

Excited-State Dynamics of J-Aggregates

Keitaro Yoshihara^{1,2} Valey F. Kamalov,² Irina A. Struganova²

*1) Japan Advanced Institute of Science and Technology,
Tatsunokuchi, Ishikawa, Japan*

2) Institute for Molecular Science, Myodaiji, Okazaki, Japan

Abstract

Frenkel exciton formed in J-aggregate of carbocyanine dye in the polyvinyl alcohol film was found to have an effective coherent size of 18 molecules at 4K. The exciton emission quantum yield drops four times when temperature increased from 20 to 60K. Independent measurements of emission quantum yield and decay were used to calculate both radiative and nonradiative rate constants in the temperature range of 4 - 140K. Radiative lifetime is found to linearly increase as temperature rises and explained by low dimensionality of J-aggregate. Nonradiative relaxation becomes efficient with rise of temperature and explained by exciton self-trapping.

Introduction

Jelly and Scheibe independently reported formation of a new absorption band in concentrated aqueous solutions of pseudo-isocyanine dye. This sharp band at the red tail of the monomer absorption spectrum is due to creation of molecular aggregates, which is often called J-aggregate and used for color sensitization in photography. The features of Frenkel excitons in molecular crystals can be used to describe exciton behavior in J-aggregates. Exciton diffusion and mechanisms of relaxation were studied in details in 1970's. A progress in technology of producing small size structures of semiconductor (at the nanometer scale) stimulated works on the exciton behavior in the low dimensional systems such as quantum wells and quantum wires. We discuss the dimensionality of J-aggregate based on the temperature dependence of the radiative lifetime with a theory developed for Frenkel exciton in the low dimensional semiconductor structures.

We present the results of the study of relaxation of exciton formed from carbocyanine (BIC) in the polyvinyl alcohol (PVA) film. We carried out optical measurements at different temperatures to determine the characteristic lifetimes and relaxation mechanisms. All measurements were done at low excitation intensity to prevent two-exciton effects observed recently in J-aggregates at high excitation intensity. We found carbocyanine dyes form crystals of micrometer size in PVA film. Radiative lifetime is found to linearly increase as temperature rises and explained by low

dimensionality of J-aggregate. Nonradiative relaxation becomes efficient with rise of temperature and explained by exciton self-trapping.

Experimental Results

J-aggregates of BIC (1,1'-diethyl-3,3'-bis(sulfopropyl) -5,5,6,6'-tetrachloro-benzimidacarbocyanine) were prepared in film of PVA by the standard spin coating method. The microcrystals were formed in the film which were observed by a fluorescence microscope. J-aggregate in the film looked like "red submarines" in shape with 10-20 micrometers in length and one third in width. They seemed to be planar. Geometrical forms and size of microcrystals depend on the conditions of film preparations, but optical characteristics were practically the same. This can be explained taking into account two parameters of J-aggregate: physical size and effective coherent exciton size. Physical size is much larger than the effective coherent exciton size. The latter is determined by interaction between molecules and is responsible to the optical properties.

The absorption maximum moved from 589 nm at 4K to 593.5 nm at 300K. The absorption bandwidth increased from 300 cm^{-1} to 500 cm^{-1} correspondingly[1]. All changes mentioned above take place at $T > 100\text{K}$. The emission maximum changes from 592 nm at 4K to 594 nm at 300K, and all changes take place at $T > 100\text{K}$ too. The emission bandwidth is increased at the all temperature range (including low temperature range, $T < 100\text{K}$) from 150 cm^{-1} (4K) to 350 cm^{-1} (300 K).

A significant decrease of relative quantum yield of about 5 times was observed in the temperature range of 4 - 150K. A small plateau can be seen at $T < 10\text{K}$, which is the reason to assume the absolute quantum yield at liquid helium temperature is unity. The data at $T > 150\text{K}$ show that the emission intensity was practically constant at higher temperatures.

The emission decays of BIC J-aggregate in PVA film were measured at different temperatures. J-aggregates were excited by a mode-locked dye laser with pulse duration of 10 ps at 580 nm. The decay at 4K was fitted by exponential curve with 102 ps with high enough fitting quality. Decay times decrease from 100 ps at $T < 40\text{K}$ to about 80 ps at

$T > 60\text{K}$. Decrease of decay lifetime is the evidence of the nonradiative decay process which takes place in J-aggregate at $T > 40\text{K}$. The similar behavior was observed for J-aggregate in glass so that the nonradiative decay characterizes the exciton itself but is not a specific feature of glass or film.

The emission quantum yield (F) is the ratio of emitted and absorbed photons and determined by two independent constants—the radiative rate constant (k_{rad}) and nonradiative rate constant (k_{nrad}), $F = k_{\text{rad}} / (k_{\text{nrad}} + k_{\text{rad}})$. Emission lifetime (τ) also depends on both radiative and nonradiative rate constants: $\tau = 1 / (k_{\text{rad}} + k_{\text{nrad}})$. The radiative lifetimes obtained by measuring both emission lifetimes and quantum efficiencies in the temperature range of 4 - 150K gave a straight line, the rise of temperature leads to increase of the radiative lifetime. The nonradiative rate constant rather steeply increases from zero at 4K and reaches a plateau with the value $1.1 \times 10^{10} \text{ s}^{-1}$ at 140K, steepest change occurs at ca. 50K.

Discussion

We will discuss the effective coherent exciton size of J-aggregate based on the comparison of the radiative lifetimes of monomer and J-aggregate. Kasha showed that the enhancement of the dipole moment of linear chain of molecules by $\mu_j = (N)^{1/2} \mu_{\text{mon}}$, where N is the effective coherent exciton size and μ_j, μ_{mon} are dipole moments of aggregate and monomer, respectively [2]. The radiative rate constant for dipole-allowed transition is given by $k_{\text{rad}} = 4\mu^2 / 3h\lambda^3 c^3$. Due to enhancement of the dipole moment the effective coherent exciton size can be found as

$$N = (k_{\text{rad}} / k_{\text{radmon}}) (\lambda_j / \lambda_{\text{mon}})^3$$

Here $\lambda_j, \lambda_{\text{mon}}$ are the absorption maxima of exciton and monomer transitions, respectively. The effective coherent exciton size at 4K is $N = 18$, which was found using radiative rate constants of exciton ($k_{\text{rad}} = 9.8 \times 10^9 \text{ s}^{-1}$) and monomer dye ($k_{\text{radmon}} = 0.8 \times 10^9 \text{ s}^{-1}$) based on the measurement of BIC monomer emission decay in methanol at 4K [3]. Deformations of all kinds (including structural inhomogeneity of the crystal and distribution of energy of dipole-dipole interaction between neighboring molecules) prevent further delocalization of excitation.

We now discuss the variation of the effective coherent exciton size with temperature. The radiative rate constant of the monomer is assumed to be temperature independent. This is usually the case due to temperature independent dipole moment of monomer. $\tau_{\text{rad}}(T)$ is then corresponds to the variation of the effective coherent exciton size with temperature. The size decreases drastically from 18 (at 4K) to 5 molecules (at 145K). The main changes take place

when the temperature of the film increased from 20 to 60 K. This corresponds to decrease of the exciton size from 16 to 9 molecules. The characteristic temperature (about 40K) gives an value of frequency which corresponds to phonon frequency populated at such a temperature, $k_B T / h = 8.3 \times 10^{11} \text{ s}^{-1}$ (30 cm^{-1}).

Theoretical background should be reconsidered to explain the temperature dependence of the radiative lifetime. One possibility is to use theories developed recently for low-dimensional systems. Therefore, for a two-dimensional system, the assumption of a thermal distribution of excitons with the requirement that only excitons with small value of center-of-mass wavevector can recombine radiatively leads to $\tau(T) \sim T$ [4]. Similar consideration for one-dimensional semiconductors (quantum wires) give $\tau(T) \sim T^{1/2}$. The obtained linear dependence on the temperature contradicts with the model of one-dimensional chain usually used for J-aggregates, which should give a square route temperature dependence. Several reasons can be considered. First the theory developed for low-dimensional semiconductors should be modified in the case of J-aggregate. Second, one-dimensional chains of J-aggregates can be packed in the crystal parallel to each other so that the effective interaction between them takes place. J-aggregate observed by atomic force microscope contained multi-chain woven or parallel located chains [5].

The temperature dependence of nonradiative rate constant has been explained by a theory of the self-trapping [6]. The rate is determined by the process in which the composite system consisting of the lattice and the exciton passes over a self-trapping barrier in configuration space. There are two distinct mechanisms for getting over the self-trapping barrier. At $T > T_c$ the process is purely one of activation, and its rate is described by $\exp(-W/k_B T)$, where W is the height of the self-trapping barrier, and the critical temperature T_c is on the order of phonon frequencies. In the temperature range of $T > 60\text{K}$ is fitted well by this mechanism. At $T < T_c$ they proposed the mechanism of thermally activated tunneling [7]. We found nonradiative rate k_{nrad} measured at $T < 60\text{K}$ in a good agreement with their thermally activated tunneling of exciton interacting with optical phonons with $\omega_0 = 25 \text{ cm}^{-1}$.

The temperature dependence of nonradiative rate constant suggests importance of low frequency mode of about 30 cm^{-1} . Because of similar frequency obtained for decreasing of the effective coherent exciton size, it is reasonable to suppose that the same low frequency mode determines both processes.

Conclusion

The emission quantum yield of BIC J-aggregate changes four times in the temperature range of 20 - 80K. With

emission decay measurement both radiative and nonradiative decay rate constants were obtained. The radiative rate constant shows linear dependence on temperature for 20 - 140K.

The effective coherent exciton size is estimated as 18 molecules at 4K based on the comparison of radiative rate constants of monomer and J-aggregate. Decrease of radiative rate constant is explained by reduction of the effective coherent exciton size down to 5 molecules at temperatures higher than 100K.

Nonradiative relaxation of exciton was observed. We suggest exciton self-trapping determines the nonradiative decay. The temperature dependence characteristics of nonradiative decay indicate passing over an energy barrier at $T > 60\text{K}$. The vibration with frequency of c.a. 30 cm^{-1} determines barrier crossing in the temperature range of 20 - 60K. The temperature dependence of both radiative and nonradiative rate constants shows the important role of low frequency vibration that decides the Frenkel-type exciton behavior. This vibration of about 30 cm^{-1} is probably intermolecular vibration, similar to the librational mode of molecular crystals. We claim this is the mode determines decrease of exciton size as well as nonradiative decay.

References

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