, 3185 (1990).
[12]J. S. Ahn, Y. Kanematsu, and T. Kushida, J. Lumin. **48/49**, 405 (1991).
[13]Y. Kanematsu, J. S. Ahn, and T. Kushida, following paper, Phys. Rev. B **48**, 9066 (1993).
[14]J.-H. Fuhrhop and D. Mauzerall, J. Am. Chem. Soc. **91**, 4174 (1969).
[15]T. Kushida and S. Kinoshita, in *Semiconductors Probed by Ultrafast Laser Spectroscopy,* edited by R. R. Alfano (Academic, New York, 1984), Vol. 2, p. 483.
[16]S. Kinoshita and T. Kushida, Anal. Instrum. **14**, 503 (1985).
[17]T. Kushida, J. S. Ahn, K. Hirata, and A. Kurita, Biophys. Biochem. Res. Commun. **160**, 948 (1989).
[18]L. Kador, J. Chem. Phys. **95**, 5574 (1991).
[19]H. M. Sevian and J. L. Skinner, Theor. Chim. Acta **82**, 29 (1992).
[20]H. M. Sevian and J. L. Skinner, J. Chem. Phys. **97**, 8 (1992).