Exciton absorption spectra of optically excited linear molecular aggregates

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Exciton absorption spectrum of optically excited linear molecular aggregate is theoretically investigated. The sum rules for the integral intensity of the absorption spectrum are derived. The dipole moments of the optical transitions from the one-exciton states to the two-exciton states are presented. The results obtained indicate an energy increase of the exciton transition after a single excitation of the aggregate. It accounts for the observed short-wavelength shift of the J-band of the pseudoisocyanine (PIC) J-aggregates after their optical excitation. The comparison of the experimental energy of the shift with its theoretical evaluation allows to estimate the number of monomers forming a typical PIC J-aggregate in the solution $N \gtrsim 20$–30.

1. Introduction

The concept of molecular (or Frenkel) excitons [1] finds a wide application in the investigation of the optical absorption spectra of different molecular aggregates forming in solutions [2–4], in mixed molecular crystals [5, 6], and in biological systems [7]. The stationary exciton absorption spectra of dimers [8, 9], polymers [8, 10, 11], and other more complex molecular aggregates [7] were theoretically investigated for many years. However, the peculiarities of their absorption spectra from the excited states were not practically studied. Only the case of the simplest molecular aggregate, i.e. dimer, was slightly considered [12, 13]. The necessity of the theoretical investigation of the transient exciton absorption spectra emerges firstly because of the experiments being carried out at present using the picosecond laser technique [14–16]. The application of ultrashort excitation pulses enables, without the destruction of the aggregates, to create a comparatively high concentration of excited molecules in the sample which is necessary to observe the changes of the absorption spectrum as compared with the stationary spectrum. The problem in question is also closely connected with the possibilities of using aggregated molecular systems as reverse saturable absorbers [13].

The object of this paper is to treat the exciton absorption spectrum of the singly optically excited linear molecular aggregate. The theoretical analysis is carried out using Wigner-Jordan transformation [17], i.e. the transition from the usual Pauli creation and destruction operators to the corresponding fermion operators. It allows to transform the initial Hamiltonian to the one of the system of noninteracting fermion excitons. That is a peculiar feature of the one-dimensional case under consideration and enables to solve the problem analytically. The results obtained are applied to explain the occurrence of the short-wavelength shift of the J-band of the pseudoisocyanine (PIC) J-aggregates after their excitation by the picosecond pulse of a relatively weak intensity [16]. The results of the paper can be applied to other objects as well, for instance, to triplet excitons in isotopically mixed quasi-one-dimensional crystals [5, 6].

2. The model

The system to be considered is a resonance-interacting molecular chain (the linear molecular aggregate) of N identical monomers. We will consider two electron states of an individual molecule of the system, i.e., the ground state and the first excited state. All the mon-

omers are in the same environment, and the exciton-phonon coupling is not taken into account. The Hamiltonian of such a system can be represented by the fermion creation and destruction operators a_n^+ and a_n or b_j^+ and b_j [17]

$$H = \sum_{n=1}^{N} \varepsilon_0 a_n^+ a_n - \sum_{n=1}^{N-1} L(a_n^+ a_{n+1} + a_{n+1}^+ a_n) \tag{1}$$

$$= \sum_{j=1}^{N} E_j b_j^+ b_j, \quad b_j b_{j'}^+ + b_{j'}^+ b_j = \delta_{jj'}, \quad b_j b_{j'} + b_{j'} b_j = 0, \tag{2}$$

with

$$b_j^+ = \left(\frac{2}{N+1}\right)^{1/2} \sum_{n=1}^{N} a_n^+ \sin\left(\frac{j\pi n}{N+1}\right),$$

$$E_j = \varepsilon_0 - 2L\cos\left(\frac{j\pi}{N+1}\right). \tag{3}$$

Here $-L$ is the excitation transfer matrix element ($L > 0$), ε_0 is the excitation energy of an individual molecule of the chain, $\delta_{jj'}$ is a Kronecker delta, and n refers to the molecules of the aggregate. The operators a_n^+ (and a_n) are related to the usual excited molecular state creation (and destruction) operators t_n^+ (and t_n) using Wigner-Jordan transformation [17]:

$$a_n^+ = (-1)^{\sigma_n} t_n^+, \quad a_n = (-1)^{\sigma_n} t_n,$$

$$\sigma_n = \sum_{l=1}^{n-1} t_l^+ t_l = \sum_{l=1}^{n-1} a_l^+ a_l. \tag{4}$$

The Hamiltonian (1) represents a system of noninteracting fermion excitons. The eigenstates of such a system are: the ground state $|g\rangle$, the one-exciton states $|j\rangle = b_j^+ |g\rangle$, the two-exciton states $|j_1, j\rangle = b_{j_1}^+ b_j^+ |g\rangle$ ($j_1 \neq j$), etc., their energies being respectively 0, E_j, $E_{j_1} + E_j$, etc.

For the investigation of the exciton absorption spectra, we will introduce the operator of the total transition dipole moment of the aggregate. In case the length of the incident electromagnetic wave is much greater than that of the chain, we have

$$M = M_+ + M_-, \quad M_- = (M_+)^+, \tag{5}$$

$$M_+ = \sum_{n=1}^{N} \mu_n t_n^+ = \sum_{n=1}^{N} \mu_n a_n^+ (-1)^{\sigma_n}, \tag{6}$$

μ_n being the projections of the transition dipole moments of individual monomers to the polarization e of the incident wave. We will assume that μ_n does not depend on n: $\mu_n = \mu$. This is the case provided the transition moments of all the molecules are of the same direction, or their projections to the polarization e are equal.

The absorption spectra of the linear aggregates formed by the transitions from the ground state to the one-exciton states (the stationary absorption spectra) have been widely investigated [8, 10, 11]. Within the model presented the dipole moments of such transitions equal to

$$\langle j|M|g\rangle = \Pi_j[1 - (-1)^j]/2,$$

$$\Pi_j = \mu[2/(N+1)]^{1/2}\text{ctg}\{\pi j/[2(N+1)]\};$$

when $j \ll N$,

$$\Pi_j \approx \mu(8N)^{1/2}/(\pi j). \tag{7}$$

In case $N \gg 1$ the transition $|g\rangle \to |1\rangle$ to the exciton state with the minimum energy yields 81 per cent contribution to the stationary absorption spectrum. It accounts for the fact that the exciton absorption band of PIC (the J-band at 573 nm) is red shifted as compared with the monomer absorption band (530 nm) [10, 11].

Further we will consider the aggregate absorption spectra from the excited (one-exciton) states. The major problem in solving the given task lies in the occurrence of the many-particle operators $(-1)^{\sigma_n}$ in (5) and (6).

3. Theoretical results

Having in consideration that the induced radiation yields a negative contribution to the absorption spectrum of the system, we will determine the lineshape of the aggregate absorption spectrum from the one-exciton state $|j_0\rangle$ as follows:

$$I_{j_0}(\omega) = I_{j_0}^+(\omega) - I_{j_0}^-(\omega),$$

$$I_{j_0}^{\pm}(\omega) = \sum_{\text{fin}} \left|\langle \text{fin}|M|j_0\rangle\right|^2 \delta[\omega \mp (E_{\text{fin}} - E_{j_0})/\hbar], \tag{8}$$

$|\text{fin}\rangle$ being all possible final states, i.e. the two exciton states or the ground state, E_{fin} being their energies, and $\hbar\omega$ being the energy of the incident photon. The function $I_{j_0}(\omega)$ obeys the following sum rule:

$$\int_0^\infty I_{j_0}(\omega)\,d\omega = (N-2)\mu^2. \tag{9}$$

The equation (9) is a particular case of the sum rule (A.5) for the lineshape of the aggregate spectrum from the many-exciton states. The comparison of (9) with the well-known sum rule for the lineshape of the stationary absorption spectrum [18]

$$\int_0^\infty I_g(\omega)\,d\omega = N\mu^2,$$

$$I_g(\omega) = \sum_j |\langle j|M|g\rangle|^2 \delta(\omega - E_j/\hbar) \tag{10}$$

shows that for the long chain ($N \gg 1$) we have $\int I_{j_0}(\omega)\,d\omega \approx \int I_g(\omega)\,d\omega$, i.e., after a single optical excit-

ation of the aggregate there are practically no changes in the integral intensity of the exciton absorption band. For a more detailed analysis of the transient absorption spectrum, it has been established that

$$M|j_0\rangle = |g\rangle\langle g|M|j_0\rangle + \sum_{j_1=2,4,\ldots} b_{j_1}^+ b_{j_0}^+|g\rangle\Pi_{j_1}$$

$$+ \sum_{j_1>j} b_{j_1}^+ b_j^+|g\rangle K_{j_1,j}, \tag{11}$$

where

$$K_{j_1,j} = 2^{-1}[(\Pi_{j_1}+\Pi_j)\delta_{j_1-j,j_0} + (\Pi_j-\Pi_{j_1})\delta_{j_1+j,j_0}] \tag{12}$$

in case $j_0 \ll N$ and $j_1 \ll N$. To satisfy the first inequality the exciton bandwidth must be considerably greater than the thermal energy: $4L \gg kT$. In this case only the lowest one-exciton levels may be occupied. The second condition excludes the discussion of hardly probable transitions to the two-exciton states with the great quantum numbers j_1 and j.

It follows from (11) and (12) that the optically allowed transitions from the one-exciton states to the two-exciton states $|j_0\rangle \rightarrow |j_1,j\rangle$ can be of three types (Fig. 1): a) when $j=j_0$, j_1 being even, b) when $j_1-j=j_0$, and c) when $j_1+j=j_0$. Moreover, some transitions, for instance $|1\rangle \rightarrow |2,1\rangle$, may belong to the first two types at the same time. The first type of the diagrams (Fig. 1a) describes the processes when the incident photon creates the second exciton without disturbing the state of the first one, i.e., these are purely one-exciton processes. The presence of the first exciton enables transitions to the states with even quantum number j_1 (compare with (7)). In the case of the processes of the second and the third types (Fig. 1b and c) the change of the initial exciton state is possible. That is due to the many particle behaviour of the operator M in the fermion representation. The constraints obtained $j_1 \pm j = j_0$ can be interpreted as a certain form of the quasi-momentum conservation law, since the quasi-momentum of the exciton $\hbar k_0 \sim j_0$ in the open molecular chain in question is determined only with an accuracy up to a sign.

The energies of these transitions are given by

$$E_{j_0 \rightarrow j_1,j} = E_j + E_{j_1} - E_{j_0} \approx \varepsilon_0 - 2L + \chi(j^2 + j_1^2 - j_0^2), \tag{13}$$

(a)   (b)   (c)

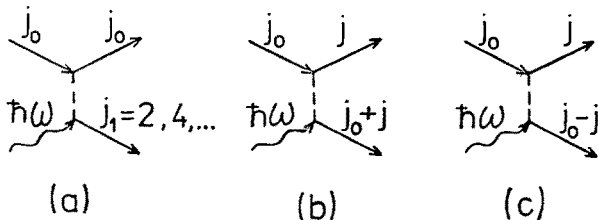Fig. 1a–c. Diagrams of the optically allowed processes

with $\chi = L(\pi/N)^2$. For the optical transitions of the first two types the energies $E_{j_0 \rightarrow j_1,j}$ exceed the energy of the most intensive transition of the stationary absorption spectrum $E_{g \rightarrow 1} \approx \varepsilon_0 - 2L + \chi$. For the transitions of the third type $E_{j_0 \rightarrow j_1,j} < E_{g \rightarrow 1}$. However, such transitions are possible only in case $j_0 \geqslant 3$. Moreover, their intensities are weak, provided j_0 is relatively small ($j_0 \lesssim 6$). For example, in case $j_0 = 4$, the intensity of the only possible transition of the third type $|4\rangle \rightarrow |3, 1\rangle$ equals respectively to 4/9 and to $\approx 1/3$ of the intensities of the most probable transitions of the first two types $|4\rangle \rightarrow |2, 4\rangle$ and $|4\rangle \rightarrow |5, 1\rangle$. It should be also pointed out that the induced radiation, occurring mainly from the state $|1\rangle$, is completely compensated by the transition of higher energy $|1\rangle \rightarrow |2, 1\rangle$, the intensity of which is one and a half times greater than that of $|g\rangle \rightarrow |1\rangle$. All these facts are indicative of the short-wavelength shift of the exciton absorption band after the optical excitation of the aggregate in case $j_0 \lesssim 6$. The minimum energy of the shift equals to

$$\Delta E_{\min} = 3\chi = 3L(\pi/N)^2. \tag{14}$$

Moreover, the transient absorption spectrum may contain new bands of the induced absorption from the first excited molecular state to the higher molecular levels. However, the neglect of such bands is quite reasonable, since, as pointed out at the end of the Appendix A, their intensities are about N times smaller than the intensity of the exciton absorption band.

So far, the excitation energies of all monomers of the aggregate have been assumed to be equal. Taking into account the changes of the excitation energies of the end molecules of the chain due to their location in the environment different from that of other molecules, we will add an extra term $\beta L(a_1^+ a_1 + a_N^+ a_N)$ to the Hamiltonian (1). It is equivalent to the imposition of the following boundary conditions on a regular infinite chain [19]:

$$C_j(0) = -\beta C_j(1), \quad C_j(N+1) = -\beta C_j(N), \tag{15}$$

where

$$b_j^+ = \sum_n a_n^+ C_j(n), \quad C_j(n) \sim \sin(k_j n + \varphi_j),$$

$$E_j = \varepsilon_0 - 2L\cos k_j, \quad j = 1, 2, \ldots, N. \tag{16}$$

For the lowest band levels, which are the most important for the absorption spectra, we have

$$b_j^+ \approx \left(\frac{2}{N+1-2n_0}\right)^{1/2} \sum_{n=1}^N a_n^+ \sin\left[\frac{j\pi(n-n_0)}{N+1-2n_0}\right],$$

$$j \ll N, \quad n_0 j \ll N, \tag{17}$$

with $n_0 = \beta/(1+\beta)$. Consequently, in (7) and (12)–(14) it is necessary to slightly change N by $N - 2n_0$ ($n_0 \ll N$). More considerable changes of these formulas are poss-

ible only in case the parameter β is near its critical value $\beta_{crit} = -1$, below which the local surface levels are split from the exciton band.

The dynamic exciton-exciton interaction V_{ex-ex} $= \sum_n \gamma a_n^+ a_n a_{n+1}^+ a_{n+1}$ for the aggregate with the cyclic boundary conditions can be taken into account by separating the movement of the center of mass of two excitons from their relative motion [20]. The problem of the relative motion is analogous to the one just discussed above. Therefore, the given type of the interaction is of no importance either.

4. Blue schift of the J-band

In aqueous solutions at concentrations higher than 10^{-3} mol/l the PIC dye is known to form thread-like J-aggregates [2]. Due to the aggregation a new, extremely narrow absorption band of exciton origin, called the J-band, appears at 573 nm in addition to the already present monomer (530 nm) and dimer (480 nm) bands. The experiment by Gadonas et al. [16] shows a transient short-wavelength shift of the J-band together with its slight bleaching after the excitation of the J-aggregates by the picosecond pulse of a relatively weak intensity not exceeding one absorbed photon per 30–40 aggregated monomers. (This shift seems to be related to the fact, pointed out in [15], that the onset of the bleaching of the long-wavelength edge of the J-band (576 nm) occurs at the excitation intensities ten time smaller than observed for its peak). The above presented theoretical results account for such a shift having assumed the exciton origin of the J-band. From the comparison of the experimental value of the shift energy $\Delta E_{exp} = 30$–60 cm^{-1} ($-\Delta\lambda_{exp} = 1$–2 nm) with (14) ($L = 910$ cm^{-1} [21]), it follows that the length of a typical PIC J-aggregate in the solution is: $N \gtrsim 20$–30. It is in agreement with the earlier evaluations obtained by means of other methods [2] and also with the fact that the bleaching of the J-band due to the multiphoton excitation of the J-aggregate occurs at the pulse energy E corresponding to one absorbed photon per several tens of the aggregated monomers [15, 16]. For example, it follows from [15] that at $\lambda_{excit} = 573$ nm $E \lesssim 10^{-5}$ J/cm^2, $\alpha = 6200$ cm^{-1} ($\alpha = \varepsilon C \ln 10$, $\varepsilon = 1.8 \times 10^5$, $C = 1.5 \times 10^{-2}$ mol/l), $n_0 = 9 \times 10^{18}$ molecules/cm^3, therefore, the number of absorbed photons per one PIC molecule equals approximately to $n/n_0 = \alpha E/(\hbar\omega n_0) \lesssim 1/30$, α being the absorption coefficient.

The explanation of the blue shift presented above is not the only possible one. Other mechanisms for the shift of the J-band upon excitation may be suggested, e.g. a change of the charge density distribution [16], a

change of the aggregate conformation, or a rise of the internal temperature of the aggregate. (Presumably, the latter mechanism cannot induce the blue shift, since so far no temperature dependence of the position of the J-band has been observed.)

However, the explanation presented seems to be more natural for us, since it is based upon the exciton origin of the J-band only, and no additional supposition is necessary.

In the present paper the projections of the transition dipole moments of all the monomers of the aggregate to the polarization of the incident light were assumed to be equal ($\mu_n = \mu$). The PIC aggregate is known to have, probably, a helical structure or two molecules per elementary cell [11, 22]. In both cases the transition dipole moments of the monomers contain a constant term $\mu_\parallel$ parallel to the aggregate axis and a rotating term $\mu_{\perp n}$ orthogonal to it. The constant term $\mu_\parallel$ is responsible for the occurrence of the J-band. The polarization of the J-band is known to be parallel to the aggregate axis [2, 11, 16]. Since our concern is the absorption of the J-band only, the assumption, that $\mu_n = \mu = |\mu_\parallel|$ does not depend on n, is completely correct.

Further, let us discuss the influence of the vibronic coupling. The exciton coupling with molecular vibrations was shown to be of great importance for the absorption spectrum $I_\perp$, polarized perpendicular to the PIC aggregate axis [11]. For the parallel polarization the vibronic coupling is not of such importance. It does not have significant (qualitative) influence on the dispersion of the exciton, and the intensity of the zero phonon line (the J-band) yields about 75 per cent contribution to the absorption spectrum $I_\parallel$ [11]. Therefore, the vibronic coupling can be roughly taken into account by simply replacing the excitation transfer term L by the vibrationally reduced one.

It should be also pointed out that the number N calculated from the experimental shift may be not a measure of an actual physical length of the aggregate, but that of the coherence length of the exciton. The excitons in PIC J-aggregates seem to have the coherence length of several tens of monomer units or greater [22], i.e. $N_{coh} > N$. In this case, the number N calculated from the experimental shift would be an actual physical length of the J-aggregate. However, since the coherence length is not exactly known, the question remains still open.

The results obtained can be applied to other systems as well, in particular, to the isotopically mixed quasi-one-dimensional 1,4-dibromonaphthalene crystal in studying the transient absorption spectra of triplet excitons in the molecular chains of the host molecules isolated by the isotopical ones. The spectral lines of such clusters of several (up to five) molecules

have been identified in the absorption spectrum of the crystal [5].

5. Conclusion

We have shown that one photon can induce the shift of the absorption band of the system consisting of $N \gg 1$ molecules. It is related to the collective properties of the coherent excitons considered, i.e., to the delocalization of the electron excitation along the chain. Locating the excitation on separate molecules of the aggregate one could observe the optical changes, such as the bleaching of the $S_0 \to S_1$ transition but not its shift. The effect under consideration is also closely connected with the fermion behaviour of one-dimensional molecular excitons. For example, in the case of the transitions from the one-exciton state of the lowest energy $b_1^+|g\rangle$, the occurrence of this shift can be easily explained by the Pauli exclusion principle.

The application of theoretical results to the PIC J-aggregates gives an explanation to the observed short-wavelength shift of the J-band and enables to evaluate the number of monomers forming the J-aggregate.

Appendix: sum rules

Let us consider the integral intensity of the exciton absorption band of singly excited aggregate

$$\int_0^\infty I_{j_0}(\omega)\mathrm{d}\omega = \sum_{\text{fin}}(|\langle\text{fin}|M_+|j_0\rangle|^2 - |\langle\text{fin}|M_-|j_0\rangle|^2)$$

$$= \langle j_0|(M_-M_+ - M_+M_-)|j_0\rangle. \tag{A.1}$$

Having in consideration the commutation rules for the Pauli operators t_n^+ and t_n [17]

$$[t_n, t_n^+]_+ = 1, \quad [t_n, t_n]_+ = 0,$$

$$[t_n, t_{n'}^+]_- = [t_n, t_{n'}]_- = 0, \quad n \neq n', \tag{A.2}$$

we find

$$M_-M_+ - M_+M_- = \sum_{n=1}^N \mu_n^2(1 - 2a_n^+a_n), \tag{A.3}$$

therefore,

$$\int_0^\infty I_{j_0}(\omega)\mathrm{d}\omega = \sum_{n=1}^N \mu_n^2 - 2\langle j_0|\sum_{n=1}^N \mu_n^2 a_n^+a_n|j_0\rangle, \tag{A.4}$$

and in case μ_n^2 does not depend on n, we get the sum rule (9). According to it the effective number of absorption molecules equals to $N-2$ independently from the initial state $|j_0\rangle$ ($N-1$ of the molecules being in the

ground state gives a contribution to the absorption, while the excited molecule takes part in the induced radiation). However, if μ_n^2 depend on n, the operator $\sum_{n=1}^N \mu_n^2 a_n^+a_n$ is not proportional to the particle number operator, and the right-hand side of (A.4) is the function of the initial state $|j_0\rangle$.

It should be pointed out that (A.4) and (9) hold when the excitation energies of the molecules and the excitation transfer matrix elements depend on n: $\varepsilon_0 \to \varepsilon_n$ and $L \to L_n$, since while deriving these formulas we did not use an explicit form of the initial states $|j_0\rangle$. Due to the same reason (A.4) and (9) can be easily generalized for the lineshape of the aggregate absorption spectrum from the many-exciton states

$$I_{j_0j_1\ldots j_{m-1}}(\omega) = I^+(\omega) - I^-(\omega),$$

$$I^\pm(\omega) = \sum_{\text{fin}}|\langle\text{fin}|M|j_0, \ldots, j_{m-1}\rangle|^2$$

$$\delta[\omega \mp (E_{\text{fin}} - \sum_{i=0}^{m-1} E_{j_i})/\hbar], \tag{A.5}$$

m being the number of excitons in the initial state. In this case in (A.4) the one-exciton states $|j_0\rangle$ should be replaced by the many-exciton ones $|j_0, \ldots, j_{m-1}\rangle$, and (9) should be modified as follows:

$$\int_0^\infty I_{j_0j_1\ldots j_{m-1}}(\omega)\mathrm{d}\omega = (N - 2m)\mu^2. \tag{A.6}$$

The sum rule (9) can be also generalized having in consideration the induced absorption of the excited molecules into the higher molecular levels. Then, in the right-hand side of (9) an extra term $\sum_t \mu_{1t}^2$ is added, μ_{1t} being the projections of the dipole moments of the intramolecular transitions $S_1 \to S_t$ ($t > 1$) to the polarization e, and the summation is extended over the transitions, whose energies are in the spectral region under consideration. Consequently, the integral intensity of the induced absorption bands is approximately N times smaller than that of the exciton absorption band which is proportional to N.

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