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DISPERSIVE LINE SHAPE OF PERSISTENT SPECTRAL HOLE-BURNING OBSERVED IN PSEUDO-ISOCYANINE BROMIDE J-AGGREGATES AND ITS EXCITON-PHONON INTERACTION

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Abstract Hole formation profiles of the exciton band of J-aggregates of pseudo-isocyanine bromide / water-ethyleneglycol system were carefully examined and significant difference of the burning sources, DC-light laser or nanosecond pulsed laser was observed. The results on the upper J-band are described mainly though the essential features are commonly observed also in the lower band. In the former case clear zero-phonon hole was formed with the width of 0.4 cm^{-1}. Assuming negligible contribution of the dephasing by phonons the homogeneous width of the one-exciton state is lifetime-limited in nature and $T_1 \sim 28$ psec. In the pulsed mode burning, peculiar feature of dispersive lineshape of the hole was observed from the initial stage of irradiation. It is described at the moment as a result of the excitation of the two-exciton band which is inherent to the excitonic state with large coherence length.

INTRODUCTION

The issue of dynamical properties of linear molecular aggregates with mesoscopic size is currently interesting. This is because these systems bridge the gap between a single molecule and a crystal. J-type linear aggregate is well known for its Frenkel type excitonic bands appearing below the lowest edge of monomeric absorption band. Since pioneering works of Jerry[1] and Scheibe[2], lots of aggregated systems have been found and investigated. They also have found technological applications as sensitizers in the photography which in turn provided the new field of science.[3] Among them pseudoisocyanine (PIC) dye exhibits the narrowest bands, i.e., ~ 1 nm at cryogenic temperatures. Recently it attracts also new attentions as a possible optoelectronic materials since large third order non-linearity was found out.[4]

Investigations of homogeneous as well as inhomogeneous natures in terms of an exciton model have mostly been proceeded by hole burning[5,6,7] as well as photon echo[8,9] techniques. In this paper we focused our attention to the careful examination of the hole formation profiles on the red J-band in PIC-Br / water-ethyleneglycol (WEG) system by using DC-light laser or nanosecond pulsed laser. The difference of the lasing mode of the burning light revealed essential difference in the excitation of the exciton state. A unique

feature observed is the formation of the hole with dispersive lineshape formed by pulsed laser irradiation. This feature is ascribed as a result of the excitation of the two-exciton band, which is inherent to the excitonic state with large coherence length.

EXPERIMENTALS

PIC-Br was purchased from Nippon Kankoh Shikiso Kenkyusho (Okayama, Japan) and used without further purification. Samples were made by dissolving PIC-Br at a concentration of 4×10^{-3} M in a mixture of distilled water and ethyleneglycol (50/50 vol%, WEG). Drops of such solutions were pressed between flat glass slides with 12 μm thickness Mylar® film as a spacer.[4] The samples were cooled down to cryogenic temperatures in a continuous flow type variable temperature optical cryostat (Oxford: CF1204). Aggregate formations were provided in the cryostat at the temperature region of 230K for blue J-band or 180 K ~ 170K for red J-band, respectively. Most of the burning experiments described in this paper were performed at 4.7 K.

The holes were burnt with two types of lasers and the results were compared. The first one was a Nd^+:YAG laser pumped dye laser (Spectra-Physics: DCR-11 + PDL-3), the width of which is about 0.07 cm^{-1}. The pulse repetition rate was 10 Hz and the average power levels were about 30 $\mu W/cm^2$ at initial burning stages. They were carefully increased step-by-step after confirming that the obtained spectral change has already exceeded ordinary observed saturation levels, by far e.g. reported in ref. 6, up to 2.4 mW/cm^2 in the final stage of burnings. Another series of experiments was performed with a single-mode ring dye laser (Coherent: 699-29) pumped with Ar^+ laser as totally DC light source. The width of the laserline was about 3 MHz. Its power densities in the burnings were tuned to follow almost similarly to those in the pulsed light burnings.

The holes as well as absorption spectra were all measured with a 1.5 m double-pass monochromator (Jovin-Yvon: THR1500) with a resolution of 0.03 cm^{-1}. It should be stressed that one has to be very careful in measuring absorption changes in the J-bands. Since they are so sharp, even a fraction of Å wavelength shift in the monochromator gives rise to some artifacts. In order to avoid this we tuned the wavelength origin of the instruments every measurements to secure the reproducibility and carried out several independent experiments for further confirmation.

RESULTS AND DISCUSSION

Figure 1 shows the visible absorption spectra for the PIC(Br) / WEG system measured at 295 K and 4.7 K in region. While the sample at room temperature shows a spectrum of typical monomeric dispersion, the spectrum at 4.7 K shows two excitonic bands. They occur as a consequence of aggregate growth at the temperature around 180 K for several

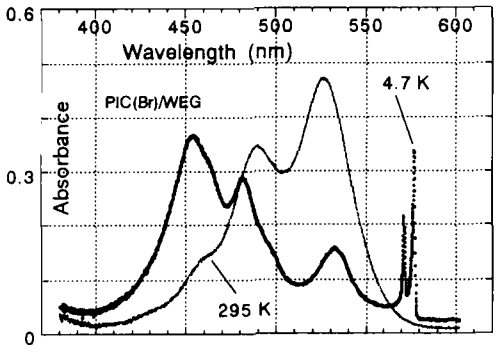

FIGURE 1 Absorption spectra of PIC-Br / WEG system observed at 295 K and at 4.7 K. The latter was obtained as a consequence of the aggregate formation at temperatures around 180 K for several minutes followed by quenching at a rate of ~ 7 K/min below 77 K.

minutes followed by quenching at a rate of ~ 7 K/min. This growth condition basically provides a lower red J-band at 576.0 nm though a some amount of upper blue J-band at 570.8 nm still remains.

The widths of the red J-band are 40 ~ 35 cm^{-1} depending upon the samples. The monomer spectrum at 295 K shows that the origin absorption has an inhomogeneous bandwidth of ~ 1200 cm^{-1}. Thus the reduction of the inhomogeneous bandwidth is characterized by a factor of 30. An exciton moving over an aggregate chain comprising N monomer molecules narrows the inhomogeneous bandwidth of the monomer absorption band by a factor of the order of $1/\sqrt{N}$.[10] Simple application of this relation yields an aggregate length of about 900 in our samples. Considering part of the inhomogeneity of monomers could be due to small rotations of the quinoline ring with respect to one another,[5] the size of the delocarization length in our sample can also be assumed in the order of 100. According to the exciton theory,[11] the energy shift of the exciton band from the monomer peak is $2V$, where V is a coupling constant between the nearest neighbor monomers in the chain. From the red shift of the red J-band, e.g. 1690 cm^{-1}, V is of the order of – 850 cm^{-1}. Hence the width of the exciton band $|4V|$ is of the order of 3390 cm^{-1}.

First, we describe the results carried out by using the pulsed laser as burning light source. Rather broad-band observations of deeply burned holes are shown in Fig. 2 compared with the exciton bands. Just to be stressed here is the total decoupling between the lower and upper exciton bands in terms of photoreaction as is also observed in PIC-Cl and PIC-I.[7] More precise hole profiles at the lower fluence regions are shown in Fig. 3. As can be seen in the figure the lineshape of holes are quite different from ordinary holes: They show ***dispersive lineshapes*** even at zero fluence limit instead of sharp zero-phonon holes in resonance with the burning light wavelength λ_B.

The notable characteristics deduced from Figs.2 and 3 can be summarized as follows:
(1) There is a conservation of oscillator strength in the low fluence limit: The area of hole is almost equal to the area of antihole.

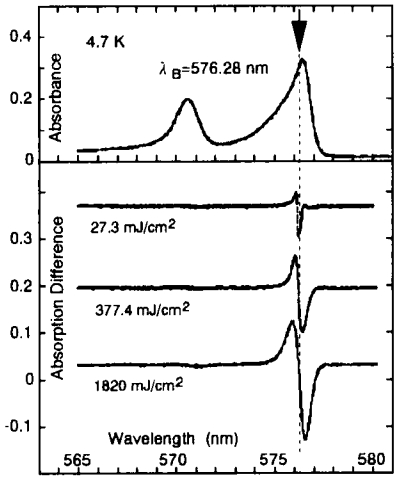

FIGURE 2 Two excitonic peaks (Top) and the hole profiles after prolonged bleaching at lower exciton peak (Bottom) indicating the two exciton bands are decoupled.

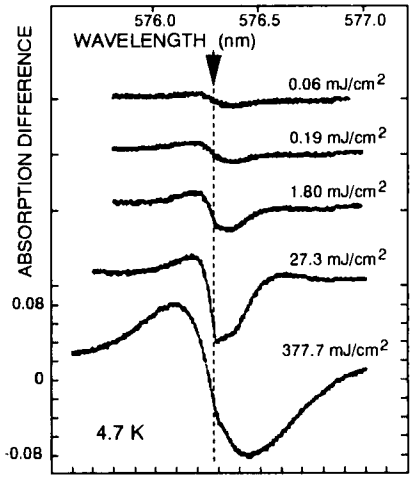

FIGURE 3 Fluence dependence of hole formation profiles obtained at 4. 7 K by the irradiation of the pulsed laser light at the peak of the lower exciton band.

(2) There is product at longer as well as at shorter wavelengths with respect to λ_B. The spectral range of the product eventually coincides with the inhomogeneous band.

(3) In the prolonged bleaching stage, a kink or a small but broad hole-like structure in resonance with λ_B appears. This could be comprehensible if rather strong linear exciton-phonon coupling (e.g. Huang-Rhys factor $S \sim 2.5$) and unusually low energy ($\Delta \sim 2.7$ cm^{-1}) for a phonon coupled to an optical transition were assumed as is suggested in ref. 6. We consider, however, that this simple model is insufficient for the description of the observed hole profile and fairly large exciton-phonon coupling inferred from the model is not consistent with other experimental findings.

In order to elucidate the nature of hole formation in the J-aggregate, we demonstrated the experiments by the DC-laser light irradiation and the results were compared. Figure 4 shows the observed hole profiles in the low fluence region. The difference is quite clear: Narrow resonance holes were obtained and this feature is rather as of ordinarily expected.

The notable characteristics deduced from Fig 4 and related data are summarized as follows:

(1) Sharp holes are formed precisely at the wavelength of the irradiated laser light within our experimental accuracy. Its full width, extrapolated to zero burning fluence, is of the order of 0.40 cm^{-1} at 4.7 K. We can safely conclude that they are zero-phonon holes and, therefore, the linewidth of the absorption band of the exciton is inhomogeneous in nature.

(2) Assuming the effective number of monomers in the aggregated chain is ~ 100, over

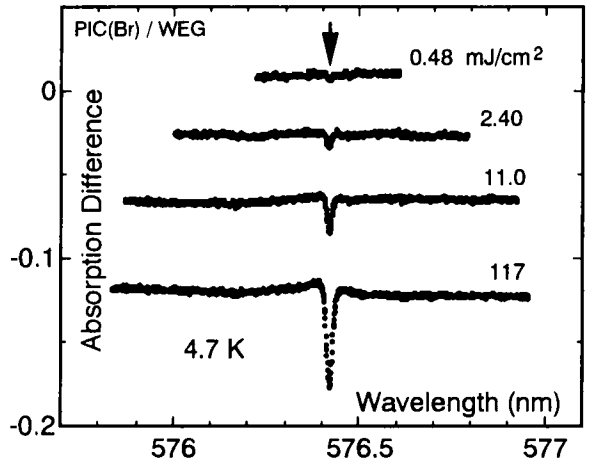

FIGURE 4 Fluence dependence of hole formation profiles obtained at 4.7 K by the irradiation of DC single-mode laser light at the peak of the lower exciton band. Other conditions such as average power density of the light was kept almost similar as in Fig. 3.

which exciton is delocalized, we can deduce a quantum efficiency of the hole formation from the data; The estimated number is 2.8×10^{-5} and is larger than that obtained for the blue J-band by a factor of 20.[12] The efficiency of the zero-phonon formation is still fairly low compared with the case of the puled laser burning.

(3) No detectable phonon or pseudo-phonon holes appeared within our experimental conditions, indicating the exciton-phonon coupling in the aggregate chain is quite small.

(4) The product appears at longer as well as shorter wavelengths from the educt.

(5) The spectral distribution range of the main product seems localized in the vicinity of the educt. Somewhat wider distribution of another product, however, is detectable which roughly coincides with the inhomogeneous width. The latter ranges the absorption change obtained by the pulsed laser burning which is described above.

(6) The oscillator strength of the product is to some extent smaller than that of the educt state.

Assuming a Lorentzian line shape and taking into account the instrumental resolution, the width of the hole 0.40 cm^{-1} yields 0.18 cm^{-1} for the homogeneous width $\Delta\omega_h$. In a one-phonon approximation the related scattering process among k = 1 exciton state and the phonons which cause the broadening of the homogeneous width is governed by the strong restrictions of energy and momentum. As a consequence at temperatures around 4.7 K no scattering processes are expected to take place.[5,6] Hence here we also assume that the $\Delta\omega_h$ observed is attributed to the residual one and we can deduce a lifetime T_1 of 28 psec, again in close agreement with ref. 6 and other time dependent experiments.[5,13]

The basic issues to be solved are as follows: Why does the difference of the operation modes of the burning lasers result in such drastic changes in the hole formation profiles even from the initial stage of burning? What is the origin for the photoreactions ? What is

the nature of the inhomogeneous line broadening? At the moment we have no definitive answers for these questions.

We consider so far that the dispersive lineshape of hole and antihole structures formed by the pulsed light irradiation is the indication of the peculiarity of the electronic state and its dynamics which are inherent to the Frenkel exciton with large coherence length. In case of the DC-light irradiation, optical excitation to the one-exciton band is enough to be considered. On the other hand, the absorption difference spectrum observed by two-color pump-probe experiment clearly shows the negative contribution due to bleaching of the ground state to one-exciton transitions, while positive contributions arise from induced absorption from the excited one-exciton state to a two-exciton state on the same aggregate.[13,14,15] Even in our nanosecond laser, the peak power of the pulse is increased over the average power by as much as a factor of ~ 10^7 (i.e. ~ 1 MW/cm^2) due to its low duty cycle. The energy per pulse becomes easily over 10 μJ/cm^2 to 1mJ/cm^2, which is sufficient to induce optically non-linear response.[6,13] Photoreaction from the two-exciton state will certainly reduce the population of the initial one-exciton state. Hence we can detect the population change at longer wavelength with respect to λ_B, the energy difference between them is roughly half of that between $k = 1$ and $k = 2$ excitons, by measuring the one-exciton spectrum with weak probe light. Further experiments and theoretical work is necessary to clarify the role of the two-exciton transition in the hole formation process as well as the nature of inhomogeneity in the absorption line.

REFERENCES

1. E. E. Jerry, Nature, 138, 1009 (1936).
2. G. Scheibe, Angew. Chem., 49, 563 (1936).
3. P. B. Gilman, Phot. Sci. Eng., 18, 418 (1974), T.Tani, J. Imaging Sci., 34, 143 (1990), A.A. Muenter, D.V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano and S. Mukamel, J. Phys. Chem., 96, 2783 (1992).
4. S. Kobayashi and F. Sasaki, Nonlinear Opt., 4, 305 (1993).
5. S. de Boer, K. J. Vink and D. A. Wiersma, Chem. Phys. Lett., 137, 99 (1987).
6. R. Hirshmann and J. Friedrich, J. Chem. Phys., 91, 7988 (1989), *ibid*, J. Opt. Soc. Am. B, 9, 811 (1992).
7. R. Hirshmann, W. Köhler, J Friedrich and E. Daltrozzo, Chem. Phys. Lett., 151, 60 (1988).
8. H. Fidder, J. Knoester and D. A. Wiersma, Chem. Phys. Lett., 171, 529 (1990).
9. S. de Boer, D. A. Wiersma, Chem. Phys. Lett., 165, 45 (1990).
10. E. W. Knapp, Chem. Phys., 85, 73 (1984).
11. J. Knoester, J. Chem. Phys., 99, 8466 (1993).
12. K. Misawa, S. Machida, K. Horie and T. Kobayashi, J. Lumines., 64, 239 (1995).
13. S. Kobayashi and F. Sasaki, Nonlinear Opt., 4, 305 (1993), F. Sasaki and S. Kobayashi, Advanced Materials '93, II/A, ed. H. Aoki et al., Trans. Mat. Res. Soc. Jpn., 15A (Elsevier, 1994) 401.
14. J. R. Durrant, J. Knoester and D. A. Wiersma, Chem. Phys. Lett., 222, 450 (1994).
15. K. Minoshima, M. Taiji, K. Misawa and T. Kobayashi, Chem. Phys. Lett., 218, 67 (1994).