Heitler Experiment in J-aggregate(Abstracts of Doctoral Dissertations,Annual Report (form April 1998 to March 1999))

Heitler Experiment in J-aggregate

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There have been a lot of theoretical studies on the resonant fluorescence spectrum because of the effectiveness in investigating the relaxation dynamics of excited states. When the pure dephasing time T_2^* is much longer than the fluorescence lifetime T_1, so-called T_1 limited case, the fluorescence line narrowing (FLN) 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. When this effect takes place, the FLN 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 Rayleigh spectra such as hole-burning and pump-probe experiments give finite homogeneous spectral width even in the T_1 limited case. Therefore, the study of the Heitler effect enables us to clarify the difference between spontaneous and stimulated optical processes. In condensed materials, however, Heitler effect has not been observed yet. So we have tried to observe the Heitler effect in J-aggregates of pseudoisocyanine bromide (PIC-Br). Since J-aggregates have a very short florescence lifetime T_1 due to the exciton superradiance, this material is promising for the Heitler experiment.

At first, we investigated optical properties of J-aggregates by numerical simulations. In this attempt, J-aggregates were treated as linear molecular chains with diagonal disorder and nearest-neighbor interactions. This simulations showed that the wave functions of states were localized on segments of the chain. This indicates that the site in resonant excitation of J-band corresponds to a segment of the chain. The average oscillator strength per state derived from the simulation indicated that the fluorescence lifetime T_1 had the wavelength dependence and the long wavelength side of the J-band had shorter lifetime. The numerical simulation of the temperature dependence of J-band line-shape indicated that the linear exciton-phonon interaction in J-band was very weak. This extremely weak linear exciton-phonon interaction was also confirmed from the study of Arbach tail in J-band.

So far, the resonant fluorescence spectrum has been mainly studied in the Raman scattering process. As the spontaneous and the stimulated optical processes give the same spectrum in the Raman process, it has been considered that there is no difference between these two processes even in other optical process. However, through the calculation of the density matrix using diagrams, we clarified that the spontaneous and the stimulated optical processes gave different spectra for the case of the Rayleigh scattering process. The spontaneous Rayleigh spectrum consists of two components whose line shapes are a δ-function for Rayleigh scattering and Lorentzian function for luminescence. In the T_1 limited case, the spontaneous Rayleigh spectrum has a δ-function Rayleigh component only. This is the Heitler effect. On the other hand, the stimulated Rayleigh spectrum consists of a single Lorentzian and always gives a finite homogeneous width even in the T_1 limited case.

Figure 1 shows that the temperature dependence of FLN spectrum in J-band of PIC-Br dissolved in a mixed solvent of ethylene glycol and water. As seen in Fig. 1, the intensity of the broad tail (luminescence) spectrum is decreasing and the δ-function-like (Rayleigh) spectrum is increasing as the temperature decreases. At around 5 K, the luminescence spectrum completely vanished and Rayleigh spectrum alone was observed. Figure 2 shows the persistent hole-burning spectrum and the FLN spectrum observed at 5 K. This clearly indicates that the FLN (spontaneous Rayleigh) spectrum is much narrower than the homogeneous spectral width determined by the hole-burning (stimulated Rayleigh) spectrum. Therefore, we can regard the FLN spectrum in Fig. 2 as the δ-function spectrum, whose width is determined by the resolution of present spectrometer. Thus we succeeded to experimentally confirm that the Heitler effect takes place in this material for temperature below 5 K. This is the first observation of the Heitler effect in condensed materials.

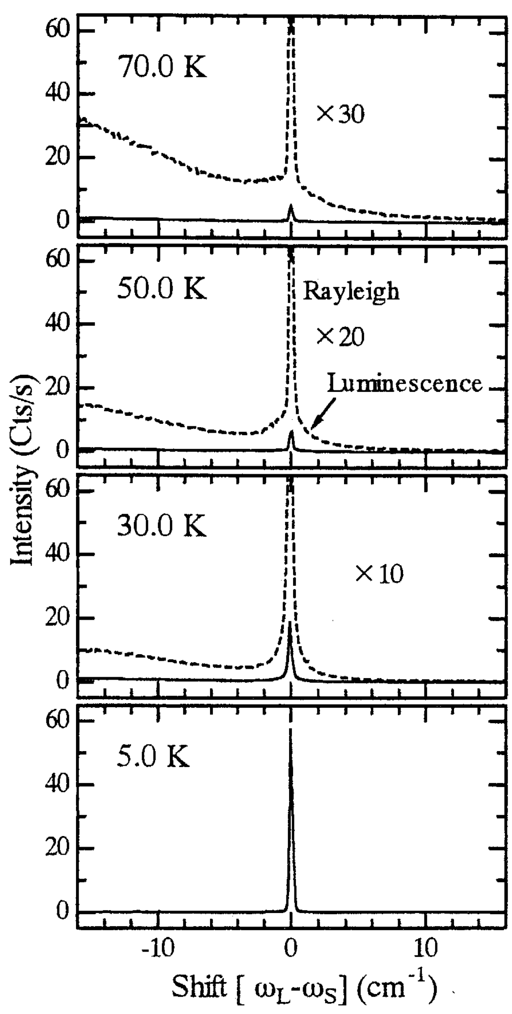

Fig. 1 The temperature dependence of FLN spectrum in PIC-Br.

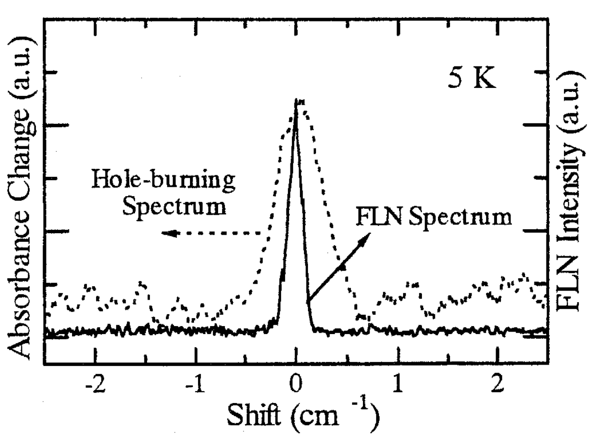

Fig. 2 Hole-burning spectrum and FLN spectrum in PIC-Br at the temperature 5 K.