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PERSISTENT SPECTRAL HOLEBURNING OF FRENKEL EXCITON SYSTEM WITH LARGE COHERENCE LENGTH: PIC(Br) J-AGGREGATES

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Abstract We found unique burning power dependence in the hole formation of linear Frenkel exciton system, J-aggregates of pseudo-isocyanine bromide, in water-ethylene glycol glasses at 4.7 K. With DC-laser light for burning, clear zero-phonon hole was formed with the width of 0.36 cm^{-1}. Once switching the laser for burning to the pulse mode operation, on the other hand, nano-second pulses e.g. can give rise to novel feature of dispersive lineshape of spectral change from the initial stage of burning: a broad and red-shifted (~3 cm^{-1} from the laser frequency ω_B) non-resonant hole accompanied by antihole with similar size at shorter wavelength side. We consider the appearance of red-shifted nonresonant hole is essential in the present situation and is due to the two-exciton excitation through one-exciton transition by two-photon absorption. Based on this model, the shift of the hole is equal to half of the difference of $k = 2$ and $k = 1$ exciton energy, from which we can estimate the coherence length of $N = 56$ in the system.

INTRODUCTION

In this paper we describe our recent findings in the burning power dependence of the hole formation of the linear Frenkel exciton system at 4.7 K.[1] Model material is J-aggregate of pseudo-isocyanine (PIC) bromide in water-ethylene glycol glasses. The issue of dynamical properties of linear molecular aggregates with mesoscopic size seems currently interesting. This is because these systems bridge the gap between a single molecule and a crystal.

Among lots of molecular aggregated systems investigated ever since by Jerry and Scheibe,[2] PIC exhibits the narrowest band, i.e. ~1 nm, below the lowest edge of monomeric absorption band. This clearly indicates that huge coherence length of the excitonic state is realized. Homogeneous as well as inhomogeneous properties have mostly been investigated by persistent hole burning[3,4,5] as well as photon echo technique.[6,7] In the present experiment the intensity dependence of hole formation profiles for burning laser light are paid much attention to by tuning the peak powers as well as average powers of nanosecond laser (~ 6 ns, 10 Hz) and compared with those obtained using cw laser. We

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consider that observed non-resonant feature of broad holes,[8] i.e. shifted several wave-numbers to the red, which can be formed at burning peak intensities above ~100 W/cm^2, is an clear indication of nonlinear excitation of Frenkel excitons with large coherence length.

EXPERIMENTALS

Samples are basically similar to those described in ref.9: (1) PIC-Br concentration is 4×10^{-3} M in distilled water and ethylene-glycol mixed solvent (50:50 vol.%, WEG), (2) Mylar® film of 12 μm thickness is used as a spacer between two flat glass slides. Growth of the J-aggregates were performed in a variable temperature cryostat (Oxford: CF1204) at ~230 K for blue J (~570.8 nm) and ~170 K for red one (~576.0 nm), respectively. They are quenched down to cryogenic temperatures with ~7 K/min for measurements.

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 0.058 cm^{-1}. The pulse repetition rate was 10 Hz and typical average power levels were about 30 μW/cm^2 at initial burning stages. 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 lasing line was about 3 MHz.

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 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(a) shows typical examples of hole profiles obtained in the blue J-band by using cw laser and the pulsed one for burning, respectively. In these observations the intensity of cw laser light is as low as ~48 μW/cm^2, while the peak power of the 6-nsec pulses is ~1.5 kW/cm^2. It is more than seven orders of magnitude lager than that of the cw light though its average intensity is tuned almost equal to that of the cw one. With cw-laser light for burning, clear zero-phonon hole was formed and the zero fluence limit of full width at half maximum (FWHM) is 0.36 cm^{-1}.

In case of the pulse laser burning, on the other hand, peculiarity of the hole spectra is clearly seen in the figure. Most notable features 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

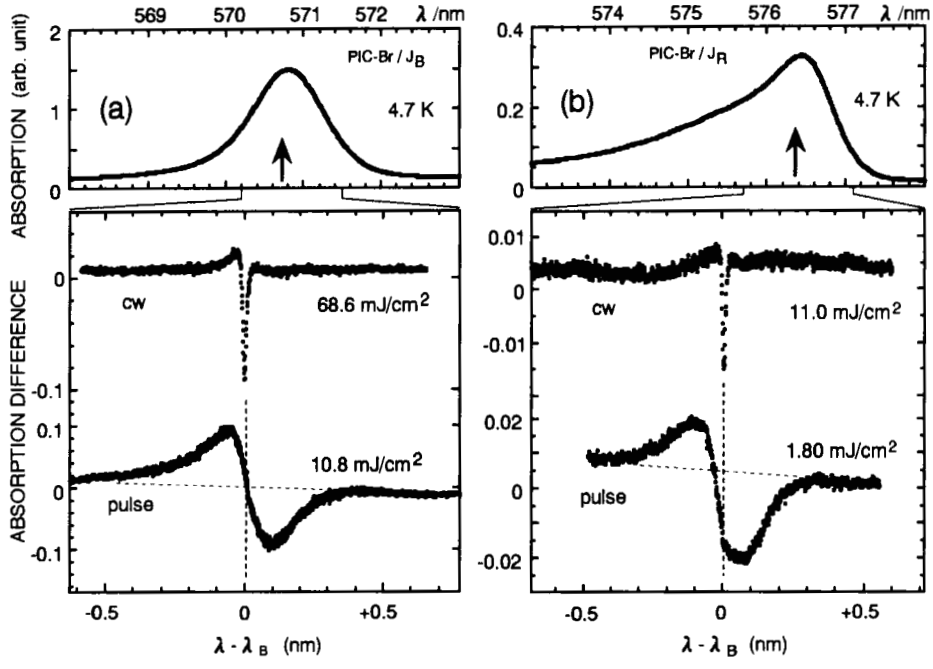

FIGURE 1 Typical examples of hole profiles obtained by cw-laser light (cw) and pulse-laser light in blue J-band (a) and red J-band (b) , respectively. Top of each panel shows an absorption spectrum of respective J-aggregates. Arrows indicate the position of burning laser wavelengths.

oscillator strength to the hole. The basic properties are similar in case of the red J-band[1] as is shown in Fig.1(b). We consider that the nonresonant red-shifted hole formation is essential to tackle the present issue because such phenomena have never been reported within our knowledge nor ordinary theories of site-selective hole formation seem insufficient for this property.

In order to see a crossover from sharp resonant hole to nonresonant red-shifted hole, we have measured the intensity dependence of the spectral profiles for more than eight orders of magnitude in burning intensity. This is done by decreasing the peak intensity of the pulsed laser light or increasing the intensity of the DC laser light under almost similar total fluence condition. Part of the results are shown in Fig. 2. By decreasing the intensity of the pulsed laser light, we also observed clear resonant hole formation at extremely weak irradiation. The FWHM is on the order of those obtained at weak cw-laser irradiation. A crossover to the nonresonant broader hole was actually observed at ~100 W/cm^2 with increasing the intensity. It should be noted here that the existence of such a crossover indicates the origin of the shift should be some kind of nonlinear effect and eliminate possibilities such as charge separation or static Stark effect. Another comment on these

data is the increase of the hole area with increasing the pulse intensity in spite of the almost similar fluence condition. This fact is exceptionally significant because in ordinary monomolecular dispersed systems such increase has never been observed. This means the apparent yield ϕ of the hole formation is increased with increasing the light intensity. Assuming the size of the aggregate is ~ 50, ϕ for DC-light burning is ~9×10^{-7} while ϕ for the nano-second pulse light seems roughly two orders of magnitude larger. In case of 13 kW/cm^2 peak intensity (i.e. 0.078 mJ/cm^2 in fluence), even a single shot of the ns-pulse light is sufficient to form clear spectral change of dispersive lineshape.

Based on the Frenkel exciton model such as by refs.10 and 11, our basic interpretations on these results are schematically shown in Fig.3. First, it can be safely concluded that the sharp resonant hole by the cw-laser burning is an ordinary 0-phonon. This means that the spectral width of the absorption is due to the inhomogeneous distribution of J's. 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.

The hole discrepancy observed by the pulsed laser burning is ascribed as a result of the two-exciton excitation through one-exciton transition by two-photon absorption. It is

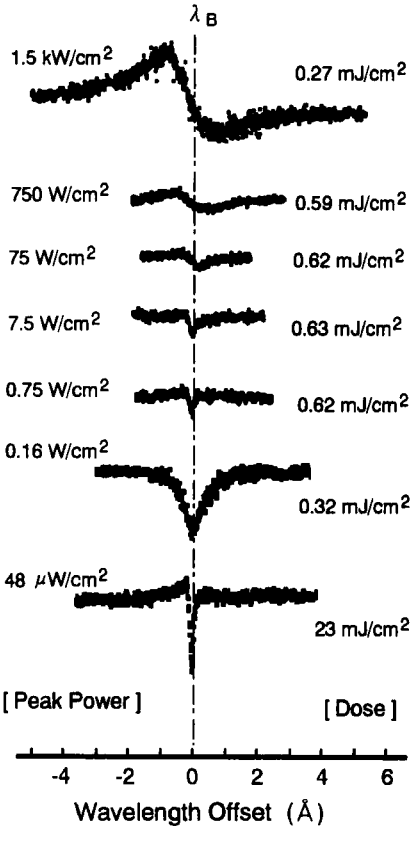

FIGURE 2 Laser light intensity dependence of the spectral change in absorption band. Top four spectra are obtained by using the pulsed laser while bottom two by cw laser, respectively. Numbers in the left indicate respective peak intensity in case of the pulsed light or intensity itself in case of the cw light burning. Those in the right indicate the total fluences being irradiated for respective spectral change. Crossover from sharp resonant hole to nonresonant broad one is observed around 100 W/cm^2. Broadening in case of 0. 16 W/cm^2 cw-burning is probably due to the heating of the sample.

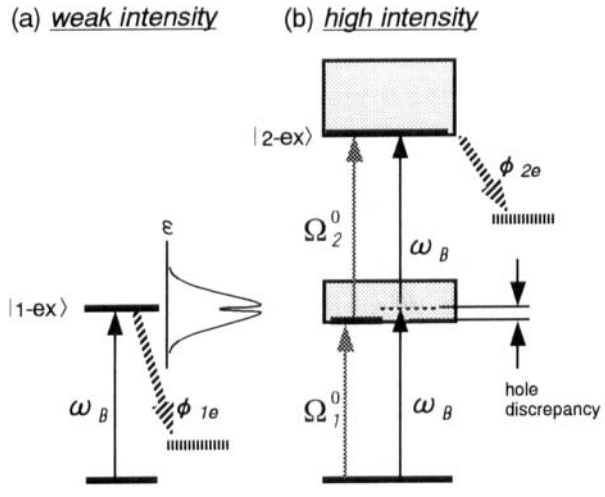

FIGURE 3 Schematic energy structure of lowest two Frenkel exciton manifolds in linear aggregate.[11] While in weak intensity limit, only one exciton is excited, at sufficiently high intensity region, two-exciton band excitation will be dominant and becomes in resonance with successive two photon absorption, which gives rise to the non-resonant red-shifted hole formation. It should be noted that this hole is eventually formed and observed in the one-exciton band , not in the two-exciton band.

surely a non-linear effect[12,13,14] and is due to the result of large coherence of the excitons. The shift of the hole, which eventually appeared in the one-exciton band and is ~3 cm^{-1} from the laser frequency ω_B , is half of the difference of $k = 2$ and $k = 1$ exciton energy[11]: $\sim(\Omega_{k=2} - \Omega_{k=1})/2 = -V \cdot 3\pi^2/2(N_{del}+1)^2$. 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}. It should be noted that this V is almost equal to - 630 cm^{-1} which is estimated from the dimer model.[15] Hence we can estimate the coherence length of $N_{del} = 56$. In this connection the width of the exciton band $|4V|$ is of the order of 2786 cm^{-1}.

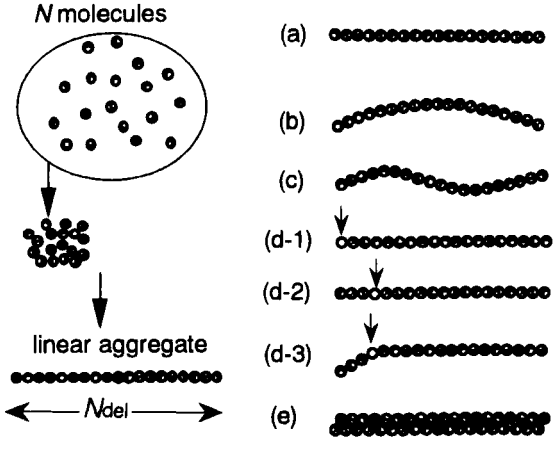

FIGURE 4 Linear J-aggregate (a) with coherence length N_{del} and possible product states (d-1, d-2). (a) is the lowest in energy among these and the photoinduced deformation such as to (b), (c) or (d-3) from (a) seems fairly hard to occur in low-temperature solid matrix.

The widths of the J-band are 35 ~ 31 cm^{-1} depending upon the preparation conditions. The monomer spectrum at 4.7 K shows that the origin absorption has an inhomogeneous bandwidth of ~ 640 cm^{-1}. Thus the reduction of the inhomogeneous bandwidth is characterized by a factor of 20. An exciton delocalization over single aggregate chain comprising N_{del} monomer molecules narrows the inhomogeneous bandwidth of the monomer absorption band by a factor of the order of $1/\sqrt{N_{del}}$.[10] Simple application of this relation yields an aggregate length of about 400 in our samples. Considering part of the inhomogeneity of monomers could be due to small rotations of the quinoline rings with respect to one another,[3] the size of the delocarization length in our sample can safely be estimated as less than 100. The obtained N_{del} seems quite consistent in this and others, which in tern confirms our interpretation.

As for the origin of the antiholes, we show some of the possibilities in Fig.4. Detailed discussions and the results such as temperature cycling experiments will be presented, part of which is related to possible mechanism of transient spectral diffusion for the appearance of broader hole width in the latter.

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