Superradiance of *J*-aggregates: correspondence between infinite disordered chain and regular chain of finite length

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The radiation decay of excitons in a slightly disordered molecule chain is considered. The degree of disordering dictates the excitonic state length that determines the enhancement of the decay rate Γ (superradiance). Γ was calculated versus disordering degree and temperature and compared with the case of a regular chain where the length of excitonic state is determined by the chain length, N. For every degree of disordering, the value of N was found that provides practically the same decay rate as a function of temperature.

A term «*J*-aggregate» denotes an almost periodic chain of organic impurity molecules in an organic matrix (*J*-aggregates are called after the name of one of their discoverers E. Jelley (1937) [1]). Since seventies, *J*-aggregates attracted attention of researchers in several aspects. Of great physical interest is a phenomenon of superradiance that consists in a shortening of the luminescence decay time of *J*-aggregates as compared with that of the corresponding monomer. The degree of shortening (considered below) depends on the chain regularity degree and can be used for the diagnostics of the chain structure and for studying the molecule−matrix interaction responsible for a slight disordering of the chain [2–11].

The study of *J*-aggregates is perspective also for biological applications; in particular, electronic relaxation processes in a molecule chain reveal some similarity with the mechanisms of light energy transformation in biological photosynthesis systems [12,13]. In 1991 , it was proposed to use the excitonic luminescence of some *J*-aggregates as a probe for the living state of biological cells [14]. *J*-aggregates are formed on the cell membrane if they are attracted to it by the membrane potential that exists only in an alive cell and disappears if the cell is dead (the formation of *J*-aggregates is revealed through their luminescence).

For all aspects of the study and applications of *J*-aggregates, of importance is the correspondence between the degree of their disordering and the shortening of the luminescence decay time τ that can be measured experimentally and used for the diagnostics of the structure. Up to now, this correspondence was established within the model of a regular (strictly periodic) chain of a finite length N (length is expressed in units of the chain period a) [2–9,15,16].

The essence of this model is physically clear and consists in what follows. Consider an one-dimensional excitonic band corresponding to the lowest excited electronic state ψ of a separate molecule. This excitonic state can be presented as a linear combination of the orthonormalized molecular states centered at the chain sites n:

$$\Psi_\alpha = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} c_{n\alpha} \psi_n \qquad (1)$$

(subscript α numbers excitonic states which for a regular chain correspond to the wave vectors k_α). At a low temperature, when only the lowest excitonic state is occupied, the rate Γ of the radiative transition to the ground state is proportional to the squared matrix element of dipole moment between the excited and ground states. For the lowest excitonic state,

since all the coefficients c_n have the same sign and the corresponding matrix element for a separate molecule is independent of n, the matrix element between the state (1) and the ground state is proportional to $N^{1/2}$; thus, Γ is proportional to the chain length N. The coefficient of proportionality can be found at $N = 1$ as the radiative decay rate, Γ_0, of a separate excited molecule. Thus, the radiative decay rate of the lowest excitonic state Γ exceeds that of a separate molecule about N times:

$$\Gamma \approx N\,\Gamma_0 . \qquad (2)$$

Relation (2) is valid only for the lowest excitonic state. For a higher excitonic state, the coefficients c_n in (1) have alternate signs and Γ is much less than the quantity (2). It follows that Γ has a decreasing temperature dependence. For a regular chain, the dependence of Γ on N and temperature is well known; below it will be inferred to compare with the case of a disordered chains of an infinite length.

The model of a regular (periodic) chain of a finite length N qualitatively describes the behavior of excitons in an infinite slightly disordered chain where the lowest excitonic state is always localized; the localization radius determines an effective value of N. This model is broadly used in view of its simplicity and illustrativity. However, up to now the model had qualitative meaning for two reasons. First, no quantitative dependence was established between N and the disordering degree of an infinite chain (this was connected with difficulties of modeling an infinite disordered chain). Second, it was not known with what accuracy the model (even with an optimally chosen N) describes the temperature dependence of the superradiance rate of excitons in a disordered chain.

The purpose of the present work is to impart a quantitative character to the model of finite chain. To that end, first, the quantitative correspondence will be established between the model chain length N and the degree of disordering of the true infinite chain. Second, the temperature dependence of the superradiance rate of excitons in a disordered chain will be calculated and compared with the case of the regular chain of the best fitting length. It is assumed that superradiance occurs under condition of the complete thermodynamic equilibrium.

This consideration will be carried on the base of general relations for the excitonic states and superradiance rate of a molecule chain with an arbitrary length M and an arbitrary degree of disordering. The chain is placed into an inorganic crystalline matrix; the discrepancy between the periods of the chain and matrix lattice is the origin of a slight aperiodicity of the chain potential. The excitonic band is assumed to

correspond to the lowest excited electronic state of a separate molecule of the chain (the higher states of the molecule are not taken into account). In the absence of disordering at $M = N$, this general case turns to the model of the regular chain of a finite length N; in the presence of disordering at a large enough M, the case of a true infinite disordered chain is realized.

The Hamiltonian of the electronic system of the chain can be written down as

$$\text{H} = \Sigma \text{H}_{0n} - V . \qquad (3)$$

Here H_{0n} is the Hamiltonian of a separate molecule including the Hamiltonian of the free molecule and the crystalline field acting on the nth molecule in the chain; term V describes interaction between electronic subsystems of different molecules. According to (1), excitonic states Ψ_α, i.e., eigenfunctions of the Hamiltonian (3), are expanded in the orthonormalized states, ψ_n, of the chain containing excited molecule in the nth site ($n = 1, ..., M$). By definition, ψ_n is an eigenfunction of the Hamiltonian H_{0n} that, hence, has no off-diagonal matrix elements, whereas V has no diagonal elements (the diagonal part of V is carried over to the first term in (3)):

$$\text{H}_{0n}\,\psi_n = \varepsilon_n\,\psi_n, \quad \text{H}_{0nm} = \varepsilon_n \delta_{nm} , \quad V_{nn} = 0. \qquad (4)$$

The interaction potential V is assumed to be of exchange character which permits one to neglect all the matrix elements V_{nm} except those between adjacent sites, $V_{n,n+1}$ and $V_{n,n-1}$. The latter take random values around their average V, and site levels ε_n take random values around their average position that is put equal to zero. In the absence of disordering, the excitonic band has the width $W = 4V$ extending from $-2V$ to $2V$.

The Shröedinger equation with Hamiltonian (3) can be written down in the site representation in a usual way. Making allowance for (1) and (4), one obtains finally a system of linear homogeneous equations relative to the expansion coefficients $c_{n\alpha}$:

$$\varepsilon_n c_{n\alpha} + V_{n,n+1} c_{n+1,\alpha} + V_{n,n-1}\,c_{n-1,\alpha} = E_\alpha c_{n\alpha} \qquad (5)$$

$$(\alpha, n = 1,..., M)$$

(subscript α numbers excitonic states with energy E_α). Equation (5) should be complemented by the boundary condition that runs for a linear chain of the length M:

$$c_0 = 0,\ c_{M+1} = 0 . \qquad (6)$$

The chain can be also closed into a ring of the length M with periodic boundary conditions

$$c_{n+M} \equiv c_n ,\ V_{n+M,\ n+M+1} = V_{n,n+1}. \qquad (7)$$

The exciton energy levels E_α can be found via equating to zero the determinant of the equation system (5). Then the orthonormalized set of solutions $\{c_{n\alpha}\}$ is obtained from equation (5) after substituting for every α the corresponding value of E_α.

The rate, Γ_α, of the radiation decay from the αth excited state to the ground state is expressed in an usual way through the solution of Eq. (5):

$$\Gamma_\alpha = \Gamma_0 \left| \sum_{n=1}^{M} c_{n\alpha} \right|^2 . \qquad (8)$$

The total decay rate $\overline{\Gamma}$ under thermodynamic equilibrium is:

$$\overline{\Gamma}(M,T) = \frac{\sum_{\alpha=1}^{M} \Gamma_\alpha \exp\left(-E_\alpha/T\right)}{\sum_{\alpha=1}^{M} \exp\left(-E_\alpha/T\right)} \qquad (9)$$

(T stands for temperature in energy units). It is the lowest excited state with $\alpha = 1$ that makes the predominant contribution to the decay rate (9) due to a constant sign of c_{n1}; hence a decreasing temperature of $\overline{\Gamma}$ follows .

In a regular chain, ε_n and $V_{n,n+1} = V$ are independent of n, and Eq. (5) has a simple solution

$$c_{nk} = \frac{\exp\left(ikan\right)}{\sqrt{M}} , \qquad (10)$$

$$E_k = 2V \cos ka, \quad k = 2\pi\alpha / Ma, \ \alpha = 1,\ldots, M .$$

The expression (8) , with allowance for (10), takes the form

$$\Gamma_k = \frac{4 \sin^2 \left[(M+1)ka/2\right] \sin^2 \left(Mka/2\right) \operatorname{ctan}\left(ka/2\right)}{M \sin\left(ka\right) - \cos\left[(M+1)ka\right] \sin\left(Mka\right)} .$$

$$(11)$$

Let us consider now an infinite slightly disordered chain. Two possible types of disordering will be considered: (1) diagonal disordering, i.e., the random, straggling of site levels ε_n around their average $<\varepsilon> = 0$ and (2) off-diagonal disordering, i.e., the straggling of the matrix elements of interaction, $V_{n,n+1}$, near their average $<V_{n,n+1}> = V \equiv 0.25W$ (W is the band width of a long regular chain). The straggling is described by the Gaussian distribution with the dispersion σ_{dia} or σ_{off} in the former or latter case, respectively.

The cases of diagonal and off-diagonal disordering were considered separately. For a given σ_{dia} or σ_{off}, 1000 realizations of the chain with random sets of ε_n or

$V_{n,n+1}$ were constructed. For every realization, the equation system (5) was solved numerically. The boundary condition (7), related to the chain closed to a ring, was used in order to avoid edge effects; such ring of the length $M \gg N$ practically exactly models an infinite chain (N is the length of the equivalent regular chain). It was numerically verified that a ring with the length $M = 100$ practically exactly models an infinite chain with the equivalent length $N \leq 35$.

The range of dispersion σ was taken from $0.05W$ to $0.3W$ for diagonal disorder, and from $0.01W$ to $0.1W$ for off-diagonal disorder. For every σ_{dia} or σ_{off}, one can indicate the equivalent regular chain length $N(\sigma)$ which provides the same decay rate at zero temperature. Figure 1 shows the dependence of N on σ_{dia} or σ_{off} . It can be seen from Fig. 1 that the off-diagonal disordering with dispersion σ_{off} is approximately equivalent to the diagonal disordering with dispersion $3\sigma_{\text{off}}$. For estimation, considering diagonal and off-diagonal disordering as independent random processes, one can reduce the simultaneous diagonal disordering with dispersion σ_{dia} and off-diagonal disordering with dispersion σ_{off} to the diagonal disordering with dispersion $(\sigma_{\text{dia}}^2 + 9\sigma_{\text{off}}^2)^{1/2}$.

It was found that the temperature dependence of the decay rate $\overline{\Gamma}(T)$ for an infinite disordered chain is well approximated by that of the regular chain of the corresponding equivalent length without restriction of the temperature range. Figures 2 and 3 show the examples of such approximation.
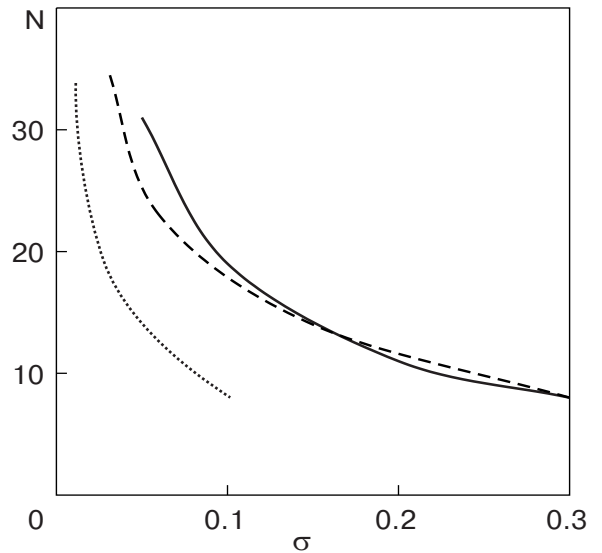

Fig. 1. The dependence of the equivalent length N of the regular chain on the disordering degree, σ, of the infinite chain. Solid curve − $N(\sigma_{\text{dia}})$ at $\sigma_{\text{off}} = 0$, dotted curve − $N(\sigma_{\text{off}})$ at $\sigma_{\text{dia}} = 0$. Dashed line shows the dependence $N(\sigma_{\text{off}}/3)$ at $\sigma_{\text{dia}} = 0$.
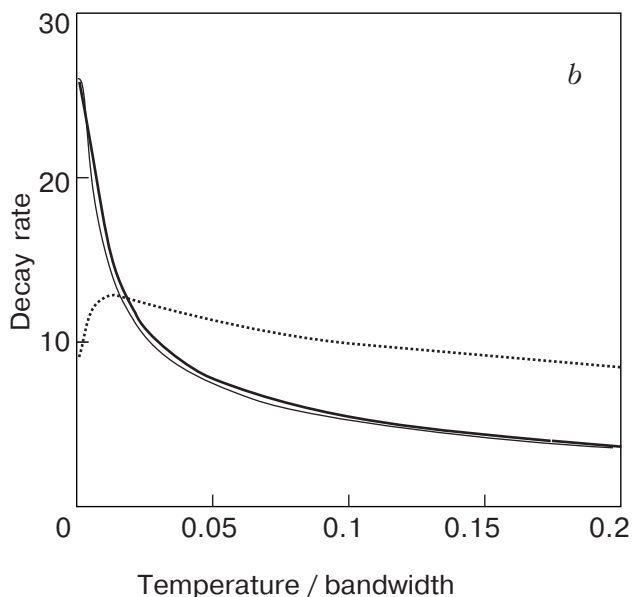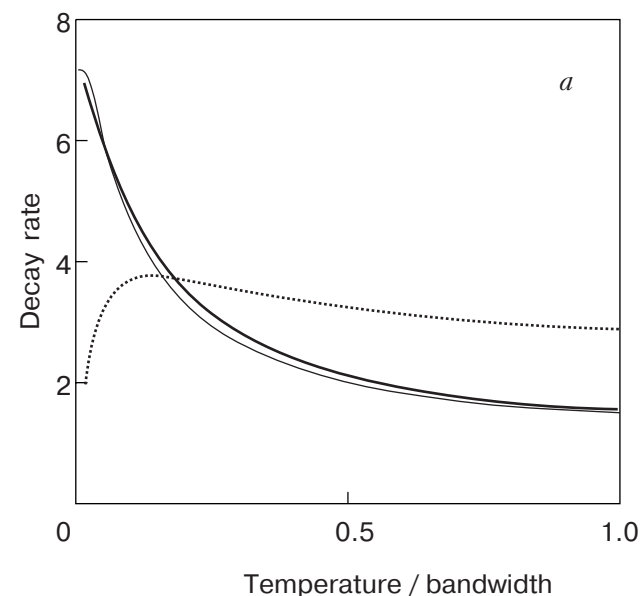
Fig. 2. Temperature dependence of radiative decay rate $\overline{\Gamma}$ for a chain with diagonal disorder in units of that of the monomer. Thick solid line relates to the infinite disordered chain with $\sigma_{dia} = 0.3$ (*a*) and 0.05 (*b*). Thin solid line relates to the regular chain with the length $N = 8$ (*a*) and $N = 31$ (*b*) that best models the disordered chain. Dotted line shows the dispersion of $\overline{\Gamma}$ over random realizations of the disordered chain.

Fig. 3. Temperature dependence of radiative decay rate $\overline{\Gamma}$ for a chain with off-diagonal disorder in units of that of the monomer. Thick solid line relates to the infinite disordered chain with $\sigma_{off} = 0.1$ (*a*) and 0.01 (*b*). Thin solid line relates to the regular chain with the length $N = 8$ (*a*) and $N = 35$ (*b*) that best models the disordered chain. Dotted line shows the dispersion of $\overline{\Gamma}$ over random realizations of the disordered chain.

It should be taken into account that Figs. 2 and 3 show the decay rate averaged over a large number of random realizations of the disordered chain. Such averaging takes place at a single excitation pulse, if it is strong enough to excite a large number of chains. If every pulse excites only one molecule (single molecule spectroscopy), observed $\overline{\Gamma}$ has a significant straggling, whose dispersion is shown in Figs. 2 and 3 by dotted lines.
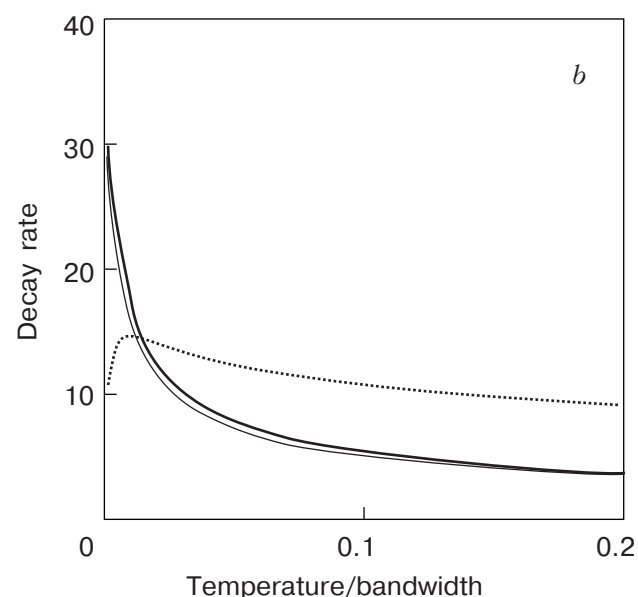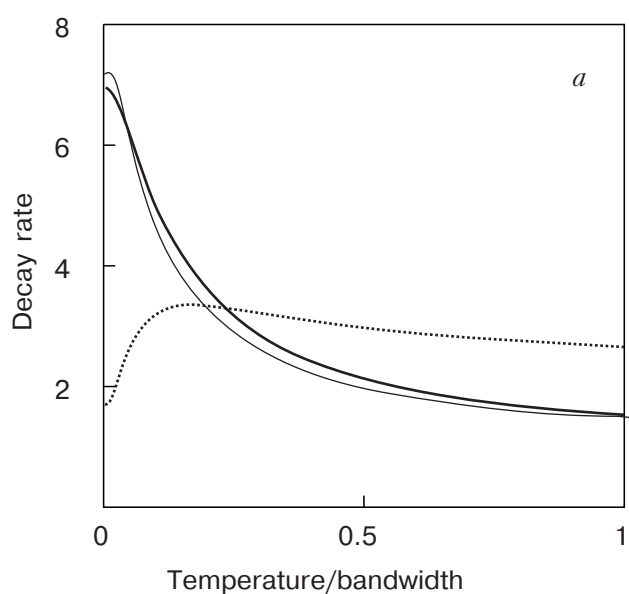
In the indicated meaning, an infinite irregular chain can be modeled by a regular chain of a finite length. However, this correspondence is restricted to the superradiance rate and cannot be extended to absorption spectrum (consisting of discrete lines for a regular chain and smeared to a band for a disordered chain).

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