

Features of low-temperature exciton dynamics in J -aggregates with topological disorder

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It is shown on the basis of an analysis of the J -band shape, luminescence spectra, and luminescence decay that self-trapping of excitons takes place in J -aggregates with strong topological disorder. A self-trapping barrier must be overcome for this to occur. A microscopic model of the self-trapped state is presented.

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1. Introduction

J -aggregates of polymethine dyes are highly ordered nanosize luminescent clusters. Because of their unusually large absorption cross section J -aggregates have been used for many years as photomaterial sensitizers [1]. In recent years, J -aggregates have been used for diagnostics of the membrane potential in living cells [2].

Since it was first discovered by Jelly and Scheibe [3,4], J -aggregate structure remains little studied. J -aggregates are usually considered to be one-dimensional molecular chains, which makes it possible to describe their optical and luminescent properties systematically. In most cases J -aggregates are characterized by a narrow resonance luminescence band, indicating the absence of relaxation of the molecular configuration of photoexcited J -aggregates. However, it was shown in [5] that in J -aggregates polaronic relaxation can take place below the bottom of an exciton band and causes the formation of a strongly-relaxed polaronic state.

In the present work the special features of 1-methyl-1'-octadecyl-2,2'-cyanineiodide (S120) J -aggregate exciton dynamics in a frozen dimethylformamide-water (DMFA-W) matrix was studied in the temperature range 1.5–80 K. S120 molecules, which are an amphiphilic analogue of PIC, allow topological disorder in S120 J -aggregates to be controlled [6].

2. Experimental

The assembly of experimental equipment used in these investigations is described in detail in [5].

3. Results and discussion

Figure 1 shows the low-temperature absorption bands of S120 J -aggregates in frozen DMFA-W solutions with different amounts of water. For low water content (Fig. 1,*a*) the low-frequency edge of the J -band is fit well by a Lorentzian contour, indicating substantial topological disorder in the J -aggregate structure [6–8]. In contrast, for high water content (Fig. 1,*b*) the J -aggregate structure becomes more perfect and the low-frequency edge of the J -band is fit well by a Gaussian contour [6–8]. At low temperatures the latter case occurs for J -aggregates of PIC [8,9], TOCBC [10] and TDBC [11]. The absorption band of S120 J -aggregates ($\Delta\nu_{FWHM} = 380 \text{ cm}^{-1}$) is much wider than that of PIC ($\Delta\nu_{FWHM} = 34 \text{ cm}^{-1}$) [8,9], TOCBC ($\Delta\nu_{FWHM} = 65 \text{ cm}^{-1}$) [10], and TDBC ($\Delta\nu_{FWHM} = 160 \text{ cm}^{-1}$) [11]. This indicates greater diagonal disorder in S120 J -aggregates [6–8].

At low temperatures only a narrow resonance luminescence J -band is observed for perfect S120 J -aggregates (Fig. 2, curve *a*). The time-resolved spectra indicate [12] that the broad luminescence spectrum of the S120 J -aggregates with topological disorder (Fig. 2, curve *b*) consists of two bands: a narrow resonance band, which coincides with the luminescence band of perfect S120 J -aggregates (Fig. 2, curve *a*), and a wide

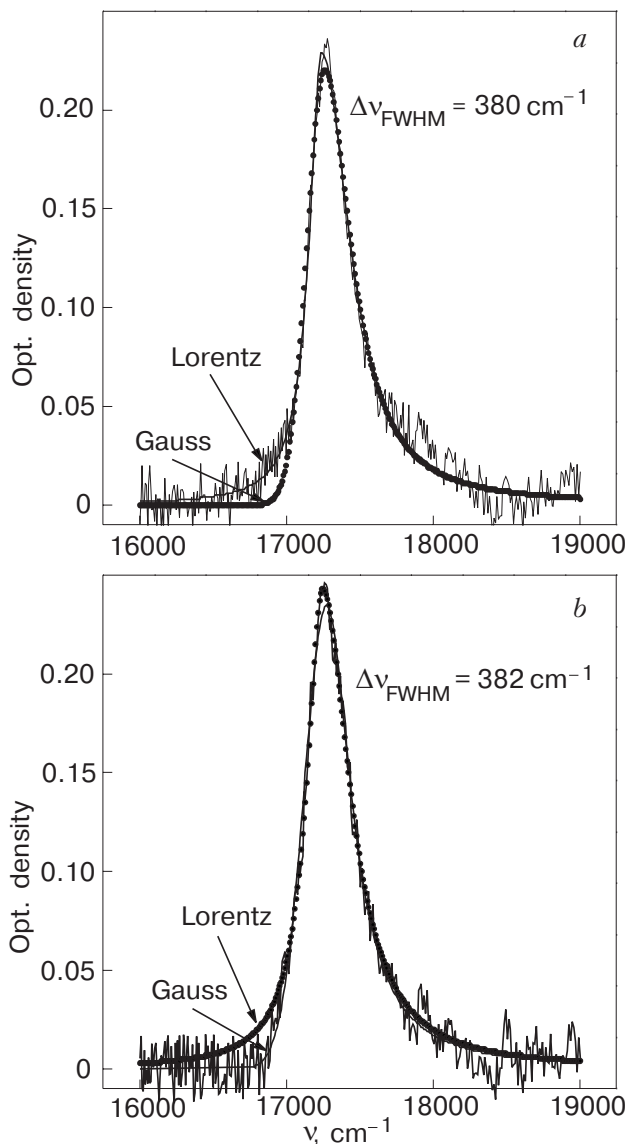


Fig. 1. The absorption band of S120 *J*-aggregates in a frozen DMFA-W matrix ($T = 1.5$ K) with different water content: 50% (a); 75% (b).

long-wavelength band. Two bands are clearly visible at 80 K (Fig. 2, curve *c*). The narrow luminescence band is strongly quenched by exciton traps [12]. Luminescence decay in this band exhibits a single exponential time dependence with a temperature-dependent decay constant (1.5–80 K) [5]. The luminescence characteristics of the narrow resonance luminescence band of S120 *J*-aggregates (Fig. 2, curve *a*) are similar to those of *J*-aggregates of PIC and TDBC [8,9,11]. On this basis the narrow luminescence band of the perfect and imperfect S120 *J*-aggregates can be ascribed to the emission of free excitons [5,13].

As temperature decreases, the spectrum represented in Fig. 2, curve *c* reversibly transforms into the spectrum shown in Fig. 2, curve *b*. Within the wide band (Fig. 2, curve *b*) the luminescence decay depends on

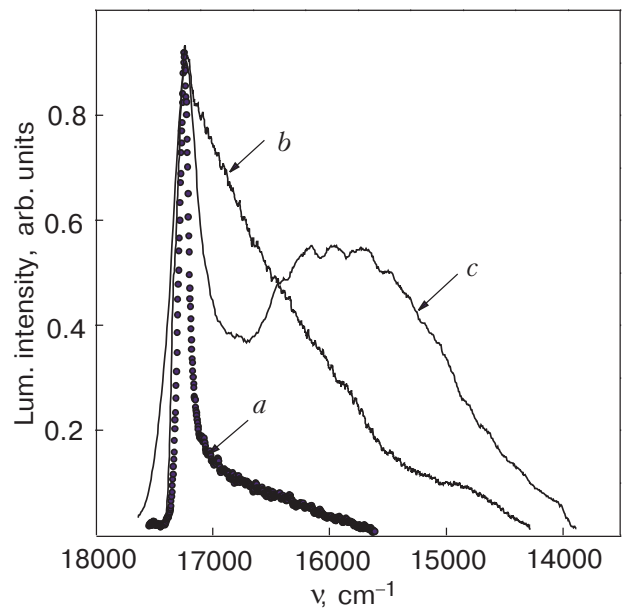


Fig. 2. The luminescence spectrum of S120 *J*-aggregates in a frozen DMFA-W matrix with different water content at different temperatures: 75%, $T = 1.5$ K (a); 50%, $T = 1.5$ K (b); 50%, $T = 80$ K (c);

the detection point and does not exhibit a simple exponential time dependence (Fig. 3). The luminescence decay recorded at the same spectral point within the wide band depends on the water content in the frozen DMF-W matrix [5]. For more imperfect *J*-aggregates the luminescence decays faster at the specified spectral point of the wide band [5].

The wide luminescence band (Fig. 2) may be associated with the emission of stationary exciton traps present in the *J*-aggregates for unknown reasons. Then the energy gap (~ 1350 cm^{-1}) between the maxima of the two bands (Fig. 2, curve *c*) is too large compared to the thermal energy kT (~ 56 cm^{-1}) to attribute its origin to the thermal depopulation of traps. The exciton traps could appear in a *J*-aggregate structure with increasing temperature. In this case reversible changes of the luminescence spectrum (Fig. 2) are impossible with inverse decreasing temperature. These and other origins of the wide luminescence band are discussed in greater detail in [5,13].

The wide *J*-aggregate luminescence band with strong topological disorder should be ascribed to the emission of dynamic (relaxing) states forming below the bottom of the exciton band. These states arise only after photoexcitation of the *J*-aggregates and after the self-trapped exciton states have lost their mobility. The simultaneous presence of two bands in the luminescence spectrum (Fig. 2, curve *c*) indicates the coexistence of free and self-trapped excitons and the existence of a self-trapping barrier [5,13]. Nevertheless, it is known that there is no self-trapping barrier in 1D

systems (which the J -aggregates in solutions are) [5,13,14]. Such a barrier is possible if the exciton self-trapping in J -aggregates involves one-dimensional electronic motion and three-dimensional lattice deformation [13].

Since Δv_{FWHM} is essentially the same for the J -bands in the cases considered (Fig. 1), it may be inferred that the topological disorder plays a key role in the development of polaronic relaxation below the bottom of the exciton band. This is due to, first and foremost, the large initial distortions in a J -aggregate structure with topological disorder. Nevertheless, this is not the only reason. It was shown [13] that self-trapping occurs when the exciton delocalization length N_{del} reaches a critical value N_{del}^{cr} . N_{del} is defined by the energy disorder and is contained in the two relations [8,9,14]:

$$\delta_{ex}^2 = \frac{3\delta^2}{2(N_{del} + 1)}, \quad (1)$$

$$\tau_J = \frac{\pi^2 \tau_{mon}}{8 N_{del}}, \quad (2)$$

where δ and δ_{ex}^2 are the effective energy disorders (Δv_{FWHM} , in fact) in the monomer and exciton bands, respectively; τ_J and τ_{mon} are the luminescence decay constants of J -aggregates and monomers.

On the basis of Δv_{FWHM} for S120, PIC and TDBS J -aggregates (see above), N_{del} for S120 J -aggregates is smallest. Using (1) and (2) and the appropriate experimental data for the S120 J -aggregates [5,6,13] we find that $N_{del} \sim 25$. The smaller N_{del} , the larger the change in the charge corresponds to one molecule under the photoexcitation of the J -aggregate is. Electric dipole transitions we implied. When $N_{del} = N_{del}^{cr}$, a substantial change in the non equilibrium charge distribution over a molecule stimulates substantial reorganization of the equilibrium molecular arrangement in the photoexcited J -aggregate. For a favorable ratio of the energy gain under polaronic relaxation and the energy gain with deformation of a solid matrix, a polaronic state is formed below the exciton band bottom [13]. Such a formation can be described by a model with a double-well adiabatic potential (Fig. 4,*a*). At 1.5 K the self-trapping rate in the AB region is low, and we observe emission from the relaxing states. As a result, a continuous luminescence spectrum is formed (Fig. 2, curve *b*). As temperature increases, the self-trapping accelerates and excitations are accumulated in the minimum C before radiative deactivation occurs. This case corresponds to the curve *c* in Fig. 2.

At the microscopic level a self-trapped exciton state in S120 J -aggregates is an excimer (Fig. 4,*b*). It is

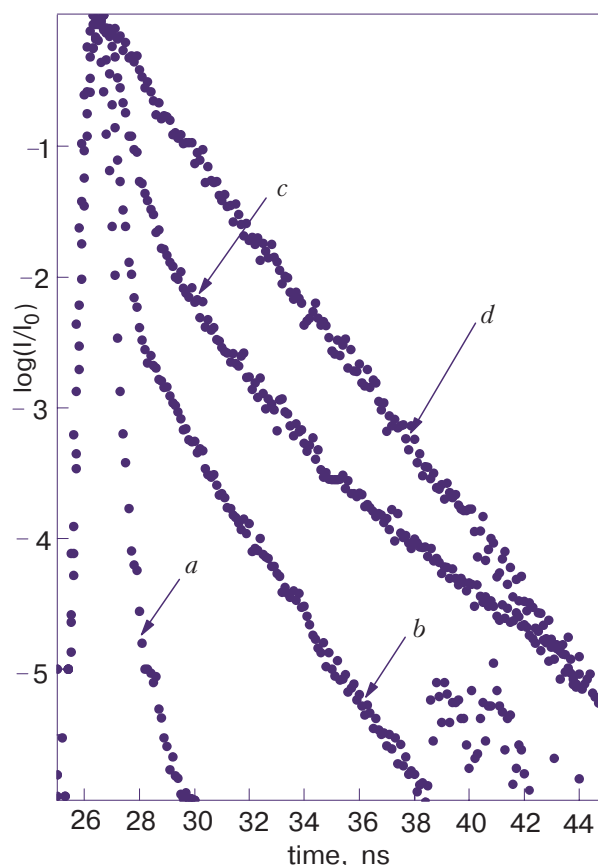


Fig. 3. The luminescence decay of S120 J -aggregates and S120 monomers in a frozen DMFA-W matrix with a 50% water content at $T = 1.5$ K: the resonant luminescence decay of J -aggregates, $\lambda_{rec} = 580$ nm (17241 cm^{-1}) (*a*); the wide-band luminescence decay of J -aggregates, $\lambda_{rec} = 600$ nm (16667 cm^{-1}) (*b*); the wide-band luminescence decay of J -aggregates, $\lambda_{rec} = 640$ nm (15625 cm^{-1}) (*c*); the luminescence decay of S120 monomers, $\lambda_{rec} = 560$ nm (17857 cm^{-1}) (*d*).

known that reversible charge modulation occurs along a polymethine chain. The fact that the S120 J -aggregate absorption bands in DMFA-W solutions [5,6,13] and LB-films [6] coincide with one another suggests that a fragment of the «brick layer» (the arrangement of molecules in a pile with their relative displacement) [15] remains for S120 J -aggregates in DMFA-W solutions. Thus excimer formation becomes possible under photoexcitation of J -aggregates because of a cross displacement of two molecules in the J -aggregate chain (Fig. 4,*b*). So, in the ground state, the adiabatic potential of J -aggregates has one minimum, and the probability of a radiative transition from a self-trapped state must decrease. Actually, at long times after an excitation pulse the luminescence decay is slower in the luminescence band of the self-trapped states (Fig. 3, curve *c*) than that in the monomer band (Fig. 3, curve *d*).

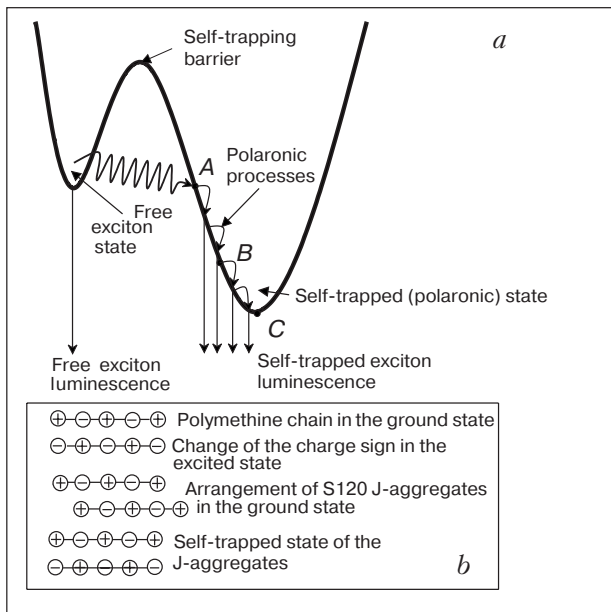


Fig. 4. The adiabatic potential describing the formation of a self-trapped exciton state in S120 *J*-aggregates (a); the formation of an excimer state in a *J*-aggregate molecular chain (b).

4. Conclusions

It has been shown that in *J*-aggregates with strong topological disorder polaronic states may be formed below the bottom of the exciton band. The topological disorder plays two roles. On the one hand the initial deformation of the *J*-aggregate structure promotes the

appearance and relaxation of polaronic states. On the other hand the energy and topological disorders decrease N_{del} , which reaches the critical value $N_{\text{del}}^{\text{cr}}$ and then the formation of self-trapped states in the 1D system becomes energetically favorable.

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