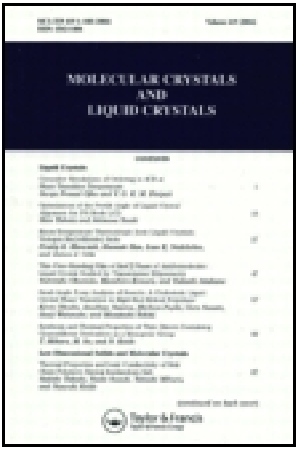

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Non-Linear Excitation Effect in Persistent Hole-Burning of Linear Frenkel Exciton System with Large Coherence Length

Toshiro Tani [a], Martin Vacha [a], Yi Liu [a], Fumio Sasaki [a], Shunsuke Kobayashi [a] & Hiroki Nakatsuka [b]

[a] Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

[b] University of Tsukuba, 1-1 Tennoh-dai, Tsukuba, Ibaraki 305, Japan

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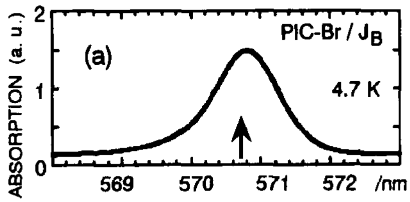
TOSHIRO TANI[a], MARTIN VACHA[a], YI LIU[a], FUMIO SASAKI[a], SHUNSUKE KOBAYASHI[a], and HIROKI NAKATSUKA[b]
[a]Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan;
[b]University of Tsukuba, 1-1 Tennoh-dai, Tsukuba, Ibaraki 305, Japan

Excitonic structure of J-bands of pseudo-isocyanine bromide J-aggregates in WEG glasses at 4.7 K has been investigated by persistent spectral hole burning. Clear crossover of hole line shape was observed in the intensity dependence of pulse laser burning (7ns, 10-Hz repetition). With decreasing the intensity the line shape changes from non-resonant red-shifted (~3 cm^{-1} from the laser frequency ω_B) broad hole to resonant sharp hole, which is similar to those obtained by cw-laser. With cw-laser light for burning, clear zero-phonon hole was formed with the width of 0.36 cm^{-1}. The hole profile seems strongly dominated by the peak intensity of the burning light. We proposed the existence of the crossover is due to switching from the $|1\text{-ex}\rangle$ state resonance by one-photon absorption to the $|2\text{-ex}\rangle$ state resonance by two-photon absorption using real dipole-allowed $|1\text{-ex}\rangle$ state. The model provides the offset of the hole is equal to half of the difference of $k = 2$ and $k = 1$ exciton energy, from which we can deduce a coherence length $N = 56$ as typical order of magnitude. Further experiments are described, which basically support the interpretation.

Keywords: persistent hole burning; pseudo-isosyanine bromide; J-aggregates; Frenkel exciton; dispersive lineshape, two-photon absorption

INTRODUCTION

In this paper we describe further support of our recent findings in the spectral hole burning in the linear Frenkel exciton system at 4.7 K [1,2]. Model material is J-aggregate of pseudo-isocyanine (PIC) bromide in water-ethylene glycol glasses. Among lots of molecular aggregated systems investigated, PIC exhibits the narrowest band, i.e. ~1 nm, separated about 1400 cm^{-1} below the monomeric absorption band edge. This clearly indicates that huge coherence length of



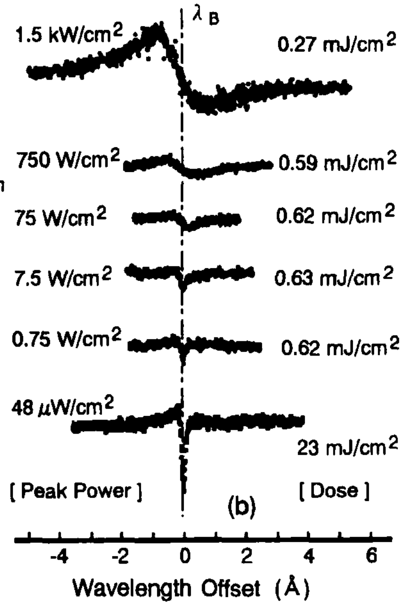


FIGURE 1 (a) Absorption spectrum of PIC-Br J-band at ~571 nm (blue band). (b) Burning light intensity dependence of the spectral change in the hole spectra. Top five spectra are obtained by using the pulsed laser while bottom one by the cw laser, respectively. Number in the left is peak intensity and in the right total fluence for each. Crossover between sharp resonant hole and non-resonant red-shifted broad one is observed in the order of 100 W/cm^2.

the excitonic state is realized. Homogeneous as well as inhomogeneous natures have mostly been investigated by persistent hole burning[3,4,5] as well as photon echo [6,7]. In the present study we have found peculiar non-resonant hole formation in ns-pulse laser burning, which we never knew to occur in monomeric dispersion systems. We consider so far the observed non-resonant hole being several wavenumbers offset to the red and its crossover to the ordinary sharp resonant hole at ~100 W/cm^2 peak intensity are the clear indication of non-linear excitation effect in the linear Frenkel exciton with large coherence length[8].

EXPERIMENTAL

Sample preparation is similar to those described in ref.2: (1) 4×10^{-3} M of PIC-Br is distilled in water and ethylene-glycol mixed solvent (50:50 vol.%, WEG), (2) 12 μm Mylar® film is used as a spacer between two glass slides. Aggregates were grown in a variable temperature cryostat (Oxford: CF 1204) at ~230 K for blue J band (~570.8 nm) and ~170 K for red one (~576.0 nm), respectively. They are quenched down to cryogenic temperatures with ~7 K/min. Holes were burnt with two types of lasers and the results were compared. The first one is a Nd^+:YAG laser pumped dye laser (pulse duration: ~7 ns, repetition rate: 10

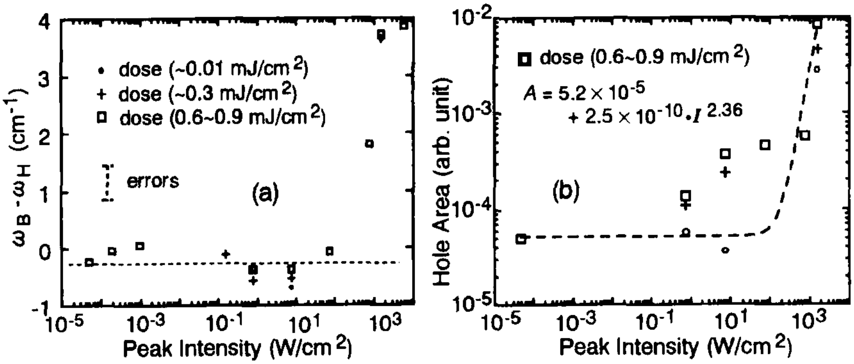


FIGURE 2 Peak power dependences of (a) the amount of hole offset from the burning laser frequency and (b) the hole area. obtained under similar fluence of ns-pulse laser typically shown in the top of Fig. 1. The offset in (a) is obtained after the line shape is corrected by the contribution of the product states, which seems to increase the number by 20 ~ 30 %. Curve fitting in (b) is obtained with using the data indicated by the squares. Fitted intensity dependence is $I^{2.36}$, indicating some kind of non-linear process undergoes.

Hz), spectral width of which is about 0.058 cm^{-1} Typical average power levels used are about 30 ~ 50 μW/cm^2. Another one is a single-mode ring dye laser (Coherent: 699-29) pumped with Ar^+ laser as cw light source. Its line width is about 3 MHz. Spectral measurements are all performed with a 1.5-m double-pass monochromator (Jovin-Yvon: THR1500) with a resolution of 0.03 cm^{-1}. It should be stressed that in measuring absorption changes in the J-bands, since they are so sharp, even a fraction of Å wavelength shift in the monochromator could give rise to some artifacts. In order to avoid this we tuned the wavelength origin of the instruments every measurements to secure reproducibility and repeated several independent experiments for confirmation.

RESULTS AND DISCUSSION

Figure 1 shows typical example of (a) the absorption spectrum of a blue J-band and (b) burning intensity dependence of the hole profiles, which is mainly obtained by decreasing the peak intensity of the ns-pulse laser while increasing the irradiation time under roughly similar fluence condition. In Fig.1 (b), peak intensity of ns pulse laser is shown for each together with total fluence. It should be noted that in case the peak power of pulse laser being 1.5 kW/cm^2 its average light intensity is about ~48 μW/cm^2, which is equal to that of the cw laser used to obtain the hole spectrum shown in the bottom. By decreasing the intensity of the pulsed laser light, we clearly confirmed that resonant hole is reformed at extremely weak irradiation. With cw-laser light for burning, clear zero-phonon hole is formed and the zero fluence limit of FWHM is 0.36 cm^{-1}.

Most notable features of holes by the pulse laser burning are as follows: (1) Instead of narrow holes in resonance with laser frequency ω_B, non-resonant broad hole red-shifted by ~3 cm^{-1} from ω_B appeared from the initial stage of burning, even by one shot of the pulse if the intensity is sufficiently large. (2) Antihole appeared at higher energy side of ω_B with almost similar oscillator strength to the hole. The basic properties are almost similar in the red J-band[1].

In Figure 2 the intensity dependencies of (a) the hole-peak offset and (b) the area of hole are summarized, the ways to deduce these numbers are briefly described in the captions. The offset as a function of the peak intensity in Fig.2 (a) clearly shows the existence of the threshold around 100 W/cm^2. Though there remains some ambiguity in deducing the precise dependence of intensity effect to the hole area from the present experiments, the tentative result gives us a power-low of $I^{2.36}$ with apparent threshold at similar power level. We consider the existence of such a crossover strongly indicates the origin of the offset should be caused by some kind of nonlinear excitation effect and eliminate other possibilities such as charge separation or some kind of Stark effect, which is intensively discussed in the field of semiconductor nano-particles.

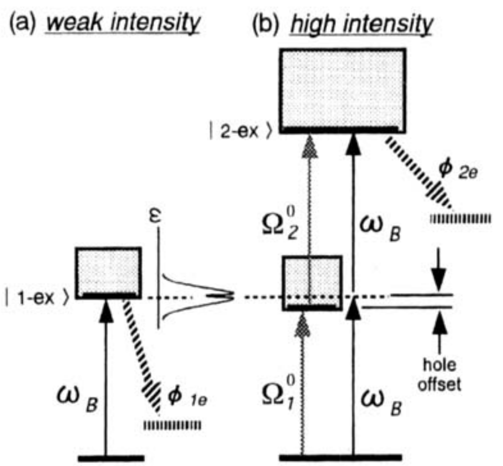


FIGURE 3 Schematic energy structure of the lowest two Frenkel exciton manifolds in linear aggregate. In weak intensity limit, only one-exciton state is excited by one-photon absorption. At sufficiently high intensity, transition to the two-exciton manifold can be possible and the resonance switchs to this successive two-exciton transition by two-photon absorption, using the real dipole-allowed 1-ex state as an intermediate one, which eventually gives rise to the non-resonant red-shifted hole in the linear 1-ex J-band.

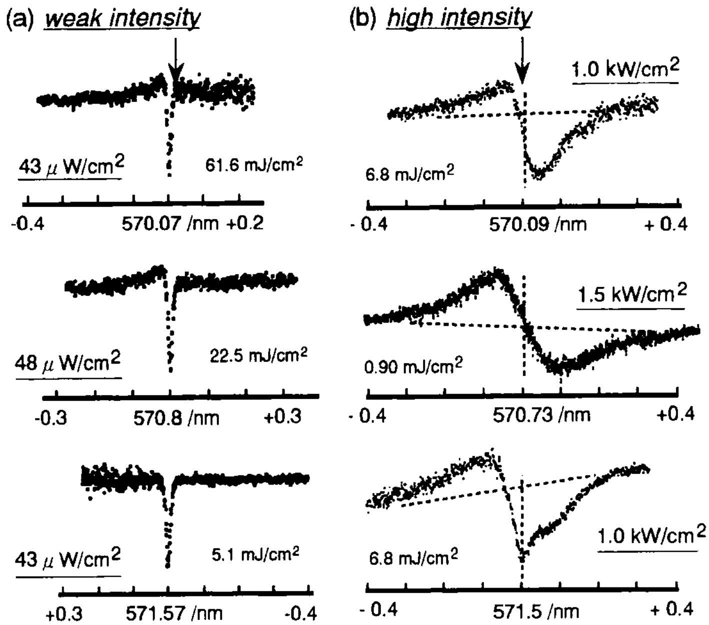


FIGURE 4 Burning wavelength dependences of hole spectra obtained by (a) cw-laser and (b) ns-pulse laser, respectively. Numbers in each figure are the peak power (underlined) and fluence for burning, respectively. The spectra are shown in arbitrary units.

Based on the Frenkel exciton model such as in refs.9 and 10, our basic interpretations on these results are schematically shown in Figure 3. First, the sharp resonant hole by the cw-laser burning is an ordinary 0-phonon hole and its origin is a dipole-allowed one-exciton transition. The spectral width of the J band is inhomogeneous in nature and size and/or shape distribution can be the cause of it. Assuming negligible contribution of the dephasing by phonons[4,7], homogeneous width of the one-exciton state is lifetime-limited in nature and T_1 ~ 28 psec is estimated.

The hole offset observed by the pulsed laser burning is ascribed as a result of site-selective resonance switching: It is due to the two-exciton excitation using real one-exciton state as an intermediate one through two-photon absorption. It is surely a non-linear effect[11, 12] and is due to the result of large coherence of the exciton. The offset of the hole, which eventually appears in the one-exciton J-band and is ~3 cm^{-1} from the laser frequency ω_B, is a half of the difference of

$k = 2$ and $k = 1$ exciton energy[10]: $\sim (\Omega_{k=2} - \Omega_{k=1})/2 = -V \cdot 3\pi^2/2(N_{del}+1)^2$. According also to the exciton theory, the energy shift of the exciton band from the monomer peak is given by $2V$, where V is a coupling constant between the nearest neighbor monomers in the chain. From the red shift of the J-band, e.g. 1393 cm^{-1}, V is of the order of – 696 cm^{-1}, which is almost equal to - 630 cm^{-1} obtained from the dimmer model[13]. Hence we can estimate the coherence length of $N_{del} = 56$. In this connection the width of the exciton band $|4V|$ is about 2790 cm^{-1}, which is almost equal to the Davydov splitting of 2650 cm^{-1}.

The model further provides us expectation about the internal structure of the J-band, which actually reveals in the ω_B dependence of hole profiles shown in Figure 4. In the absorption wing at longer wavelength, the contribution from the process shown in Fig.3 (b) should become less significant and the hole profile turns back to the one more dominated by 0-phonon components. We will also describe possible origin of the antiholes, intensity as well as ω_B dependences of burning yield, effect of further higher intensity etc. in more details.

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