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OPTICAL INFORMATION TECHNOLOGIES AND SYSTEMS

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INTRODUCTION

Optical phenomena in chromophore molecules (dyes) are of a great variety and interest (see, for instance, [1–4]). The chromophore study is also important from an applied point of view because they are utilized as probes and labels [5, 6], for macromolecule modification [7], in active laser media [8].

The present paper is devoted to a theoretical description of the optical processes in an infinite linear chromophore chain. The monomers which constitute the chain are assumed to be isolated (discernible) quantum mechanically, however due to weak overlapping of electron clouds they can radiativelessly exchange an electron excitation energy with the nearest neighbors in the chain. This exchange causes the cooperative processes. In particular, the summation of the energy of two neighboring monomers in one of them (a cooperative excitation) is a cooperative process. Another side of this process is nonlinear quenching (an energy loss by a monomer) by an energy donor. Besides the process mentioned above, an excitation energy migration along the chain is also possible. It does not lead to a change in the populations of electron levels and thereby is not taken into account in the paper.

Photoprocesses in bichromophores, dye dimers, were considered in [9, 10]. The monomer population correlation which appeared due to the energy exchange was taken accurately into account in these papers. However, the method of balance equations, which was applied in [9, 10] for description of the populations of electronic levels of a bichromophore, cannot be extended to a chain because of a growing number of equations. To overcome this difficulty, in the present paper we use an analogy with the Ising model. The results obtained are verified by numerical simulation.

Definition of the model. At first, let us consider an individual chromophore (hereafter we will call it a monomer). As is well-known [11], in the complex organic molecules which are impurities in a condensed phase, a rate of dephasing in electronic excited states is significantly higher than that of other relaxation processes. Hence, taking also into account the quantum mechanical discernibility, one may conclude that the monomers are in certain "pure" electronic states at any instant. Let us denote these states as S_i, where i is a level number.

The following processes proceed in a monomer. Firstly, radiative transitions with cross-sections σ_{ij}:

$$S_j + \hbar\,\omega \stackrel{\sigma_{ij}}{\to} S_i, \quad i \neq j. \tag{1}$$

For $i > j$, (1) describes a radiative excitation, for $i < j$, a stimulated emission. A differential probability that the radiative transition (1) occurs in a time interval dt is $\sigma_{ij} I dt$, where I is an intensity of the exciting radiation. Therefore, the quantity $\sigma_{ij} I$ is a rate of the process described by (1).

We will assume, according to observed values, that the rates of relaxation via the vibrational sublevels $\Gamma_i^{(v)}$ are significantly higher than the rates of spontaneous relaxation of the electronic states Γ_i. That is why the electronic states decay from the ground vibrational sublevels:

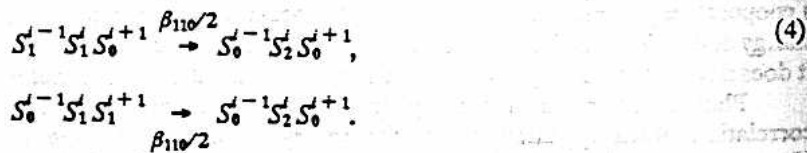$$S_j \stackrel{\Gamma_{ij}}{\to} S_i, \quad i < j, \tag{2}$$

where Γ_{ij} are partial rates and $\Gamma_j = \Sigma_i \Gamma_{ij}$. Because of the condition $\Gamma_i^{(v)} \gg \Gamma_i$, the excitation of the higher electronic levels occurs via the ground vibrational sublevels of the lower ones in stepwise processes of the (1) type: $S_0 \to S_1 \to S_2$; the two-photon (not stepwise) processes have a small probability in terms of the parameter $\Gamma_i^{(v)}/\Gamma_i$. Hereafter we suppose that a photon energy is not so high that the topmost levels are populated bypassing the cascade, i.e., in a one-quantum process.

In complex chromophore molecules, a lifetime of the first singlet state Γ_1^{-1} is of the order of 10^{-8}–10^{-9} sec while the higher excited states have lifetimes shorter than 10^{-12} sec. Therefore, one may demand that the excitation radiation intensity I be not so high as to saturate the second excited level but sufficient for saturating the first one:

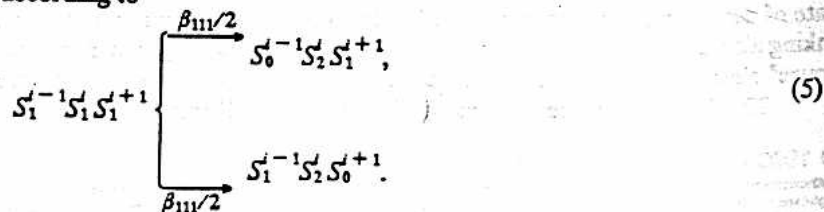$$\Gamma_2 \gg \Gamma_1, \ \sigma_{ij} I. \tag{3}$$

This allows us to restrict the consideration only to the first three electronic states: S_0, S_1, and S_2. Note, that the rates of the photochemical conversions which can proceed only from the higher excited states (for instance, the reactions which are caused by the transfer of a two-quantum excitation energy [12, 13]) are proportional to the population of the S_2 level; the fluorescence intensity is proportional to the population of S_1.

Let us now proceed to the cooperative processes which are specific for a chromophore chain. They are described by two rate constants. Firstly, if an ith monomer and one of its nearest neighbors are in the S_1 state, while the other nearest neighbor in the S_0 state, then the electron excitation energy can accumulate in the ith monomer, with the latter moving to the S_2 state and its neighbor, which is an energy donor, to S_0. Let us designate the rate of such a process by $\beta_{110}/2$:

$$S_1^{i-1} S_1^i S_0^{i+1} \stackrel{\beta_{110}/2}{\to} S_0^{i-1} S_2^i S_0^{i+1}, \tag{4}$$

$$S_0^{i-1} S_1^i S_1^{i+1} \underset{\beta_{110}/2}{\to} S_0^{i-1} S_2^i S_0^{i+1}.$$

Here the upper indices number the monomers. The factor 1/2 is introduced because the energy may accumulate in both the ith monomer and its neighbor with an equal probability. The constant β_{110} is completely analogous to the constant β_{11} which was used in [9, 10] for a bichromophore description.

If the ith monomer and both its neighbors are in the S_1 state, then the energy summation in the ith monomer is described by the rate constant β_{111} according to

$$S_1^{i-1} S_1^i S_1^{i+1} \begin{cases} \stackrel{\beta_{111}/2}{\to} S_0^{i-1} S_2^i S_1^{i+1}, \\[2ex] \underset{\beta_{111}/2}{\to} S_1^{i-1} S_2^i S_0^{i+1}. \end{cases} \tag{5}$$

It is supposed here that the probability of the summation of the three-quantum energy in one monomer is low.

The energy conditions on 0–0-transition frequencies, which provide the proceeding of the cooperative processes in the directions indicated in (4) and (5), at the same time prohibit the reverse processes.

Populations and reduced balance equations. Let us introduce the following notation. Let $n_{i_1 i_2 \dots i_m}$ ($i_k = 0, 1, 2$) be a combined probability that m monomers, which constitute a chain fragment and follow one after another, are in the states $S_{i_1} S_{i_2} \dots S_{i_m}$, respectively. It follows from the properties of chain symmetry and the condition of conservation of the number of particles that:

$$n_{i_1 i_2 - i_m} = n_{i_m i_{m-1} - i_1}, \tag{6}$$

$$\sum_{i_1, \dots, i_m = 0}^{2} n_{i_1 \dots i_m} = 1. \tag{7}$$

For $l < m$ the following relationship also takes place

$$n_{i_1 \dots i_l} = \sum_{i_{l+1}, \dots i_m} n_{i_1 \dots i_l \dots i_m}. \tag{8}$$

In particular, n_i is an individual chromophore population which characterizes the probability that an arbitrary monomer in the chain is in the S_i state. The quantity n_{ij} is a simultaneous pair correlator and describes the bichromophore states completely. In paper [9], which is devoted to bichromophores, a system of balance equations for quantities n_{ij} was obtained and solved, after which the populations n_i were calculated according to (8).

Let us now obtain the equations which describe the populations of energy levels of monomers constituting an infinite chain. In this case we will take into account condition (3) (see also [9]). Suppose that the monomer found in the S_2 state returns instantaneously either with a probability r_0 to the S_1 state or with a probability r_1 to the S_1 state, where r_0 and r_1 are branching coefficients:

$$r_0 = \Gamma_{\omega}/\Gamma_2, \quad r_1 = \Gamma_{12}/\Gamma_2, \quad r_0 + r_1 = 1. \tag{9}$$

Proceeding from the balance of the processes (1), (2), (4), (5), and taking into account the above reasoning, we will obtain in the steady state (for stationary excitation conditions):

$$\begin{cases} dn_1/dt = -n_1/\tau_1 + n_0/\tau_0 - (1 + r_0)\beta_{110} n_{110} - (1 + r_0)(\beta_{111}/2)n_{111} = 0, \tag{10} \\ dn_2/dt = -\Gamma_2 n_2 + \sigma_{21} I n_1 + \beta_{110} n_{110} + (\beta_{111}/2)n_{111} = 0, \tag{11} \end{cases}$$

$$1/\tau_0 = \sigma_{10} I, \quad 1/\tau_1 = \Gamma_1 + (\sigma_{01} + r_0 \sigma_{21})I, \tag{12}$$

$$n_0 + n_1 = 1, \quad n_2 \ll 1. \tag{13}$$

Here we introduced the quantities τ_0 and τ_1, the lifetimes of an individual chromophore in the states S_0 and S_1 without regard to the cooperative processes and also took into account that $n_{110} = n_{011}$. Relationships (13) are obtained from the condition of conservation of the number of particles (7) with regard to (3) and express the fact that a monomer is almost always either in the S_0 state or in the S_1 state.

System (10), (11) cannot be solved because it involves more unknown quantities than equations. However, it allows one to obtain a very useful relationship between n_1 and n_2. Really, since (10) and (11) involve n_{110} and n_{111} in one and the same combination, we have

$$n_2 = \frac{1}{\tau_1 \Gamma_2 (1 + r_0)} \left\{ \kappa + n_1 \left[\frac{\kappa}{\kappa_c} - 1 \right] \right\}, \tag{14}$$

$$\kappa = \tau_1/\tau_0, \quad \kappa_c = \frac{\sigma_{10}}{\sigma_{21}/(1 + r_0) - \sigma_{10}}, \tag{15}$$

where the parameter κ of saturation of the first level is introduced. As it follows from (12), with growing intensity of the excitation radiation, κ approaches the value $\kappa_{max} = \sigma_{10}/(\sigma_{01} + r_0\sigma_{21})$. Usually, $\Gamma_{02} \ll \Gamma_2$ in organic chromophores, and, consequently, $r_0 \ll 1$. As a rule, a nonzero value of r_0 is explained by transfer of the energy of two-quantum excitation of a chromophore to a surrounding medium (a solvent). Moreover, if the excitation is carried out beyond the chromophore fluorescence band, than the cross-section of the stimulated emission is small, i.e., $\sigma_{01} \ll \sigma_{10}$. Therefore, κ_{max} may exceed unity significantly. Further all steady-state populations will be considered as functions of κ, while a dependence on the excitation radiation intensity I can be obtained with the aid of (12) and (15); when $I \ll \Gamma_1/(\sigma_{01} + r_0\sigma_{21})$, we have $\kappa = \sigma_{10}I/\Gamma_1 \ll \kappa_{max}$.

It follows from (14) that the population n_2 of the higher excited state S_2 may lower as well as grow with increasing rates of the cooperative processes. Since it is clear from the general considerations that the quantity n_1 always decreases as a rate of the cooperative processes grows, the behavior of n_2 depends on the κ/κ_c ratio. When $\kappa > \kappa_c$, the cooperative processes always lead to a decrease in a population of the S_2 level; if $\kappa_c > 0$, then there exists a range $0 < \kappa < \kappa_c$ in which the cooperative processes bring about an additional population of S_2. For $\kappa_c > 0$ all plots of the function $n_2(\kappa)$, which are obtained for different rates of the cooperative processes, intersect at the point $\kappa = \kappa_c$.

The result obtained above is explained by the fact that for a sufficiently high intensity of excitation radiation and, consequently, a value of κ the radiative channel of populating the S_2 state is more efficient than the cooperative one. Really, in the case of the cooperative population of S_2, a monomer which is an energy donor moves to the S_0 state and is thereby removed from all channels of populating S_2; to excite it back to the first level an additional time is needed. A similar result was obtained for a bichromophore in [9]. Note, that formula (14) is valid not only for a chain but for any regular structure with interaction of the nearest neighbors as well.

Relationship (14) allows one to simplify the problem and consider further a chain of two-level systems. Then, with the cooperative excitation, as equations (10), (11) imply, the energy donor moves to the S_0 state, while the accepter remains with a probability r_1 on the level S_1 and moves to S_0 with a probability r_0. Therefore, it suffices to find a population n_1 of the first level in the two-level model and then to express n_2 in terms of n_2 and κ according to (14). In the approximation under consideration the quantity n_2 is small in terms of the parameter $1/\tau_1\Gamma_2$.

Thermodynamic analogies. A closed system of balance equations for a chain, which consists of N two-level monomers, should involve 2^N variables $n_{i_1 \dots i_N}$ ($i_k = 0, 1$) and the same number of equations. Solution of such a system seems to be an impracticable task. Instead of this we will use an analogy with the one-dimensional Ising model.

The difficulty in drawing this analogy consists in the fact that the radiation and chromophore system under consideration is not at thermodynamic equilibrium, and, consequently, the introduction of temperature is not legitimate. In other words, in the general case we cannot find such a constant T which would yield a correct distribution for all possible values of the energy ε in the expression for a distribution function $f \sim \exp(-\varepsilon/T)$. In this case ε may be considered as a function of a set of indices $(i_1, \dots, i_N)$. However, the stationary character of the problem allows one to choose the function $\varepsilon(i_1, \dots, i_N)$, which will no longer have a meaning of energy, so that the kinetic coefficients found from the distribution function correspond exactly to the kinetic coefficients in balance equations of the (10), (11) type. Then $\exp(-\varepsilon/T)$ will be a correct function of chain distribution in the configurations $(i_1, \dots, i_N)$, and with its aid, one will be able to calculate the populations.

Each monomer may be in one of two states: S_0 or S_1, and the probability of a transition from one state to the other depends, as well as in the Ising model, on an external parameter (an intensity of excitation radiation), an initial state of the monomer, and a state of the nearest neighbors. Therefore, we will seek ε in the form $\varepsilon = N_1 E + N_{11}\Delta$, where N_1 is the number of monomers in the S_1 state; N_{11} is the number of pairs of the nearest neighbors in the S_1 state; E and Δ are some coefficients ("thermodynamic variables").

Below we will find the relation between optical and thermodynamic variables, using a monomer, a dimer, and a trimer as examples (the relation between the thermodynamic variables and the probabilities of transitions

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between possible states of a system in the Ising model is described, for instance, in [14]). Here by the optical variables are meant the quantities $\tau_0, \tau_1, \beta_{110}$, and β_{111}; the steady-state populations depend only on three dimensionless combinations of these quantities: $\kappa = \tau_1/\tau_0, \ \tau_1\beta_{110}, \ \tau_1\beta_{111}$. There are merely two independent dimensionless combinations of the thermodynamic quantities: $E/T, \ \Delta/T$, where T is an effective temperature. Since there are one less independent thermodynamic variables, the quantities β_{110} and β_{111} are not independent (they both are expressed in terms of one and the same thermodynamic variable Δ).

Monomer. At first, let us consider a two-level system (a monomer isolated from other monomers) in a thermostat at temperature T. Let the degrees of degeneracy of the ground and first excited states be g_0 and g_1, respectively. We will reckon the energy from the ground state and assume that the energy of the first excited level is E. Then the canonical statistical sum Z_1 has the form

$$Z_1 = g_0 + g_1 \exp(-E/T). \tag{16}$$

For the average energy $\langle \varepsilon \rangle$ of the two-level system we have

$$\langle \varepsilon \rangle = \frac{1}{T^2} \frac{d\ln(Z_1)}{dT} = E\frac{\kappa_T}{1 + \kappa_T}, \tag{17}$$

$$\kappa_T = \frac{g_1}{g_0} \exp(-E/T). \tag{18}$$

A thermodynamic saturation parameter κ_T is introduced in (17), (18). The population n_1 of the first level is expressed according to

$$n_1 = \langle \varepsilon \rangle/E = \kappa_T/(1 + \kappa_T). \tag{19}$$

Let us now obtain an expression for n_1 in terms of optical variables. The balance equations for the chromophore which is not included in a chain have the form

$$dn_1/dt = n_0/\tau_0 - n_1/\tau_1 = 0, \quad n_0 + n_1 = 1, \tag{20}$$

whence it follows:

$$n_1 = \kappa/(1 + \kappa). \tag{21}$$

Since formulas (19) and (21) must lead to the same result, we assume $\kappa = \kappa_T$. Therefore, the first equation which relates the thermodynamic and optical variables is obtained:

$$\kappa = \frac{\tau_1}{\tau_0} = \frac{g_1}{g_0}\exp(-E/T) = \kappa_T. \tag{22}$$

Dimer and trimer. We now turn to a relationship for the rate constant β_{110}. With this aim in view, we will consider a dimer (a bichromophore). The latter may be in one of the four states: $(S_0^1 S_0^2), (S_1^1 S_0^2), (S_0^1 S_1^2)$ or $(S_1^1 S_1^2)$. Suppose that the latter state has an additional energy Δ. Whence we find the statistical sum Z_2:

$$Z_2 = g_0^2 + 2g_0 g_1 \exp(-E/T) + g_1^2 \exp(-(E + \Delta)/T), \tag{23}$$

and also the average energy and the population n_1 of the bichromophore:

$$\langle \varepsilon \rangle = 2En_1 + \Delta n_{11} = \frac{1}{T^2}\frac{d\ln(Z_2)}{dT} = \frac{2E\kappa_T + (2E + \Delta)\kappa_T^2/B}{1 + 2\kappa_T + \kappa_T^2/B}, \tag{24}$$

$$n_1 = \frac{\kappa_T(1 + \kappa_T/B)}{1 + 2\kappa_T + \kappa_T^2/B}, \tag{25}$$

$$B = \exp(\Delta/T). \tag{26}$$

The balance equations for the bichromophore populations n_{ij}, which describe its state completely have the form [9]

$$\begin{cases} dn_{00}/dt = -2n_{00}/\tau_0 + 2n_{10}/\tau_1 + r_0\beta_{110}n_{11} = 0, & (27) \\ dn_{10}/dt = -(1/\tau_0 + 1/\tau_1)n_{10} + n_{00}/\tau_0 + n_{11}/\tau_1 + r_1(\beta_{110}/2)n_{11} = 0, & (28) \\ dn_{11}/dt = -2n_{11}/\tau_1 + 2n_{10}/\tau_0 - \beta_{110}n_{11} = 0, & (29) \end{cases}$$

$$n_0 = n_{00} + n_{10}, \quad n_1 = n_{11} + n_{10}, \quad n_0 + n_1 = 1. \tag{30}$$

The solution to system (27)–(30) was obtained in [9]:

$$n_1 = \frac{\kappa(1 + \kappa/(1 + \tau_1\beta_{110}/2))}{1 + 2\kappa + \kappa^2/(1 + \tau_1\beta_{110}/2)}. \tag{31}$$

The equation relating β_{110} with Δ/T follows from the comparison of (25), (26), and (31):

$$1 + \tau_1\beta_{110}/2 = \exp(\Delta/T) = B. \tag{32}$$

It remains to find an expression for β_{111}. This quantity describes cooperative processes of the (5) type which do not occur in a bichromophore. Therefore a trimer, a chain of three chromophores, should be considered. The trimer is a minimal formation in which the processes (5) take place. Omitting the calculations, which are completely analogous to those considered above when deriving formulas (22), (32) but somewhat more cumbersome, we will give only the final result:

$$1 + \tau_1\beta_{111}/2 = \exp(2\Delta/T) = B^2. \tag{33}$$

Thus, formulas (22), (32), and (33) establish the complete relationship between the thermodynamic and optical variables. These relationships do not contradict to the exact solutions for the chains consisting of four and five monomers.

Note, that formulas (22), (32), and (33) are not a trivial substitution of variables because they allow one to express the distribution function $f \sim \exp(-N_1 E/T - N_{11}\Delta/T)$ in terms of the optical variables.

Let us present some results which follow from (22), (32), and (33). At first, we will find the relation between the variable E/T which describes the interaction between chromophores and radiation, and an intensity I of the excitation radiation. Assuming that $g_1/g_0 = \sigma_{10}/(\sigma_{01} + r_0\sigma_{21})$, we will obtain from (22)

$$E/T = \ln\left[1 + \frac{\Gamma_1}{(\sigma_{01} + r_0\sigma_{21})I}\right] \xrightarrow[I \to \infty]{} \frac{\Gamma_1}{(\sigma_{01} + r_0\sigma_{21})I} \tag{34}$$

As it was noted already, the quantities β_{110} and β_{111} are not independent. It follows from relationships (32), (33) that

$$\beta_{110} = \frac{\sqrt{1 + \tau_1\beta_{111}/2} - 1}{\tau_1/2} \xrightarrow[\tau_1\beta_{111} \to 0]{} \frac{\beta_{111}}{2}. \tag{35}$$

Formula (35) imposes a restriction on β_{110} and β_{111}. However, one may demand that these quantities be independent. To do this, one should introduce instead of one thermodynamic variable Δ two variables: Δ_1 and Δ_2 which characterize the monomer interaction with one and two neighbors. Here $\Delta_2 \neq 2\Delta_1$; in this case Δ_1 and Δ_2 are governed by arbitrarily defined β_{110} and β_{111}. However, such a statement of the problem leads to considerable complications in calculating the statistical sum (see Appendix) and will not be considered.

Calculation of populations for an infinite chain. Now we will calculate the level populations for an infinite chain, and using relationships (22), (32), and (32), express them in terms of the optical variables. Below we will apply the conventional procedure for calculating a statistical sum, which was first used by Ising [15, 16].

Let us consider an infinite chain as a limit for the chain consisting of N monomers with $N \to \infty$. For the sake of simplicity, we will speak about a sequence of N zeros and unities, with the S_0 state corresponding to zero while S_1 to unity. Let us introduce the following notation. Let N_0 and N_1 be the numbers of zeros and unities in the sequence; N_{10}, N_{01}, N_{11}, the numbers of pairs of the nearest neighbors corresponding to the lower indices; $N_{10}^+ = N_{10} + N_{01}$. Thus, for instance, for the sequence

$$0010100111011,$$

$N = 13, N_0 = 6, N_1 = 7, N_{10} = 3, N_{01} = 4, N_{11} = 3$, and $N_{10}^+ = 7$. The normalization condition has the form $N_0 + N_1 = N$; besides, odd N_{10}^+ (as in the above example) satisfy the relationship $N_1 = N_{11} + (N_{10}^+ + 1)/2$; $N_1 = N_{11} + N_{10}^+/2$ is valid for even N_{10}^+. In the limit $N \to \infty$ one may not distinguish between even and odd N_{10}^+ and use the latter formula, neglecting the addend 1/2. For the energy of a configuration with given $N_1 N_{11}$ and $\varepsilon(N_1, N_{11})$ we have

$$\varepsilon(N_1, N_{11}) = N_1 E + N_{11}\Delta = N_1(E + \Delta) - N_{10}^+\Delta/2. \tag{36}$$

Let us write the statistical sum Z_N in the following way:

$$Z_N = \sum_{N_1=0}^{N} \sum_{N_{10}^+} g_0^{N-N_1} g_1^{N_1} \nu(N, N_1, N_{10}^+) \exp\left[-(N_1(E + \Delta) - N_{10}^+\Delta/2)/T\right], \tag{37}$$

where ν is the number of configurations with given N_1 and N_{10}^+.

For the sake of definiteness, let N_{10}^+ be an odd number. It is easy to verify that in this case the whole chain is divided into $L = (N_{10}^+ + 1)/2$ groups of zeros and the same number of groups of unities, each containing at least one zero or unity. In particular, the sequence, given above as an example, is divided into groups in the following way:

$$00 \mid 1 \mid 0 \mid 1 \mid 00 \mid 111 \mid 0 \mid 11.$$

It can be seen that altogether there are $N_{10}^+ + 1 = 8$ groups, including $L = 4$ groups of zeros and L groups of unities. For large N, as it was already noted above, one may not distinguish even and odd N_{10}^+ and assume that $L = N_{10}^+/2$.

Therefore, the problem of calculating the function $\nu(N, N_1, N_{10}^+)$ is reduced to a combinatorial problem of distributing $N - N_1$ zeros in L groups and N_1 unities also in L groups. One important point to remember is that each group should contain at least one zero (or unity). In fact, $N - N_1 - L$ unities should be placed in L groups (including 0 unities in a group), and zeros in a similar way. It is self-evident that to find ν, one should multiply the numbers of arrangements of zeros and unities. Finally we have:

$$\nu(N, N_1, N_{10}^+) = 2 \frac{N_1! (N - N_1)!}{[(N_{10}^+/2)!]^2 (N - N_{10}^+)! (N - N_1 - N_{10}^+)!}. \tag{38}$$

The factor 2 emerges because of the symmetry of the chain with respect to the "start-for-end" substitution (cf. formula (6)).

To calculate the average (equilibrium) energy $\langle \varepsilon \rangle$ of the chain, one should compute $\ln Z_N$. Introducing the notation $Q = g^{N-N_1} g^{N_1} \nu \exp(-\varepsilon/T)$, we write

$$\ln Z_N = \ln \Sigma Q(N, N_1, N_{10}^+) \approx \ln Q_{max}(N, N_1, N_{10}^+),$$

$$\tag{39}$$

$$Q_{max}(N, N_1, N_{10}^+) = Q(N, \overline{N}_1, \overline{N}_{10}^+),$$

where $\overline{N}_1, \overline{N}_{10}^+$ are the values of N_1, N_{10}^+ with which the maximum value of Q is reached. Finally, we find $\langle \varepsilon \rangle$:

$$\langle \varepsilon \rangle = T^{-2} d \ln(Q_{max})/dT = \overline{N}_1(E + \Delta) - \overline{N}_{10}^+ \Delta/2, \tag{40}$$

whence (comparing with (36)),

$$n_1 = \overline{N}_1/N, \quad n_{10}^+ = n_{10} + n_{01} = 2n_{10} = \overline{N}_{10}^+/N. \tag{41}$$

It remains to find $\overline{N}_1, \overline{N}_{10}^+$ which are defined by the condition $Q(N, \overline{N}_1, \overline{N}_{10}^+) = $ max. To do this, we set the derivatives $\partial \ln Q/\partial N_1$ and $\partial \ln Q/\partial N_{10}^+$ equal to zero. In calculating $\ln \nu$, we will use the Stirling formula and drop all the terms which are less than $N \ln N$ in the order of magnitude. Finally, we obtain the following system (let us write it immediately in terms of the variables $n_1, n_{10} = n_{10}^+/2$):

$$\begin{cases} \dfrac{n_1(1 - n_1 - n_{10})}{(1 - n_1)(n_1 - n_{10})} = \dfrac{\kappa}{B}, & \tag{42} \\[3mm] \dfrac{(n_1 - n_{10})(1 - n_1 - n_{10})}{n_{10}^2} = \dfrac{1}{B}. & \tag{43} \end{cases}$$

Relationship (22) $\kappa = \kappa_T$ was used in (42). The relation between B and the rates β_{110} and β_{111} is given by (32) and (33).

The solution to system (42), (43) for n_1 has the form

$$n_1 = \frac{1}{2}\left\{1 + \frac{\kappa/B - 1}{\sqrt{4\kappa + (\kappa/B - 1)^2}}\right\}. \tag{44}$$

The population n_2 of the higher singlet level is related with n_1 by (14). Let us also write the solution for the reduced correlator $K = (n_{11} - n_1^2)/n_1^2$:

$$K = -\frac{B}{B - 1}\left\{\frac{[\sqrt{4\kappa + (\kappa/B - 1)^2} - \kappa/B]^2 - 1}{4\kappa}\right\}^2. \tag{45}$$

Let us discuss the obtained results (44), (45). In the case of the absence of the cooperative processes ($B = 1$), (44) is transformed into (21). An increase in the rate of the cooperative processes always leads to a decrease in the population of the S_1 level (n_1 decreases). As it is seen from the comparison with the results [9] for a bichromophore (formulas (25), (31)), the cooperative processes play a more significant role in the chain especially at high saturation. The population n_1 lowers in passing from the dimer to the chain. As for the population n_2, according to (14) its value decreases in passing from the dimer to the chain if $\kappa > \kappa_c$, and it increases if $\kappa < \kappa_c$. Below, some asymptotics for n_1, n_2, and K are presented for the chain and the bichromophore; the results for the chain are marked with the upper index ch while for the bichromophore – with bic.

a) $\kappa \ll 0$:

$$n_1^{ch} \approx \kappa\,[\,1 - \kappa\,(3 - 2/B)\,], \quad n_1^{bie} \approx \kappa\,[\,1 - \kappa\,(\,2 - 1/B)\,],$$

$$n_2^{ch} \approx \frac{\kappa^2(1/\kappa_c + 3 - 2/B)}{\Gamma_2(1 + r_0)}, \quad n_2^{bie} \approx \frac{\kappa^2(1/\kappa_c + 2 - 1/B)}{\Gamma_2(1 + r_0)},$$

$$K^{ch} \approx K^{bie} \approx -B/(B - 1);$$

b) $\kappa \gg 1$:

$$n_1^{ch} \approx 1 - B^2/\kappa, \quad n_1^{bie} \approx 1 - B/\kappa,$$

$$n_2^{ch} \approx \frac{\kappa\,[\,1 + 1/\kappa_c - (1 + B^2/\kappa_c)/\kappa\,]}{\Gamma_2(1 + r)}, \quad n_2^{bie} \approx \frac{\kappa\,[\,1 + 1/\kappa_c - (1 + B/\kappa_c)/\kappa\,]}{\Gamma_2(1 + r)},$$

$$K^{ch} \approx -B^3(B - 1)/\kappa^2, \quad K^{bie} \approx -B(B - 1)/\kappa^2;$$

c) $B \gg 1$:

$$n_1^{ch} \approx (1 - 1/\sqrt{1 + 4\kappa})/2, \quad n_1^{bie} \approx \kappa/(1 + 2\kappa),$$

$$K^{ch} \approx -1 + \sqrt{1 + 4\kappa}/B,$$

$$K^{bie} \approx -1 + (1 + 2\kappa)/B.$$

The plots of the function $n_1(\kappa)$ for the chain and the dimer are presented in the figure.

Numerical simulation. The result (44) was verified by numerical simulation. A chain of 100 two-level monomers with periodical boundary conditions was used. Probabilities of the transitions were calculated according to schemes (1), (3), (4), and (5). All times (τ_0, τ_1) were measured in units of a certain discrete step which was selected so that the probability of the transition of each particular monomer from one state to another is sufficiently low at a given step. The value of n_1 was calculated by the monomer and time averaging over the intervals which were much longer than all characteristic times of the system, i.e., under statistical equilibration.
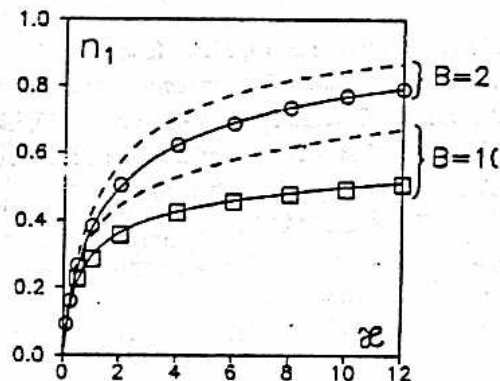
Population n_1 of the first excited state as a function of saturation parameter κ for different rates of cooperative processes: the solid line is the result of calculations by formula (44) for the infinite chain; the dashed – by formula (25) for the dimer; the circles are the results of numerical calculations for the infinite chain.

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Numerical and theoretical results for the function $n_1(\kappa)$ are shown in the figure. As it is seen from the figure, the agreement is very good. The small fixed deviation for $B = 10$ is attributed to the finiteness of the chain. The good agreement between the numerical and analytical results is an indirect confirmation of the legitimacy of the use of the distribution function $f \sim \exp(-N_1 E/T - N_{11}\Delta/T)$ with the parameters E/T and Δ/T defined by (22), (32), and (33).

APPENDIX

If we seek for ε in the form $\varepsilon = N_1 E + N_{110}\Delta_1 + N_{111}\Delta_2$, then the quantities β_{110} and β_{111} will be independent. In this case the relation between the variables has the form

$$1 + \beta_{110}/2 = \exp(\Delta_1/T) = B_1, \quad 1 + \beta_{111}/2 = \exp(\Delta_2/T) = B_2$$

and the following system of three equations is obtained instead of (42) and (43):

$$\frac{(n_1 - n_{10})(1 - n_1 - n_{10})}{(1 - n_1)(n_1 - n_{10} - n_{110})} = \frac{B_2}{\kappa}, \quad \frac{(1 - n_1 - n_{10})(n_1 - n_{10} - n_{110})}{(n_1 - n_{10})(n_{10} - n_{110})} = B_2,$$

$$\frac{(n_{10} - n_{110})(n_1 - n_{10} - n_{110})}{n_{110}^2} = \frac{B_1^2}{B_2}.$$

Although the solution of this system is not a difficult mathematical problem, it is very cumbersome and, besides, the rate of the cooperative processes is governed in it by two independent variables rather than one as it is in the solution (44).

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