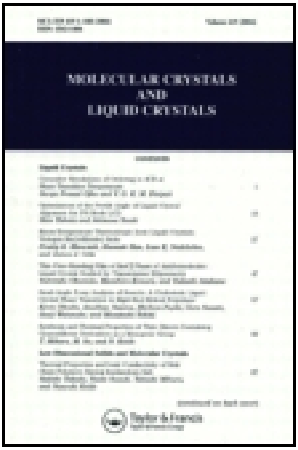

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Heitler Experiment in J-Aggregate : Difference Between Fln and Hole-Burning Spectra

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HEITLER EXPERIMENT IN J-AGGREGATE : DIFFERENCE BETWEEN FLN AND HOLE-BURNING SPECTRA

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Abstract We have observed Heitler effect in the fluorescence line narrowing spectrum of J-aggregate for temperatures below 5K. The spectrum shows complete vanish of luminescence and predominant Rayleigh scattering. From the observed hole-burning spectrum and the Rayleigh spectrum, we discuss the difference between spontaneous and stimulated optical processes.

When the pure dephasing time (T_2^*) is much longer than the fluorescence life time (T_1), which corresponds to the so called T_1 limited case, the fluorescence line narrowing spectrum of a two-level system subjected to monochromatic radiation is expected to have a δ-function spectrum in spite of the finite homogeneous spectral width. This effect is sometimes referred to as the Heitler experiment. [1] When this effect takes place, the fluorescence line narrowing spectrum, i.e. the spontaneous Rayleigh spectrum does not provide the homogeneous spectral width because of its δ-function spectrum. On the other hand, stimulated optical processes such as hole-burning and pump-probe experiments, which can be regarded as resonant stimulated Rayleigh scattering, give finite homogeneous spectral width even in the T_1 limited case. Therefore, the study of Heitler effect enables us to clarify the difference between spontaneous and stimulated optical processes.

The Heitler effect was first observed by Gibbs and Venkatesan, [2] and also by Wu, Grove and Ezekiel[3] for atomic vapors. Subsequently, Hegarty et .al.[4] employed the resonant Rayleigh scattering to reveal the variation of the homogeneous spectral width within the exciton absorption band. As will be discussed later, materials that have a small value of $2T_1/T_2^*$ are preferred to observe the Heitler effect. As samples for the present experiment, we chose aggregates of pseudo-isocyanine bromide (PIC-Br) because the relaxation parameters for this material have been previously investigated by Wiersma's group[5] and it has been found that T_1 of this material rather shortens with decreasing temperature due to the delocalization of exciton, and oppositely T_2^* increases at liquid He temperature. Hence, this material is promising for the Heitler experiment.

Figure 1 shows the temperature dependence of fluorescence line narrowing spectrum in red J-absorption band of PIC-Br dissolved in a mixed solvent of ethylene glycol and water. [6] To reduce the surface scattered laser light, we detected the fluorescence polarized perpendicular to that of the excitation light. The contamination of the fluorescence spectrum due to the surface scattering was less than 30 counts/sec as seen in the spectrum at the temperature of 150 K, at which temperature the Rayleigh component is expected to vanish due to the increased dephasing process. The power of the excitation laser was reduced to about 100 nW so as to avoid the persistent hole burning effect. As seen in Fig.1, the relative strength of the broad spectrum (luminescent part) and δ-function-like spectrum (Rayleigh part) varies as the temperature decreases. Below 5K, the luminescent part completely vanished and the Rayleigh spike alone was observed.

To clarify the difference between spontaneous spectrum and the stimulated spectrum, we performed an experiment of persistent spectral hole-burning. Figure 2 shows the observed hole-burning and fluorescence line narrowing spectra at 4.5 K. This clearly indicates that the resonant spontaneous Rayleigh spectrum is much narrower than the homogeneous spectral width determined by the hole-burning experiment. The fluorescence life time in PIC-Br has been reported to be about 65 ps at temperature below 40 K. The T_1 limit Lorentzian spectrum which takes into account the spectral resolution of the spectrometer (0.085 cm^{-1}, HWHM) is also shown in Fig.2

as a dotted line. Therefore, we can regard the fluorescence line narrowing spectrum in Fig.2 as the δ-function spectrum, whose width is determined by the resolution of the present spectrometer. Thus we succeeded to experimentally confirm that the Heitler effect takes place in this material for temperatures below 5 K.

We are now in a position to discuss theoretically the difference between spontaneous and stimulated resonant Rayleigh spectra. As is well known, spontaneous resonant Rayleigh spectrum can be obtained by using three diagrams of density matrix depicted in Fig.3 in which ω_2 denotes the frequency of spontaneous emission and ω_1 is the frequency of the excitation light. The reason why the δ-function spectrum appears in the resonant spontaneous Rayleigh scattering can be ascribed to the fact that No.3 diagram contains the ground-state propagator over the interval (t_2,t_3). The fluorescence line narrowing spectrum can be obtained by virtue of Fig.3.

$$I(\omega_1-\omega_2)=\pi T_2\delta(\omega_1-\omega_2)+\frac{2T_1}{T_2^*}\left(\frac{2}{(\omega_1-\omega_2)^2+4/T_2^2}\right) \quad (1)$$

where T_1 is the fluorescence life time, T_2^* is pure dephasing time, T_2 is the dephasing time which is related to T_1 and T_2^* by the relation of $1/T_2=1/2T_1+1/T_2^*$. In the derivation of eq.1, we have assumed that the inhomogeneous spectral width is extremely broad compared with the homogeneous width. The δ-function and the Lorentzian function in eq.1 are, respectively, associated with Rayleigh scattering and luminescence. Equation 1 indicates that the relative intensity of the two components integrated over the frequency ω_2 depends on the ratio $2T_1/T_2^*$, and the Rayleigh scattering becomes prominent as the temperature decreases, since usually T_2^* increases at lower temperatures. These results explain quite well the observed spectra of Fig.1.

On the other hand, the persistent hole burning process can be represented by the diagrams of Fig.4. In Fig.4, ω_1 and ω_2 denote frequencies of excitation light and probe light, respectively. Note the difference in the meaning of the diagrams from those of Fig.3, in which ω_2 denotes the frequency of the spontaneous emission. Figure 4 shows that No.6 and No.7 diagrams also contain the ground-state propagator over the interval (t_2,t_3) which was responsible for the appearance of δ-function spectrum in spontaneous Rayleigh scattering. However, in the stimulated process, there are two diagrams of No.8 and No.9 which take into account the spontaneous decay of the excited state. These diagrams represent the renormalization of the ground-state population due to the spontaneous decay of the excited state. As was already discussed by Kayanuma, [7] the diagrams of No.8 and No.9 can be decomposed into No.4-No.6 and No.5-No.7 diagrams, respectively. Consequently, the contribution of No.6 and No.7 diagrams to the hole-burning spectrum are canceled by No.8 and No.9 diagrams. Therefore, the only two diagrams of No.4 and No.5 give the persistent hole-burning spectrum, and the spectrum results in

$$H(\omega_1 - \omega_2) = \frac{1}{(\omega_1 - \omega_2)^2 + 4/T_2^2} \tag{2}$$

Here the extreme inhomogeneous broadening was assumed again. The spectral shape of the persistent hole-burning is a single Lorentzian and does not include the δ-function spectrum. Hence, the measurements based on the stimulated optical process always give the homogeneous spectral width even in the T_1 limited case.

Summarizing, it was experimentally confirmed that Heitler effect takes place in aggregate samples of pseudo-isocyanin bromide for temperature below 5K. The spectral difference between fluorescence line narrowing and hole-burning was ascribed to the fundamental difference between spontaneous and stimulated optical processes.

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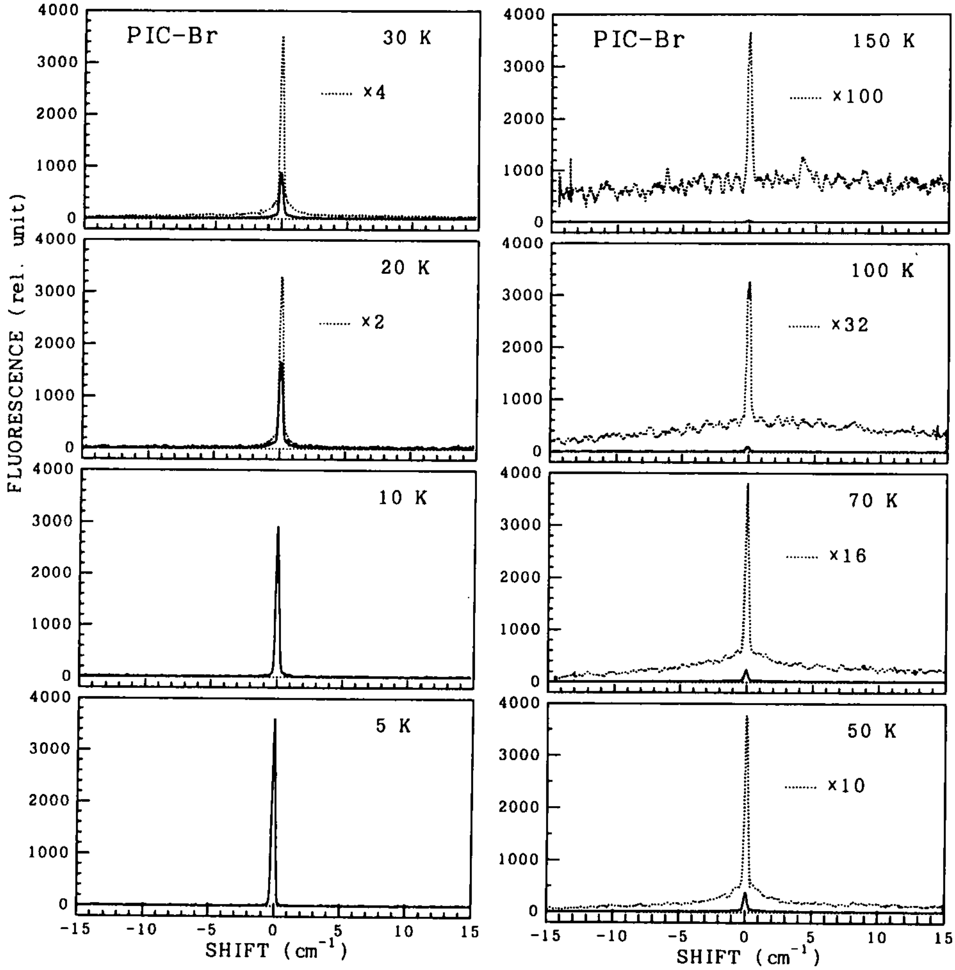

Fig.1 Temperature dependence of fluorescence line narrowing spectrum in PIC-Br (in solid lines). Ordinate is enlarged for dotted lines.

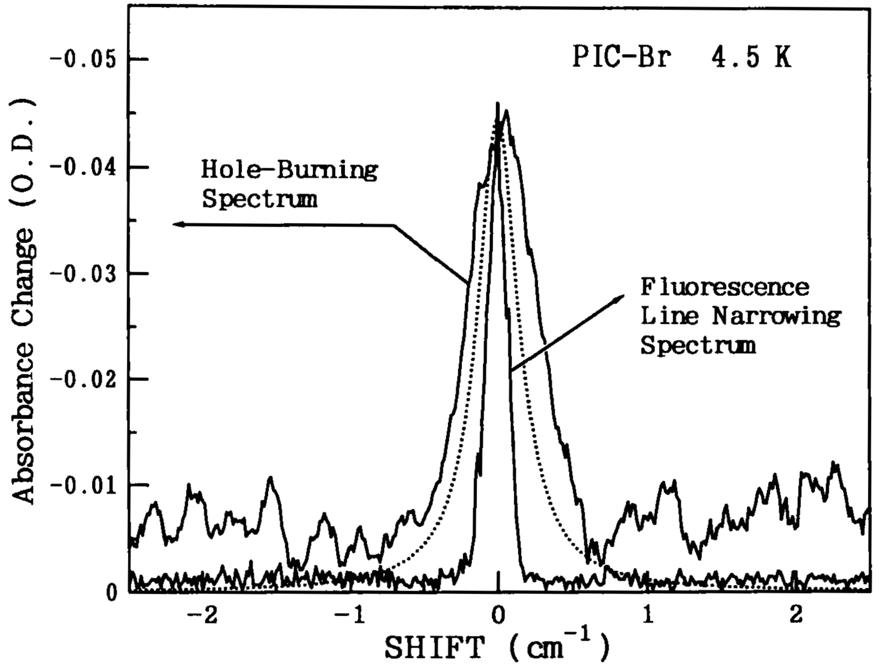

Fig.2 Hole-burning spectrum and fluorescence line narrowing spectrum in PIC-Br at the temperature 4.5 K.
This spectral difference indicates that Heitler effect takes place in this material. Dotted line denotes T_1 limit Lorentzian spectrum.

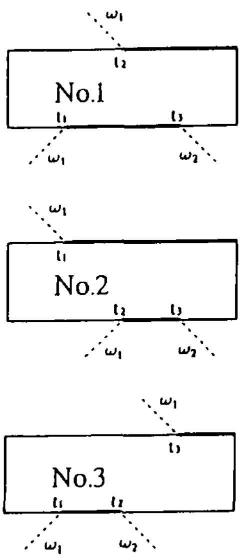

Fig.3

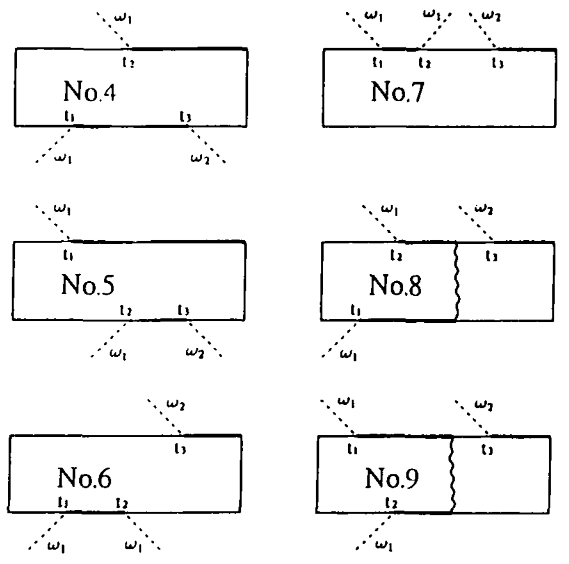

Fig.4

Fig.3 Diagrammatic representation for spontaneous Rayleigh scattering. ω_1 and ω_2 denote the frequencies of excitation light and spontaneous emission, respectively. The system propagates in the ground (excited) state in the interval shown by the thin (bold) solid lines.

Fig.4 Diagrammatic representation for stimulated Rayleigh scattering (persistent spectral hole burning). ω_1 and ω_2 denote the frequencies of excitation light and probe light, respectively. The wavy lines in Nos.8 and 9 diagrams represent the spontaneous decay.