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Site-selective fluorescence spectroscopy in dye-doped polymers. II. Determination of the weighted density of states of the vibrational modes

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The density of states of vibrational modes weighted by the coupling strength between the guest molecule and the host polymer has been obtained in dye-doped polymer films by solving an integral equation numerically using experimentally determined single-site fluorescence spectra at 4 K. The temperature dependence of the laser-induced fluorescence spectrum has been found to be reproduced by a simulation based on the linear electron-phonon coupling theory using the determined weighted density of "phonon" states. This result supports the validity of our procedures of experiment and analysis. The spectral profiles of the obtained weighted density of states of the vibrational modes will be discussed.

I. INTRODUCTION

The weighted density of "phonon" states (WDOS), i.e., the density of states of vibrational modes of the host material weighted by the coupling strength between the optical center and the host modes, is important, because it gives us valuable information on the dynamics of the host material and the nature of the electron-phonon interaction. This can be obtained from the analysis of the phonon sideband of the optical spectrum of a localized center in solids. However, the WDOS for disordered systems such as glasses and polymers has not yet been reported, because it is not easy to obtain accurately the phonon-sideband spectrum due to the large inhomogeneous broadening of the optical spectra.

There exist interesting attempts to obtain the phonon-sideband profile by analyzing hole-burning spectra.[1,2] For example, Lee, Hayes, and Small reconstructed the phonon-sideband spectra using Lorentzian profiles for the one-phonon profile, which corresponds to the WDOS, and the multiphonon profiles on the basis of a linear electron-phonon coupling theory.[2] In addition to the employment of tentative phonon-shape functions, an approach from hole-burning spectroscopy has drawbacks due to the effects of photoproducts and dispersive hole-burning kinetics, as pointed out in the preceding paper.

Recently, we have succeeded in the determination of the single-site fluorescence spectrum in dye-doped polymers, eliminating the inhomogeneous broadening by means of a site-selective fluorescence technique. The experimental methods and analytical procedures for obtaining the single-site fluorescence spectra have already been described in detail in the preceding paper.[3] In the present paper, we analyze these single-site fluorescence spectra and determine the WDOS for dye-doped polymers. A part of the results of the present work have already been reported briefly.[4]

II. PROCEDURES OF ANALYSIS

The single-site absorption and fluorescence spectra generally contain multiphonon sidebands in addition to the one-phonon sideband, and we cannot neglect the former contribution when the Debye-Waller factor is smaller than ~ 0.9. In order to determine the WDOS, it is necessary to extract the one-phonon sideband profile from the single-site spectrum. A method of doing this by solving an integral equation numerically has been devised by Kukushikin,[5,6] and has been applied to dye-doped crystals by Personov and co-workers.[7,8]

Let us consider the case in which the concentration of the localized center in a solid is so low that the interaction between the centers can be neglected. We treat the optical transition between the electronic ground and excited states of the center by adopting the adiabatic and Condon approximations. The optical transition energy of the host material is assumed to be sufficiently large, and the following linear electron-phonon interaction is employed:

$$H_{e-p}=\sum_j \gamma_j (b_j^+ + b_j) \ , \tag{1}$$

where b_j^+ and b_j are the creation and annihilation operators of the phonons in the jth mode. Furthermore, we confine ourselves to first-order perturbation, and assume that the low-frequency vibrational modes of the host can be regarded as an ensemble of normal-mode harmonic oscillators. Then the fluorescence spectral shape function at temperature T is expressed as

$$f_T(\omega_p;\omega_0)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\omega_0-\omega_p)t+S_T(t)-S_T(0)} \ , \tag{2}$$

where

$$S_T(t)=\int_0^{\infty} d\omega\, s(\omega)[\{n_T(\omega)+1\}e^{-i\omega t}+n_T(\omega)e^{i\omega t}] \ , \tag{3}$$

with

$$s(\omega)=\sum_j (\gamma_j/\hbar\omega)^2 \delta(\omega-\omega_j) \ . \tag{4}$$

Here $\hbar\omega_p$ is the photon energy, $\hbar\omega_0$ is the peak energy of the zero-phonon line, ω_j is the angular frequency of the jth normal mode of the host material, and $n_T(\omega_j)$ is the occupation number of the corresponding phonon at temperature T. Since the dimensionless quantity $(\gamma_j/\hbar\omega)$ can be regarded as the coupling coefficient between the opti-

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cal center and the host matrix, we call $s(\omega)$ the weighted density of "phonon" states (WDOS). In the approximation being discussed, the Debye-Waller factors in the absorption and fluorescence spectra are given by

$$\alpha_T=\alpha'_T=e^{-S_T(0)} . \tag{5}$$

Assuming that the fluorescence spectral shape function is site independent, we separate it into a δ-function-like zero-phonon line and a phonon sideband as

$$f_T(\Omega)=\alpha'_T\delta(\Omega)+\Phi_T(\Omega) , \tag{6}$$

where $\Omega=\omega_0-\omega_p$. Let us expand the factor $e^{S_T(t)}$ in Eq. (2) as $\sum_{m=0}^{\infty}[S_T(t)]^m/m!$, and express $S_T(t)$ by its inverse Fourier transform $s_T(\Omega)$, i.e.,

$$\begin{aligned} s_T(\Omega)&=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, S_T(t)e^{i\Omega t} \\ &=s(\Omega)[n_T(\Omega)+1]+s(-\Omega)n_T(-\Omega) . \end{aligned} \tag{7}$$

Then $\Phi_T(\Omega)$ is given in the form of the sum of convolutions of $s_T(\Omega)$ as follows:

$$\Phi_T(\Omega)=\sum_{m=1}^{\infty}\Phi_T^{(m)}(\Omega) , \tag{8}$$

$$\Phi_T^{(m)}(\Omega)=\frac{\alpha'_T}{m!}\int_{-\infty}^{\infty}d\Omega_1\int_{-\infty}^{\infty}d\Omega_2\cdots\int_{-\infty}^{\infty}d\Omega_m s_T(\Omega_1)s_T(\Omega_2)\cdots s_T(\Omega_m)\delta(\Omega-\Omega_1-\Omega_2\cdots-\Omega_m) , \tag{9}$$

where $\Phi_T^{(m)}(\Omega)$ denotes the contribution of the m-phonon process to the phonon sideband.

If we multiply $\exp(-i\Omega t')$ to both sides of Eq. (6) and integrate it over Ω, we obtain

$$\int_{-\infty}^{\infty}d\Omega\,\Phi_T(\Omega)e^{-i\Omega t'}=\alpha'_T[e^{S_T(t')}-1] , \tag{10}$$

where we used Eq. (2). If we further differentiate both sides of Eq. (10) with respect to t' and perform the Fourier transform, the following integral equation is obtained:

$$\Omega\Phi_T(\Omega)=\alpha'_T\Omega s_T(\Omega)+\int_{-\infty}^{\infty}d\Omega'\Phi_T(\Omega-\Omega')\Omega' s_T(\Omega') . \tag{11}$$

At $T=0$, this reduces to

$$\Omega\Phi_0(\Omega)=\alpha'_0\Omega s_0(\Omega)+\int_0^{\Omega}d\Omega'\Phi_0(\Omega-\Omega')\Omega' s_0(\Omega') , \tag{12}$$

because both $s_0(\Omega)$ and $\Phi_0(\Omega)$ are zero for $\Omega\leq 0$. Since $s_0(\Omega)=s(\Omega)$, as seen from Eq. (7), it is possible to determine the WDOS by solving Eq. (12) numerically using the phonon-sideband profile of the single-site fluorescence spectrum obtained at low temperatures. For this purpose, it is convenient to introduce dimensionless quantities as

$$x=\frac{\Omega}{\Omega_0} ,\quad y=\frac{\Omega'}{\Omega_0} ,\quad \tilde{s}(x)=xs(\Omega_0 x) ,\quad \phi(x)=c\frac{\Phi_0(\Omega)}{\Phi_0(\Omega_1)} ,$$

where Ω_0 and Ω_1 are arbitrary fixed frequencies and the constant c is chosen so that the area of $\phi(x)$ is normalized to $1-\alpha'_0$ using a new scale x. Then Eq. (12) is rewritten in the form

$$\tilde{s}(x)=\frac{1}{\alpha'_0}\left[x\phi(x)-\int_0^x dy\,\tilde{s}(y)\phi(x-y)\right] . \tag{13}$$

If we take a sufficiently small step ε along the x axis, this changes into

$$\tilde{s}(n\varepsilon)=\frac{\varepsilon}{\alpha'_0}\left[n\phi(n\varepsilon)-\sum_{m=1}^{n-1}\phi\{(n-m)\varepsilon\}\tilde{s}(m\varepsilon)\right] , \tag{14}$$

with the boundary condition $\tilde{s}(0)=0$.

III. DETERMINATION OF WDOS IN DYE-DOPED POLYMERS

We determined the WDOS for polystyrene (PS) and polymethyl-methacrylate (PMMA) doped with Mg-octaethylporphyrin (MgOEP) employing Eq. (14). In the actual calculation, we used the single-site fluorescence spectra obtained at 4 K and made a correction for the effect of the nonzero temperature using Eq. (7). This is considered to be a good approximation because, at

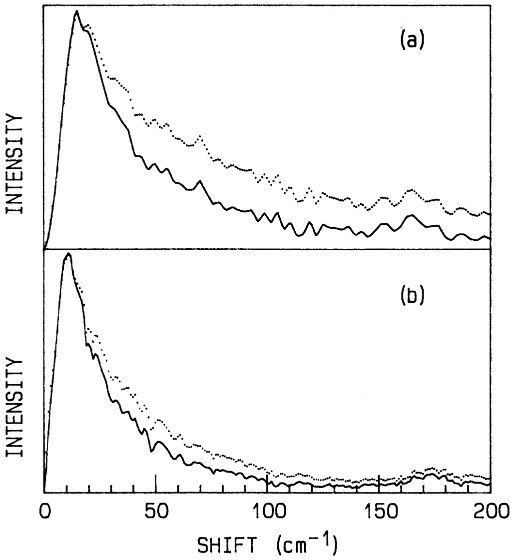

FIG. 1. The single-site fluorescence spectrum (dashed line), and weighted density of "phonon" states (solid line) obtained for (a) PMMA and (b) PS doped with MgOEP.

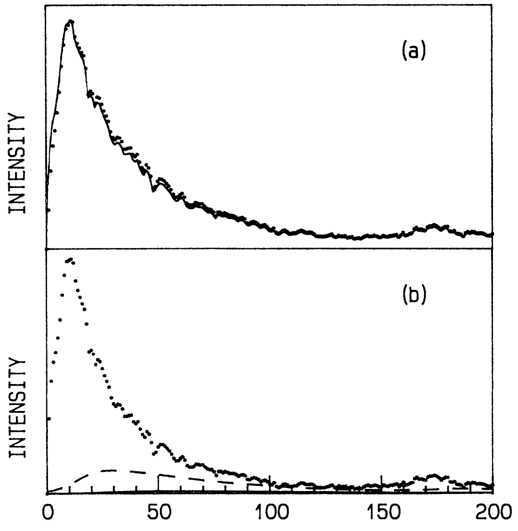

FIG. 2. (a) The phonon-sideband profile of the single-site fluorescence spectrum of MgOEP in PS at 4 K. The solid line has been calculated using the weighted density of "phonon" states in Fig. 1. (b) The one-phonon (dots), two-phonon (dashed line), and three-phonon (solid line) sidebands included in the calculated spectrum in (a).

sufficiently low temperatures, the temperature dependence of $\Phi_T(\Omega)$ is expected to be weak and present only in the vicinity of $\Omega=0$. For the same reason, we used the Debye-Waller factor obtained at 4 K. The WDOS's thus determined are plotted in Fig. 1. together with the phonon-sideband profiles of the single-site fluorescence spectra obtained in the preceding paper.[3]

If the WDOS is correctly obtained, the single-site fluorescence spectrum must be reconstructed by the calculation of Eqs. (6), (8), and (9). We performed this calculation using the above-determined WDOS. As shown by solid lines in Figs. 2 and 3, the experimentally determined phonon-sideband profiles of the single-site fluorescence spectra are well reproduced by this calculation. Also shown in Figs. 2 and 3 are the spectra due to the one-, two-, and three-phonon processes calculated through Eq. (9) using the above WDOS. We see that the contributions of the multiphonon processes are not negligible in our samples. As far as we know, this is the first case in which the WDOS is reported for dye-doped amorphous systems, although Personov *et al.*[7] obtained the WDOS for n-paraffin crystals doped with organic molecules from the phonon-wing profiles of the fluorescence spectra under mercury lamp excitation.

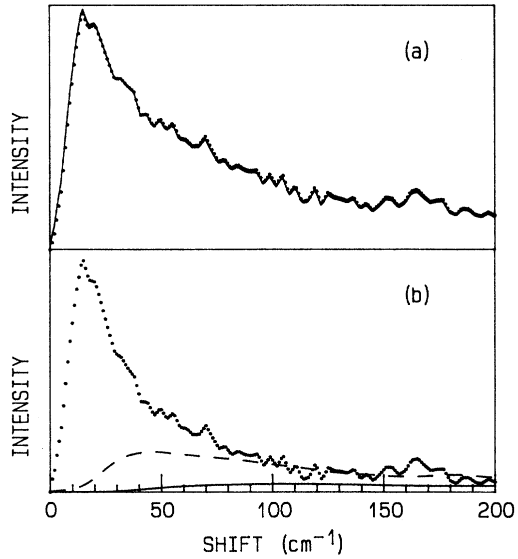

FIG. 3. The same as in Fig. 2 for MgOEP in PMMA.

IV. TEMPERATURE DEPENDENCE OF LASER-INDUCED FLUORESCENCE SPECTRA

The scattered dots in Fig. 4 show the fluorescence spectra measured for a MgOEP/PS film under laser excitation in the low-energy region of the absorption band at various temperatures. We notice that the fraction of the sharp resonance line decreases with increasing temperature. Almost the same temperature dependence was observed for a MgOEP/PMMA film (Fig. 5). We calculated the temperature dependence of the laser-induced fluorescence spectrum using the site-energy distribution function $G_T(\omega')$ and WDOS $s(\omega)$. The site-energy distribution function was assumed to be independent of temperature.

The details of the calculation are as follows. The phonon-sideband profiles of the fluorescence shape function at various temperatures were calculated by Eqs. (7), (8), and (9) using the experimentally determined WDOS. The Debye-Waller factors α'_T at various temperatures

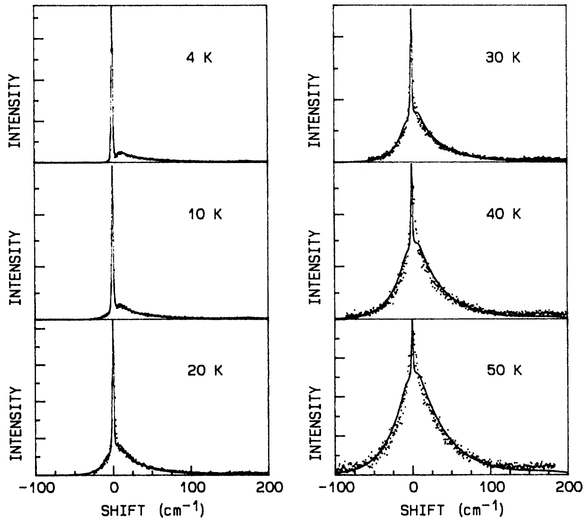

FIG. 4. Laser-induced fluorescence spectra of MgOEP in PS at various temperatures. The excitation wave number is 17 126 cm^{-1}. The solid lines show theoretical curves obtained from the WDOS of Fig. 1 under the assumption of linear electron-phonon interaction.

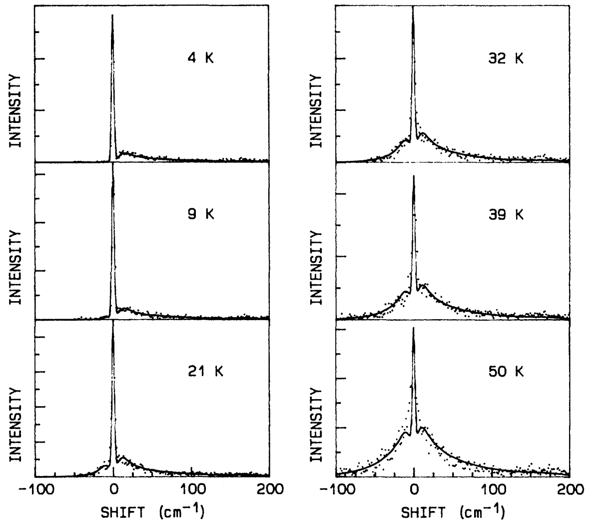

FIG. 5. The same as in Fig. 4 for MgOEP in PMMA excited at 17 117 cm^{-1}.

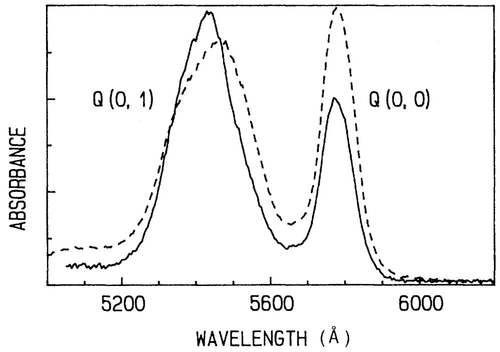

FIG. 6. Absorption spectra of two films of MgOEP-doped PMMA. The dashed curve is for the specimen containing more triethylamine, which was employed for the measurement of the temperature dependence of the laser-induced fluorescence spectrum.

were obtained using Eq. (5) from the WDOS and α'_T at 4 K. Then the fluorescence shape function was obtained by Eq. (6). Using this function and the experimentally determined $G_T(\omega')$, we obtained the laser-induced fluorescence spectra at various temperatures by performing the following convolution:

$$F_T(\omega;\omega_L) \propto \int d\omega' G_T(\omega')\omega_L g_T(\omega_L;\omega')\omega^3 f_T(\omega;\omega') \ , \tag{15}$$

where we assumed that the mirror-symmetry relation holds between the absorption and fluorescence shape functions, and also that they are site independent. The calculated laser-induced fluorescence spectra were further convoluted using a Gaussian function with the width corresponding to the resolution of the experimental equipment. The results are plotted by solid lines in Figs. 4 and 5.

The general features of the observed laser-induced fluorescence spectra are well reproduced by the simulated curves over all the temperature region studied. This result assures the validity of our experimental and analytical methods of determining the WDOS. At temperatures higher than about 20 K, the observed resonance fluorescence lines appear to have broader spectral widths than the experimental resolution. This will be discussed in Sec. V. The MgOEP/PMMA specimen used for the measurement of the spectra of Fig. 5 was not the same one as that used for the experiment reported in the preceding paper.[3] The absorption spectrum of the former is shown in Fig. 6 by a dashed line, whereas that of the latter is plotted by a solid line. In the preparation of the MgOEP/PMMA sample, we added several drops of triethylamine to the PMMA solution in order to avoid decomposition of MgOEP, as mentioned previously. We found that the intensity ratio of the $Q(0,0)$ absorption band to the $Q(1,0)$ band increases with increasing quantity of the added triethylamine. It should be noted, however, that the temperature dependence of the laser-induced fluorescence spectrum is reproduced well by the calculation as in Fig. 5.

V. DISCUSSION

As seen in Fig. 1, the WDOS's determined for two samples are very similar to each other, although the peak positions and the slopes in the high-energy side are a little different. Furthermore, the shapes of the WDOS's we obtained for dye-doped amorphous systems are very similar to those of the n-paraffin crystals doped with organic molecules.[8] In the latter case, it has been found, from the comparison of the WDOS with the Raman spectrum of the host crystal, that the contribution of the optical vibrations to the WDOS is small, and the main contribution comes from the acoustic branch. Taking into account the effect of the quadratic electron-phonon interaction, Osad'ko, Al'shits, and Personov[8] approximated the WDOS as the sum of the single-phonon and two-phonon contributions, and estimated the limiting energy for the acoustic vibrations as 40 cm^{-1} for n-heptane and 50 cm^{-1} for n-hexane. Moreover, from the comparison between the obtained one-phonon contribution and a calculation based on a simple model, these authors assigned the principal peaks of the WDOS's as being due to the density of n-paraffin phonon states in certain cases, and to a quasilocal vibration in certain other cases.

As for the main peaks of the WDOS in Fig. 1, it should be noted that the peak frequencies nearly coincide with those of the hole-burning spectra of dye-doped PS and PMMA. Previously, we pointed out that the peak frequency of the sideband hole in the hole-burning spectrum of a dye-doped polymer is insensitive to the species of the guest molecule, and that it corresponds to the boson peak frequency in the Raman spectrum of the host material.[9,10] Therefore, the main peaks of the WDOS's in Fig. 1 are considered to correspond to the peaks in the density of states of the vibrational modes of the host polymer. It is possible that they are due to the quasilocalized vibrational modes.

Recently, an interpretation of the Raman spectra of disordered materials from the fractal viewpoint has appeared.[11–13] According to this, the boson peak is attributed to the phonon-fracton crossover. We compared the WDOS's with the Raman spectra of the host materials, and found that there exists a correlation between the high-energy slopes of the WDOS and the Raman spectrum both for PMMA and PS. We tentatively discussed this result based on the fracton picture of the vibrational modes in disordered systems.[14] Since it has become possible by our method to obtain an accurate WDOS, it is very interesting to compare our method with other experiments such as Raman scattering and neutron scattering in many systems.

In the discussion of Sec. II, we employed a linear electron-phonon coupling theory, in which the energy difference between the adiabatic potential surfaces for the electronic ground and excited states is assumed to contain only the linear terms of the normal coordinates of the harmonic vibrations in addition to a constant term. In this case, the zero-phonon line has no spectral breadth irrespective of the sample temperature. However, as seen in Figs. 4 and 5, the spectral widths of the zero-phonon lines are not negligible in our samples, especially at elevated temperatures. In order to explain this, it is necessary to take into account the quadratic terms in the normal coordinate in the energy difference between the adiabatic potential surfaces. However, since the spectral analysis based on the linear electron-phonon coupling theory gives satisfactory results, as explained in the present and previous papers, the effect of the quadratic coupling is considered to be small enough not to affect the WDOS and the shape of the broad band in the single-site fluorescence spectra, as well as that of the laser-induced fluorescence spectra.

We have recently applied the technique described in the present paper to a chromoprotein, and obtained the WDOS for a chromophore surrounded by polypeptide chains. The result will be reported elsewhere.

VI. CONCLUSION

By solving an integral equation numerically, we have determined the one-phonon sideband profile of the single-site fluorescence spectrum at 0 K for dye-doped polymers. This corresponds to the density of "phonon" states weighted by the frequency-dependent electron-phonon coupling strength between the host polymer and the guest molecule. We believe that this is the first case in which the weighted density of "phonon" states has been determined in dye-doped amorphous systems. Furthermore, it has been confirmed that the Debye-Waller factor as well as the shape of the observed laser-induced fluorescence spectra at ≤ 50 K are well reproduced by the simulation based on the linear electron-phonon coupling theory using the determined WDOS. From this result, it is confirmed that the WDOS has been determined correctly by our experiment and analysis.

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