

Self-trapping of excitonic excitations in *J*-aggregates

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A self-trapping of excitonic excitations is shown to occur in *J*-aggregates of quino-2-monomethine cyanin at low temperatures. This effect is manifested by the appearance of a broad, structureless fluorescence band with a nonexponential decay kinetics.

Several convincing experiments have now been carried out on the self-trapping of excitonic excitations in crystals, but there has been little work on systems with a reduced-dimensionality exciton transport.¹ Moreover, despite the diversity of entities and the actual microstructure of the self-trapping state, the overwhelming majority of the experiments have not made use of laser spectroscopy, with its extremely high time resolution. Consequently, some fundamental questions concerning the dynamics of the self-trapping state have yet to be taken up. There is accordingly interest in studying excitonic excitations in systems with a reduced-dimensionality exciton transport. Some pertinent entities here may be *J*-aggregates (Shaibe polymers), which are molecular chains of (up to 10^6) polymethine dye molecules (the monomers).² Because of the purely geometric structure of these chains, the exciton transport in them is strictly one-dimensional.

In this letter we are reporting direct experimental observation of a self-trapping of excitonic excitations in systems with a 1D exciton transport: *J*-aggregates of quino-2-monomethine cyanin produced in frozen binary solutions. The possible manifestation of a self-trapping of excitonic excitations in pinacyanol diethylchloride *J*-aggregates was discussed many years ago by Rashba.³

In the present experiments, spectral and kinetic measurements were carried out on a spectrofluorimeter consisting of a cw-pumped, *Q*-switched Nd:YAG laser with active mode locking, a synchronously pumped dye jet laser, and an emission detection system which operates by a time-correlated photon counting method.

Some distilled water was added to the original dimethylformamide solution to produce the aggregation of the quino-2-monomethine cyanin monomer molecules.⁴ The formation of the *J*-aggregates was monitored by means of the narrow, long-wavelength absorption band which is characteristic of these entities. The original solutions, in cells which were not sealed off, were slowly lowered into a helium bath. Some vitrifying samples of good quality were obtained as a result.

The low-temperature spectrum of a test sample consisted of three characteristic bands: an intense long-wavelength band corresponding to the exciton absorption of the *J*-aggregates and some less intense absorption bands of monomers and dimers (Fig. 1).

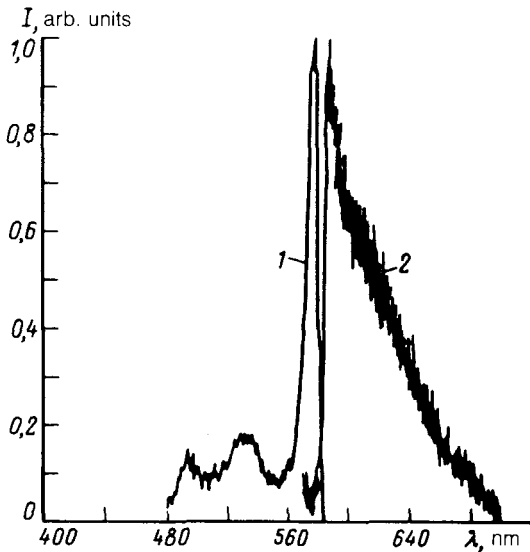


FIG. 1. Absorption (1) and luminescence (2) spectra of the solutions studied.

The half-width found experimentally for the absorption band of the *J*-aggregates was 295.60 cm^{-1} .

During excitation of luminescence directly in the *J*-aggregate absorption band, a broad, structureless band with a half-width of 944.36 cm^{-1} was observed in the emission spectrum. This half-width is greater than that of the corresponding absorption band (Fig. 1).

There were differences in the kinetics of the emission in the broad, structureless band measured at different points in the spectrum. As we move in the low-frequency direction, the kinetics becomes noticeably slower (Fig. 2). These kinetic curves are clearly not exponential, as can be seen from the circumstance that it is not possible to find a satisfactory approximation of these curves by a set of exponential functions. (The emission kinetics was measured at low excitation densities, to rule out possible exciton-exciton annihilation.) In contrast, the emission kinetics of the monomers of quino-2-monomethine cyanin is strictly a single-exponential process (Fig. 2).

A study of time-resolved emission spectra during selective excitation in the *J*-aggregate absorption band showed that the peaks of the corresponding time spectra as well as their shape depend on the shift of the measurement time interval with respect to the laser pulse (Fig. 3).

There is a trivial way to explain these results: to suggest that the structureless band which is observed is the result of the emission of intrinsic defects of the molecular chain of the *J*-aggregate, which act as low-energy trapping centers for excitonic excitations. (These centers might be monomer molecules which have not assumed regular positions in the *J*-aggregate chain and instead lie near it.) However, that suggestion must be rejected simply because this band was not found in the absorption spectrum⁵ in the course of a detailed study of the long-wave edge, and the emission kinetics measured in this band is different from that of monomers (Fig. 2).

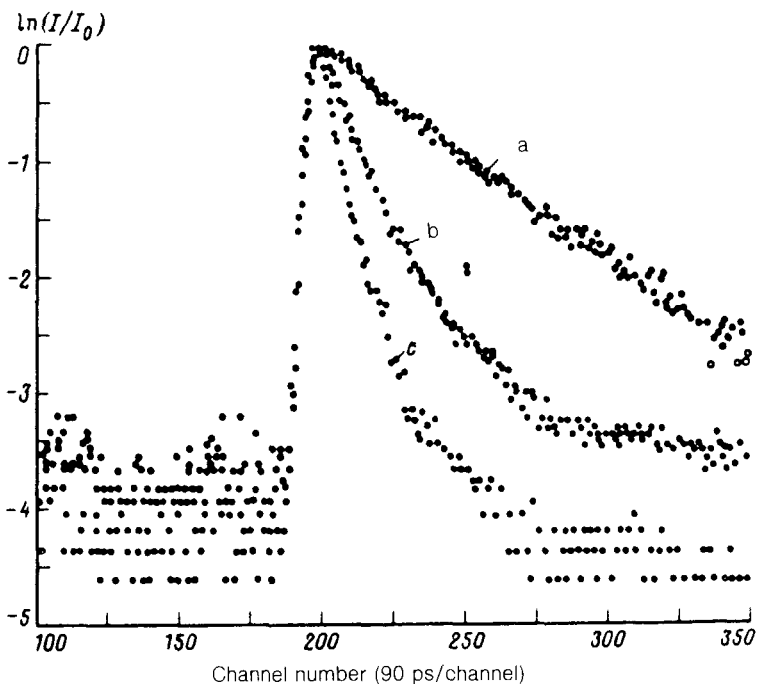


FIG. 2. Emission kinetics of the solutions studied. a: Emission kinetics of the monomer, $\tau \approx 3.2$ ns. b: Emission kinetics in the broad, structureless band, $\lambda_{\text{det}} = 640$ nm. c: Emission kinetics in the broad, structureless band, $\lambda_{\text{det}} = 590$ nm.

Apparently the most reasonable way to explain the results is to suggest that these experiments are revealing a self-trapping of excitonic excitations in the *J*-aggregate chain. Since the width of the exciton band in the *J*-aggregates is $1000\text{--}2000\text{ cm}^{-1}$ according to estimates of the oscillator strength, the excitons involved in this self-trapping are “light” excitons. Since the time scales of the emission of excitonic excitations in the *J*-aggregates are fairly short,⁶ they are apparently comparable to the self-trapping rate. The broad emission band observed is therefore due to the emission of photons from a relaxing self-trapping state. Support for the idea that we are seeing an emission from a “hot” self-trapping state comes from the nonexponential nature of the observed emission (Fig. 2) and the slight shift of the peaks in the time-resolved spectra (Fig. 3).

The structure observed in the broad-band luminescence spectrum with a characteristic steep high-frequency side and a monotonically decaying low-frequency edge, without any inflection points or additional peaks, seems to support the idea of a barrier-free self-trapping of excitons in systems with a 1D exciton transport.¹

In summary, these experiments have shown that a self-trapping of excitonic excitons is exhibited in *J*-aggregates of quino-2-monomethine cyanin, which have a purely 1D exciton transport in binary solutions at low temperatures. This self-trapping

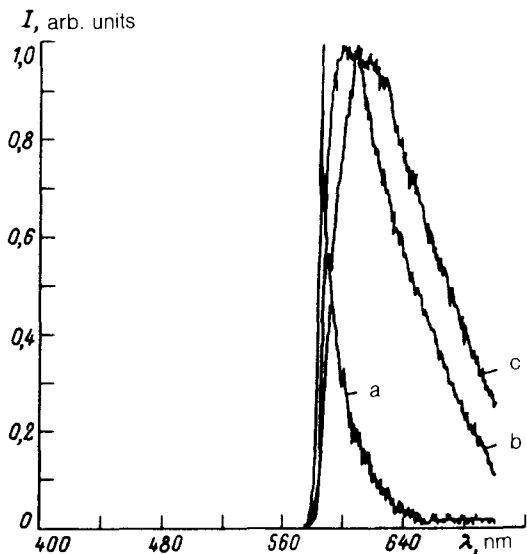


FIG. 3. Time-resolved emission spectra. a—Measurement time of 0.0-0.3 ns; b—1.0-2.9 ns; c—2.9-5.9 ns.

is manifested in the appearance of a broad, structureless long-wavelength band with a nonexponential emission kinetics.

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¹É. I. Rashba, *Self-Trapping of Excitons* (Nauka, Moscow, 1985).

²A. N. Terenin, *Photonics of Dye Molecules and Related Organic Compounds* (Nauka, Leningrad, 1967).

³É. I. Rashba, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **21**, 37 (1957).

⁴A. A. Ishchenko, *Usp. Khim.* **60**, 1708 (1991).

⁵A. A. Ishchenko, M. A. Kudinova, Yu. V. Malyukin *et al.*, "Spectroscopy of *J* aggregates of cyanin dyes in frozen binary solutions," Preprint IMK-93-8, Institute of Single Crystals, Ukrainian Academy of Sciences, Kharkov, 1993.

⁶S. de Boer and D. A. Wiersma, *J. Lumin.* **45**, 241 (1990).

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