

Manifestations of the self-trapping of exciton excitations in *J* aggregates

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The results of an investigation of low-temperature exciton dynamics in *J* aggregates, which are characterized by strictly one-dimensional exciton transport, have been presented. A systematic interpretation of the special features observed in the low-temperature spectra and the luminescence kinetics has been given on the basis of a hypothesis of the self-trapping of exciton excitations. © 1995 American Institute of Physics.

The study of the self-trapping of exciton excitations in crystals is a vast area of research.^{1,2} The overwhelming majority of experimental studies conducted in this area dealt with crystals with isotropic exciton transport. For this reason, there would be great interest in an investigation of the self-trapping of excitons in systems with low-dimensional transport since the latter may have some specific features.^{1,3–5} Owing to their molecular structure, *J* aggregates of polymethine dyes have one-dimensional exciton transport.^{6,7} The latter are characterized by a fairly narrow exciton absorption band, strong resonance fluorescence, extremely short radiative lifetimes,^{8–10} and an anomalously high cubic susceptibility.¹¹ The most extensive experimental material has been amassed for *J* aggregates of pseudoisocyanine (PIC), which form at high concentrations (10^{-2} M/l) in aqueous solutions. The earlier publications^{12–16} contained contradictory information regarding the luminescence decay times of *J* aggregates of PIC measured at room temperature. The decay constants obtained in Refs. 12–15 differed by an order of magnitude from those obtained in Ref. 16. The contradictions were resolved in Ref. 17, where it was shown that in the general case the luminescence decay kinetics of *J* aggregates of PIC have a biexponential character and that the short-term exponential function appears only at high excitation densities (above 10^{20} photons/cm²·s) and is attributable to an exciton annihilation effect. When solutions containing *J* aggregates of PIC are cooled, the radiative lifetimes shorten significantly.¹⁸ It was found that the conception developed in Ref. 19 of the cooperative radiative relaxation of exciton excitations in *J* aggregates is important for explaining these phenomena. The fact is that the number of coherently interacting molecules in the molecular chain of a *J* aggregate varies with the temperature due to the development of dephasing processes, as a result of which the radiative relaxation rate also varies with the temperature.¹⁹ There has not yet been a thorough analysis of the character of the luminescence decay of *J* aggregates at low temperatures.

Our results, specifically the nonmonoexponential decay of the luminescence of the samples investigated, which is observed even at low excitation densities (10^{16} photons/cm²·s), as well as the dependence of the kinetics on the recording point in the luminescence spectrum, differ considerably from those previously obtained for *J* aggregates of PIC at low temperatures.^{8,9,18} These features were described in Ref. 20, which also contained a preliminary interpretation

of the results based on an hypothesis of the self-trapping of exciton excitations. In this report we present more extensive experimental material, as well as a detailed analysis of the results obtained.

The experimental investigations of the luminescence spectra and kinetics were performed on a spectrofluorometer that included a continuously pumped YAG laser with active mode synchronization, which can also operate simultaneously in a *Q*-switched mode, a synchronously pumped organic-dye jet laser, and a system for recording the luminescence that operates in a time-correlated photon counting mode.

In our experiments we obtained *J* aggregates from 1-methyl-1'-octadecyl-2,2'-cyanine iodine molecules [see the inset in Fig. 1(a)], which are distinguishable from PIC molecules by the presence of a C₁₈H₃₇ grouping. This made it possible to achieve the aggregation of 1-methyl-1'-octadecyl-2,2'-cyanine iodide molecules in a binary dimethylformamide-water (DMFA/W) solvent at a sufficiently low, of the order of 10^{-4} M/l, initial concentration in DMFA. Following Ref. 21, we shall henceforth use the shortened name S120 for 1-methyl-1'-octadecyl-2,2'-cyanine iodide.

The low-temperature absorption spectrum of the samples investigated contained three characteristic bands: a narrow long-wavelength band corresponding to the absorption of the *J* aggregates, as well as broad absorption bands of the monomers and dimers (Fig. 1). Variation of the concentration of water in the DMFA/W binary solvent resulted in variation of the intensity of these bands, but the shape and spectral position of the absorption band of the *J* aggregates remained nearly unchanged (Fig. 1). Similarly, we did not observe any significant changes in the absorption spectrum of solutions in any of the binary solvents, regardless of the concentration of water, when the temperature was varied in the 1.5–100 K range. Here we shall not consider the finer details of the temperature-induced transformation of the contour of the long-wavelength absorption band of the *J* aggregates, which we reported in Ref. 22.

Under selective excitation in the absorption band of the *J* aggregates, the luminescence band of the samples investigated underwent significant variation as the concentration of water in the binary solvent was varied. These changes essentially consist of considerable broadening of the luminescence band as the proportion of water added to the original DMFA

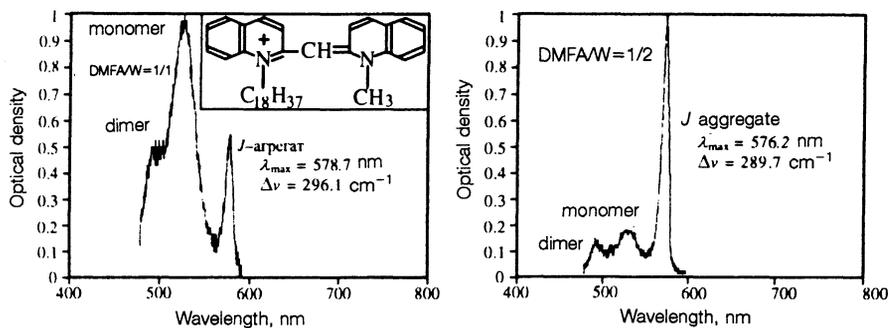


FIG. 1. Absorption spectra of the samples investigated at $T=1.5$ K (the molecule of 1-methyl-1'-octadecyl-2,2'-cyanine iodide is shown in the inset).

solution is diminished (Fig. 2). At the same time, the position of the short-wavelength boundary of the luminescence spectrum remained unchanged. Differences were also observed in the temperature-induced transformation of the luminescence band in comparison with the absorption band of the J aggregates. At 80 K a characteristic maximum appeared in the long-wavelength part of the luminescence spectrum (Fig. 2).

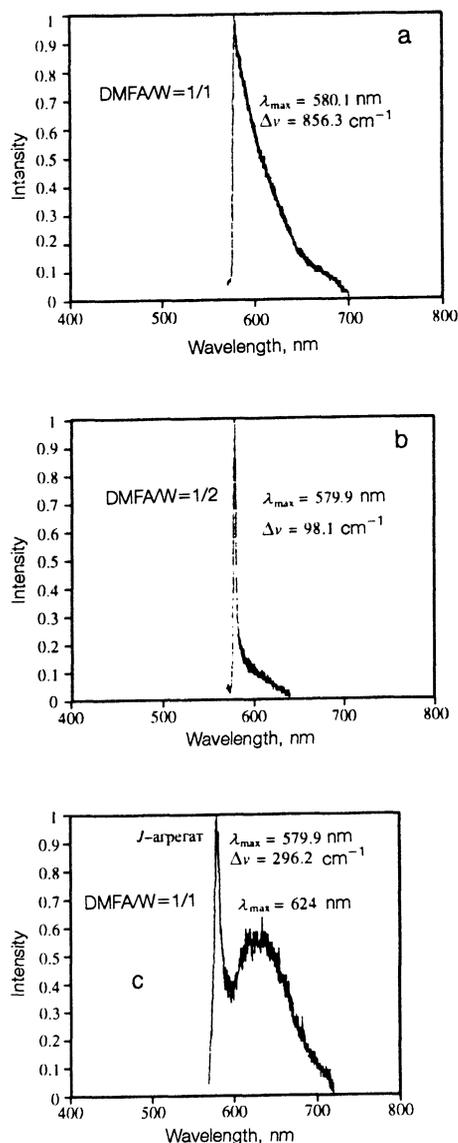


FIG. 2. Luminescence spectra of the samples investigated: a,b) at $T=1.5$ K; c) at $T=80$ K.

The radiative decay curves recorded in the luminescence band at different wavelengths under low excitation densities (less than 10^{16} photons/cm²·s) differed from one another (Fig. 3). As we moved toward lower frequencies in the luminescence spectrum, the radiative decay kinetics became appreciably more protracted, but maintained an explicitly non-monoexponential decay law. The luminescence kinetics recorded for solutions in binary solvents with different concentrations of water at the same wavelength did not coincide (Fig. 4). We observed acceleration of the radiative kinetics in the luminescence band only when the density of the exciting radiation was increased to a level above 10^{20} photons/cm²·s.

The luminescence decay kinetics of S120 monomers at low temperatures, unlike those of the J aggregates, had a monoexponential character (Fig. 3).

We investigated time-resolved luminescence spectra of the samples (Fig. 5). The spectra were recorded with selective excitation in the absorption band of the J aggregates. The maxima of the corresponding time-resolved spectra, as well as their half-widths, depended on the displacement of the recording time interval relative to the laser excitation pulse.

1. ANALYSIS OF THE EXPERIMENTAL RESULTS

The most trivial explanation for the experimental results obtained might be based on the hypothesis that there are low-energy traps for exciton excitations in the molecular chain of a J aggregate. However, a more thorough and comprehensive analysis of the results obtained on the basis of this hypothesis reveals serious contradictions. To demonstrate this, we consider the situation using two approaches. Under the first we assume that there are traps for exciton excitations in the chain of a J aggregate, and under the second we assume that the self-trapping of exciton excitations occurs in J aggregates. It should be noted that the possibility of the self-trapping of excitons in J aggregates of pinacyanol fluoride was previously examined in Ref. 4, but it appears that no experimental research was subsequently performed in this area.

To complete the presentation, one more approach, whose unsuitability is obvious, should be considered briefly. Its essential point is the hypothesis that J aggregates of different structure exist in solutions in the binary solvents. However, in such a case, at a concentration of the J aggregate macromolecules low enough to rule out any energy-transfer mechanisms (less than 10^{-5} M), the forms of the bands in the

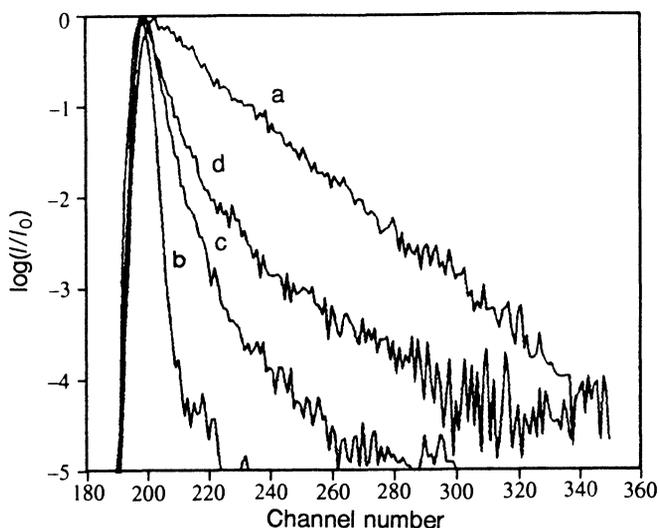


FIG. 3. Luminescence kinetics of a solution in a 1:1 DMFA/W binary solvent at $T=1.5$ K (the channel width is 98 ps) and $\lambda_{\text{reg}}=560$ nm (luminescence band of S120 monomers) (a), 580 nm (b), 600 nm (c), and 640 nm (d).

absorption and luminescence spectra should coincide. This conclusion totally contradicts the available experimental results (Fig. 1 and 2).

1.1. Trap model

We assume that the J aggregates of S120 have an identical structure in solutions in the binary solvents; however, the molecular chains contain defects, which play the role of low-energy traps of exciton excitations, and the experimentally observed broad luminescence band (Fig. 2) is attributable to their luminescence.

In the general case S120 molecules with a different isotopic composition, undetectable impurity molecules, and finally, defects in the structure of the molecular chain of a J

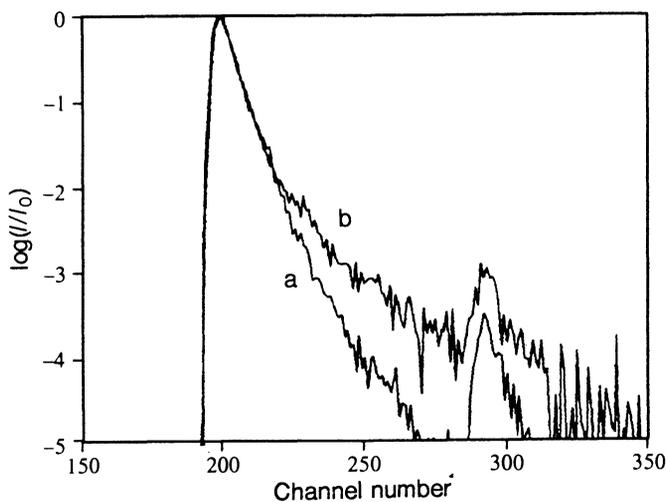


FIG. 4. Luminescence kinetics recorded at one wavelength ($\lambda_{\text{reg}}=640$ nm) and $T=1.5$ K (the channel width is 98 ps). DMFA/W=1/1 (a), 1/2 (b).

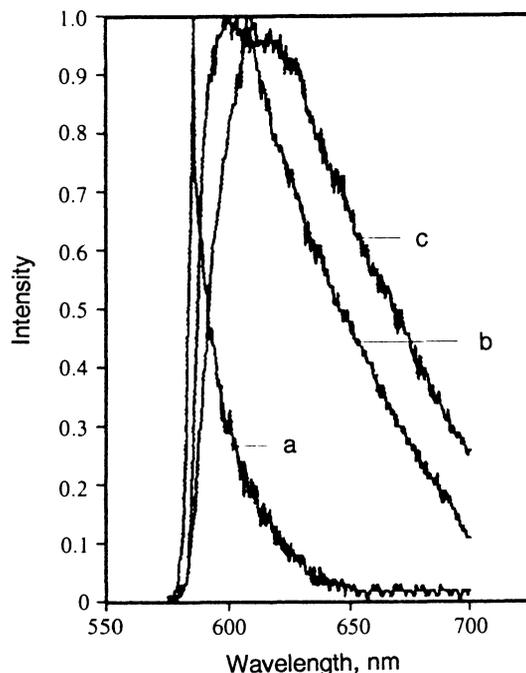


FIG. 5. Time-resolved luminescence spectra of a solution in a 1:1 DMFA/W binary solvent at $T=1.5$ K: a) recording window at 0–0.3 ns; b) recording window at 1–2.9 ns; c) recording window at 2.9–5.9 ns.

aggregate can act as traps. All of these trap models are characterized by one common property: they are present in a J aggregate regardless of whether the latter is excited or not. However, there is also a fundamental difference between them: the number of molecules with a different isotopic composition and the number of undetectable impurity molecules must remain fixed in relation to the number of normal S120 molecules. Therefore, the experimentally recorded variation of the intensity of the luminescence band of the traps (Fig. 2) in solutions with different concentrations of water unequivocally indicates that only defects in the molecular chain of a J aggregate can be considered as traps. It is perfectly reasonable to assume that the number of such defects varies with variation of the proportion of water in the binary solvent.

The structure of the energy levels with consideration of the traps and the corresponding channels for the relaxation of exciton excitations in the J aggregates are shown in Fig. 6. The model adopted accounts for the differences in the shape and structure of the absorption band and the luminescence band of the J aggregates. In fact, the concentration and absorption cross section of the traps may be such that the traps are not manifested on the background of the intense exciton absorption band of the J aggregates. Such a situation is common in work on the spectroscopy of excitons and traps in crystals²³ and should not raise any special objections. However, the recorded temperature-induced transformation of the luminescence spectrum (Fig. 2) cannot be explained under this approach. First, it is unlikely that a change in the concentration of the corresponding traps which would result in the observed changes in the luminescence spectrum would occur in the 1.5–100 K range. Second, consideration of another mechanism, which is associated with temperature-

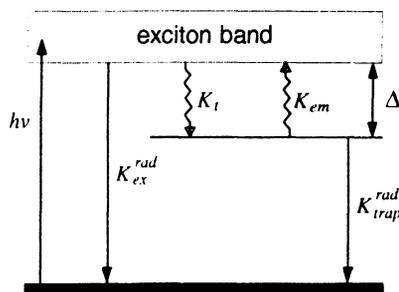


FIG. 6. Model of energy levels with consideration of the exciton and trap bands. Here K_{ex}^{rad} is the radiative decay constant in the exciton band; K_{trap}^{rad} is the radiative decay constant in the trap band; K_t is the capture constant of excitons in traps; K_{em} is the constant for the thermal ejection of the trap excitations into the exciton band; Δ is the depth of the trap level.

induced ejection of the trap excitations into the exciton band (Fig. 6), likewise does not permit description of the temperature-induced transformation of the luminescence spectrum. To demonstrate this, we write a system of kinetic equations, which describe the evolution of the populations $n(t)$ and $N(t)$ in the exciton and trap bands, respectively, in accordance with the model adopted (Fig. 6):

$$\begin{aligned} \frac{dn}{dt} &= -(K_{ex}^{rad} + K_t)n + K_{em}N, \\ \frac{dN}{dt} &= -(K_{trap}^{rad} + K_{em})N + K_t n. \end{aligned} \quad (1)$$

For stationary excitation, system (1) is easily solved, and the population of the trap level is given by the expression

$$N = \frac{I_0 K_t}{K_{ex}^{rad} K_{trap}^{rad} + K_t K_{trap}^{rad} + K_{ex}^{rad} K_{em}}, \quad (2)$$

where I_0 (photon/s) is the intensity of the exciting radiation.

In relation (2) there is one parameter which depends on Δ and T (T is the temperature of the sample), viz., K_{em} . As was shown in Ref. 24, an exponential temperature dependence is expected for K_{em} , i.e., $K_{em} \propto \exp[-(\Delta/k_B T)]$. Thus, in the ranges of Δ (of the order of 1500 cm^{-1}) and experimentally attainable temperatures of interest to us, the last term in the denominator in (2) can be neglected; therefore, the variations in the luminescence spectrum (Fig. 2) cannot be attributed to the thermal activation of trap excitations.

Moving on to a discussion of the luminescence kinetics of the samples investigated using the trap model, we must analyze two experimental findings, viz., the dependence of the kinetics on the recording point in the luminescence spectrum and the deviation of the luminescence kinetics from a monoexponential law. The trap model presented in Fig. 6 clearly does not contain an explanation for these features. Therefore, an additional hypothesis must be considered. In principle, in most cases in which the depth of the trap level Δ is greater than the width of the exciton band and the latter is relatively narrow (less than 100 cm^{-1}), the radiative decay constant of the traps does not depend on Δ . In our case, a

situation in which the width of the exciton band (1300 cm^{-1}) is comparable in magnitude to the depth of the trap levels Δ is realized. In addition, the minimum of the exciton band corresponds to $k \approx 0$ (k is the wave vector of the Brillouin zone) and the J aggregates of S120.²² Manifestation of the Rashba effect is possible under these conditions,²³ and then the decay constant K_{trap}^{rad} should depend on Δ . More specifically, K_{trap}^{rad} should decrease with increasing Δ . This correlates with the experimentally observed protraction of the kinetics (Fig. 3) upon movement toward lower frequencies in the luminescence spectrum. On the other hand, the absorption band of the trap levels should become evident under the Rashba effect. In addition, according to the Rashba effect, the luminescence decay kinetics obtained for solutions in different binary solvents (Fig. 4) at the same wavelength should also coincide. These features are not confirmed by the experimental findings; therefore, even with the additional hypothesis of the possibility of manifestations of the Rashba effect, it is not possible to give a satisfactory explanation for the nonuniformity observed in the luminescence decay kinetics of the J aggregates.

As for the character of the luminescence decay kinetics, a nonmonoexponential decay law may appear for exciton and trap luminescence in systems with one-dimensional exciton transport.²⁵ The main cause of such behavior of the luminescence kinetics is the presence of scattering centers for exciton excitations, which results in "locking" of the excitons.²⁵ In this case²⁶ the probability function of the capture of excitons by traps is given by the expression

$$K_t = A t^{-1/2}, \quad (3)$$

where A depends on the factor of the transition and can be evaluated from experimentally observed quantities, and t is the current time.

In the case of J aggregates, the ends of the molecular chain must be regarded as scattering centers, since the efficiency of scattering by molecules with a different isotopic composition is negligibly small when the exciton band is broad. In such a case a formalism which has been embodied in several well known models²⁷⁻²⁹ can be utilized to analyze the kinetics of exciton and trap luminescence in J aggregates. In our specific case we utilize the Wieting-Fayer-Dlott (WFD) model,²⁸ which reduces to the solution of system (1) for $K_{em} = 0$ and K_t taken in accordance with (3). The numerical solution of (1) is presented in Fig. 7, and an example of the experimental kinetics is presented in this figure for comparison. One characteristic feature of trap luminescence in the WFD model is the negative value of the second derivative $d^2[\ln N(t)]/dt^2$, which is maintained for any values of the parameters varied. However, the value of $d^2[\ln N(t)]/dt^2$ for the experimental plot is positive. From a strictly mathematical standpoint, the theoretical curves of trap luminescence in logarithmic coordinates are convex, while the experimental plots are concave. This property of the theoretical curves is preserved in both the Kenkre model²⁹ and in the Movaghar-Sauer-Wurtz model.²⁷

Concluding the discussion of the trap model, we can state that the following effects are still inexplicable under this approach: the temperature-induced transformation of the

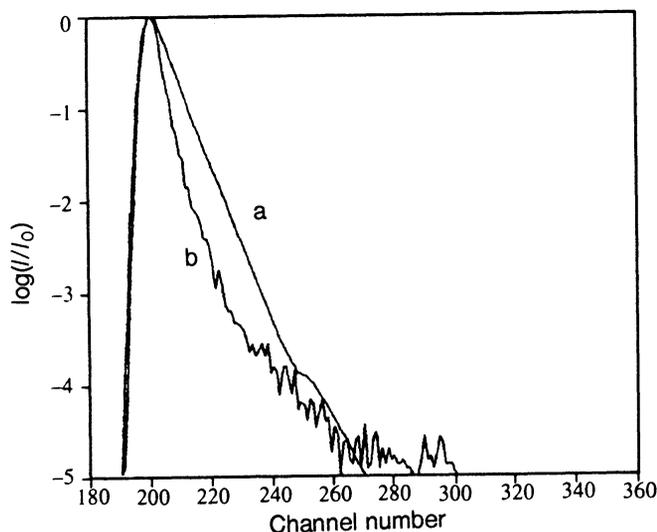


FIG. 7. Luminescence kinetics of traps: a) results of the numerical solutions of system (1); b) experimental results (DMFA/W=1/1, $\lambda_{\text{reg}}=600$ nm, $T=1.5$ K).

luminescence spectrum (Fig. 2), the deviation of the luminescence kinetics from a monoexponential law with characteristic concavity (Fig. 3), and, finally, the variation of the kinetics with motion along the luminescence spectrum (Fig. 3).

1.2. Model of the self-trapping of exciton excitations

Without going into the details of the microscopic structure of a self-trapped state, we assume that the self-trapping of excitons occurs in the J aggregates of S120 obtained in a solution in a DMFA/W binary solvent. From a formal standpoint it signifies the appearance of a dynamic defect in the molecular chain of J aggregate with an energy level lying below the bottom of the band of free excitons. The dynamic defect is a local distortion of the structure of the J aggregate, which is associated with an exciton wave packet and is caused by strong exciton-photon coupling. It is known³ that barrier-free self-trapping occurs in one-dimensional systems; nevertheless, the structure of the dynamic defect varies, passing through a number of states before completion of the self-trapping process. It was shown in Ref. 30 that the relaxation rate of a "hot" self-trapped state K_{aut} , which is associated with a multiphoton process, is determined by the multiplier $\exp(-\Delta_a/\omega_d)$, where Δ_a is the energy lost as a result of self-trapping (Fig. 8) and ω_d is the Debye frequency of the acoustic phonons. By analogy to organic crystals we assume that $\omega_d \leq 150$ cm^{-1} . Then the luminescence spectrum (Fig. 2) can be used to evaluate the exponent Δ_a/ω_d , which is of the order of 10. Therefore, it is perfectly possible that K_{aut} , which characterizes the radiationless relaxation of the self-trapped state, is comparable to $K_{\text{aut}}^{\text{rad}}$, which determines the probability of radiative transitions from the self-trapped state. The assumptions made are sufficient for explaining all the experimentally observed spectral features and the kinetics.

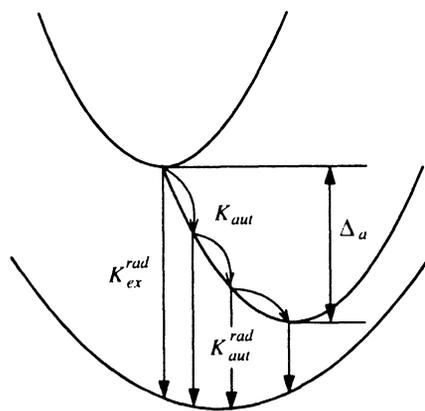


FIG. 8. Diagram of adiabatic potentials showing relaxation of a "hot" self-trapped state.

Under the assumptions made the long-wavelength absorption band corresponds to transitions to the bottom of the band of free excitons (Fig. 8). Absorption corresponding to transitions directly to the self-trapped state is not displayed, since there is a prohibition in accordance with the Franck-Condon principle.²³ After photoexcitation of a J aggregate, the process of the self-trapping of the exciton begins, and due to the fact that $K_{\text{aut}} \sim K_{\text{aut}}^{\text{rad}}$, we observe luminescence from a relaxing "hot" self-trapped state. Therefore, the half-width of the luminescence band (Fig. 2) significantly exceeds the half-width of the long-wavelength absorption band (Fig. 1). The self-trapping rate increases with increasing temperature.³¹ In the limiting case of $K_{\text{aut}} > K_{\text{aut}}^{\text{rad}}$, radiation can already be observed after completion of the relaxation process. When the condition $K_{\text{ex}}^{\text{rad}} \sim K_{\text{aut}} > K_{\text{aut}}^{\text{rad}}$ is satisfied, two characteristic maxima form in the luminescence spectrum. One corresponds to the luminescence of free excitons, and the other corresponds to self-trapped excitons. These conditions are clearly realized in our experiments (Fig. 2) when the temperature of the samples investigated arises.

The hypothesis of the self-trapping of excitons makes it possible to proceed with explaining the nonuniformity of the luminescence decay kinetics in a natural manner (Fig. 3 and 4). In fact, the relaxation of the "hot" self-trapped state signifies a continuously increasing degree of localization of the exciton wave packet. This should result in a decrease in $K_{\text{aut}}^{\text{rad}}$, since the number of coherently interacting molecules in the molecular chain of a J aggregate decreases according to the hypothesis of the cooperative radiative effect.¹⁹

The model of the self-trapping of excitons has another significant difference from the model of a low-energy trap. It is the fact that the energy level of the "hot" self-trapped state has an additional channel for radiationless relaxation in comparison with a trap level. The appearance of K_{aut} should result in a nonmonoexponential type of luminescence decay and fulfillment of the condition $d^2[\ln I(t)]/dt^2 \geq 0$, which is unattainable in the trap model.

To analyze the microstructure of the self-trapped state in J aggregates of S120, their structure must first be examined. Unfortunately, there have not been any direct experimental investigations of the structure of J aggregates in solutions. However, there are reliable results on the structure of J aggregates of S120 in Langmuir films. The "brick-wall" model, which was proposed in Ref. 32 and characterizes the packing of S120 molecules in Langmuir molecular monolayers, was confirmed experimentally in Ref. 21. On the basis of the fact that the spectral characteristics of the J aggregates of S120 in a Langmuir film and in a solution in a DMFA/W binary solvent are nearly identical, we suggest that at least a fragment of the "brick-wall" packing is realized in the structure of a J aggregate in solution, i.e., a J aggregate is a stacked structure, in which the S120 molecules are packed with a small displacement.

We also note another feature of the S120 molecule, which may have direct bearing on the problem under consideration. According to the theoretical ideas in Ref. 7, symmetric polymethine dyes, such as S120, exist in the so-called polymethine state, which is characterized by the alternation of positive and negative charges on the atoms. When a molecule passes from the ground state to the first excited state, the charges on the atoms are reversed. The reversal of the signs of the charges can result in a change in the energy of the intermolecular interaction in the J aggregate. The energy decreases, if one of the molecules in the excited state moves in the plane of the stack to form a local mirror-image structure. Thus, an excimer forms in the molecular chain of the J aggregate. Therefore, we assume that one of the possible mechanisms of the self-trapping of excitons in our experiments is associated specifically with the formation of excimers. Such a mechanism was previously discovered in Ref. 33 for pyrene crystals, where the molecules are arranged in pairs and they can approach without overcoming considerable energy barriers. In J aggregates this is promoted not only by the stacked structure, but also by the reversal of the signs of the charges on the atoms in the excited state of the S120 molecule.

Since water molecules play a key role in the formation of J aggregates, variation of their concentration in the binary solvent causes variation of the energy of the intermolecular interaction and thereby results in variation of the elasticity of the molecular chain of the J aggregate, which can be expressed in the form

$$W = \frac{\partial^2 u(\theta)}{\partial \theta^2}, \quad (4)$$

where $u(\theta)$ is the potential of the intermolecular interaction in the J aggregate and θ is the generalized coordinate.

According to Ref. 34, the energy of a self-trapped state lies below the bottom of the exciton beam, and in the case of rigidly fixed molecules, the distance between them is

$$\Delta a = \frac{s^4 D^4}{W^2 d^4 L}, \quad (5)$$

where D is the change in the energy of the intermolecular interaction in the J aggregate when the molecule passes to

the excited state, L is the magnitude of the resonant integral, d is the distance between molecules, and s is a positive parameter.

According to (5), a decrease in W due to a decrease in the concentration of water in the binary solvent will promote the self-trapping of excitons and the appearance of a band associated with luminescence from a relaxing self-trapped state. Conversely, an increase in W will suppress self-trapping, and the effect of the self-trapping of excitons may not be manifested. The difference between the luminescence kinetics (Fig. 4) recorded at the same wavelength for solutions in different binary solvents is also attributable to the different values of W for these solutions, which determines the radiationless relaxation rate of the "hot" self-trapped state.

Thus, it has been shown on the basis of a comparative analysis of the experimental results obtained under two approaches that the hypothesis of the self-trapping of excitons in J aggregates offers the most systematic interpretation. It should also be noted that due to the large number of features considered, the arguments frequently had a qualitative character. This was partly due to the total lack of any treatment of several theoretical aspects of the problem analyzed in the present paper.

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