Kinetics of two-photon excitation of impurity centers in a condensed medium

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Two-photon stepwise excitation of an energy donor in a condensed medium of acceptors is considered. The acceptors are in quasiresonance with the second (but not the first) excited electron singlet state of the donor. It is shown that quasiresonant excitation proceeding through two real donor levels is the leading process. The kinetic equations are obtained in the balance approximation. They include terms representing relaxation, nonlinear donor photodegradation, migration of excitation over acceptors and its return to the donor, and attenuation of the incident radiation by donor absorption. A self-consistent solution of these equations is found for the evolution in space and time of the donor and acceptor populations, and the intensity of the exciting radiation. The main parameter of the theory that permits an analytic solution is the long lifetime of the first singlet state of the donor as compared with the other relaxation time constants of the system. This long lifetime is characteristic of organic-dye impurities in condensed media. Some applications of the theory, including sensitized selective photomodification of macromolecules, are examined.

1. INTRODUCTION

Energy transport phenomena in a system of donors and acceptors of excitation have been examined in detail, for example, in the monograph by Agranovich and Galanin[1] and in the review by Burshteĭn.[2] The usual approach is to consider the evolution in time of the initial state in which the entire excitation is localized on donors. This state can be "prepared" by a short (δ-function of time) pulse of radiation that is absorbed by the donors alone.[1,2] For problems that are linear in the radiation intensity, the convolution of the response to the δ-pulse and the excitation intensity $I(t)$ as a function of time gives the solution for arbitrary $I(t)$ (see Ref. 2). This was noted by Galanin in relation to the description of phosphorescence kinetics.[3]

In this paper, we shall consider quasiresonant two-photon excitation of donors in a medium of acceptors by an incident light pulse of arbitrary shape. The attenuation of incident radiation by donor absorption will not be assumed to be small and will be taken into account. The problem is nonlinear, so that the excitation kinetics at a particular point has a nontrivial dependence on the radiation intensity at preceding instants of time, and the intensity itself depends on the state of the donor subsystem at preceding (along the direction of propagation of the exciting radiation) points in space. It follows that what is required is a self-consistent determination of the state of the system and of the intensity of light both in space and time.

Figure 1 shows the level diagram for a donor-acceptor pair and the processes that occur under excitation. Each of the singlet electron levels consists of a quasicontinuum of vibrational sublevels. The exciting radiation is quasiresonant with both $S_0 \to S_1$ and $S_1 \to S_2$ transitions in the donor, but is not absorbed directly by the acceptor (in the one-photon process). The second excited singlet of the donor S_2 is in quasiresonance with the acceptor level S_1^M (quantities referring to acceptors will be indicated by the index M for medium). Two-photon step-wise excitation of the state S_2 occurs with appreciable probability when the exciting intensity is high enough. Coupled ("simultaneous") nonradiative transitions in the donor ($S_2 \to S_0$) and acceptor ($S_0^M \to S_1^M$) are then possible and lead to the transfer of the two-photon excitation energy from the donor to the acceptor. We note that, in the dipole-dipole (Foerster) process, the $S_2 \to S_0$ transition is the radiationless analog of two-photon excited fluorescence. To conserve parity, this process requires the participation of nonfully symmetric vibrational sublevels, which reduces its probability to some extent as compared with the fully allowed transition.[4]

We shall suppose that the density of donors is low enough to enable us to neglect energy transport over them. However, energy migration over the acceptors is important and will be taken into account because it facilitates the outflow of excitation from the donor and thus prevents its return to the donor and its consequent total loss. This results in

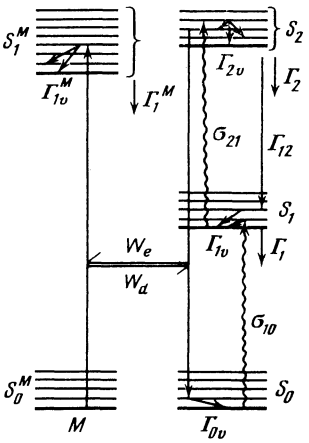

FIG. 1. Donor (right) and acceptor (left, labeled M) level schemes. See text for notation.

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an increase in the number of events in which excitation remains in the acceptor subsystem.

Let us examine some interesting systems that can be described by the above model. The donor can be a molecule of an organic dye. There are, in fact, many dyes in which absorption bands due to the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transitions are found to overlap strongly (see, for example, Refs. 5 and 6). This means that such transitions can be excited by quasimonochromatic light. However, this is not fundamental and is introduced here only for simplicity. Actually, quasiresonant stepwise excitation of a donor can always be accomplished with bichromatic radiation (see Refs. 5 and 6).

We may suppose that the acceptor medium is a molecular crystal or a solution. The constituent molecules must not absorb the incident radiation, but should exhibit quasiresonant absorption at twice the frequency (minus the Stokes shift at S_1), which should lie in the range 250–160 nm in the UV/VUV (when the incident radiation lies in the visible or near UV). There is an enormous number of moleucles that satisfy this condition. Naphthalene in benzene, anthracene (or its heterocyclic analogs, such as rhodamine and acridine) in naphthalene, and others are examples of possible donor-acceptor pairs.

The energy of the two-photon excitation of a donor (5–7 eV) is sufficient to break chemical bonds in both donor and acceptor molecules, which may lead to their nonlinear photochemical degradation. This effect will be taken into account for donors because it is precisely this process that restricts the maximum number of acceptor excitation events whilst the exciting pulse is present. Because of the large number of acceptors, their degradation is of little significance for the kinetics of the process, and will not be taken into account. However, the photo modification of acceptors may itself be of applied interest.

The method of two-photon affinity modification (TAM) proposed in Ref. 7 for the selective (at a given point in primary structure) photomodification of macromolecules is based on precisely this process. The acceptors are then chromophoric groups of a macromolecule that are nonlinearly excited by a donor in the form of a dye molecule bonded ("addressed") to a given segment of the macromolecule. We note that there are various ways of addressing the dye molecules to a segment of the macromolecules that are of applied interest. Some of them were discussed by the present author in Ref. 7 and by Rautian and the present author in Ref. 8.

We note that, in approaches that were known prior to the publication of Ref. 7, the selective optical excitation of large polymeric molecules (macromolecules) encountered the fundamental difficulty that monomeric residues of a particular type with practically identical optical properties are repeatedly encountered in different segments of the macromolecule. It follows that, even when it is possible to excite only the residues of a particular type, the excitation will still be distributed over the entire macromolecule. In the TAM method, this problem is solved by exploiting the fact that, in the one-photon process, the macromolecule does not absorb the incident radiation and the probability of direct (without donor participation) two-photon absorption as well as other secondary processes is small in comparison with the useful quasiresonant process (see Refs. 7 and 8 and Sec. 2). The energy is transferred to the macromolecule in the small neighborhood of the donor. For example, according to the estimate given in Ref. 7, the Foerster radius of DNA is $R_F = 3\text{–}5$ Å, and the radius is smaller still when transport is accomplished by the resonant-exchange mechanism.[9] In the case of DNA, estimates[8] show that diffusion over the macromolecular chain does not delocalize the excitation to any great extent.

The physical foundations of the TAM method were confirmed by experiments with unaddressed[10] and addressed[11] dyes. Cleavages were found in the molecular chains of nuclei acids, induced by two-photon excitation of complexes of these molecules with different dyes. It became clear that TAM was of considerable applied interest. The theory presented below is directly applicable to the description of this method.

2. CHOICE OF MODEL AND BASIC EQUATIONS

The essential assumption in this thoery is that the lifetime of the ground vibrational sublevel in the first excited electronic state S_1 (but not in the higher S_2) is long in comparison with the lifetimes of the other sublevels that are typical for dyes (see, for example, Ref. 12):

$$\Gamma_1 \ll \Gamma_{0v},\ \Gamma_{1v},\ \Gamma_{2v},\ \Gamma_2,\ \Gamma_{1v}^M, \tag{1}$$

where Γ_i is the rate of depopulation of the electronic state S_i, Γ_{iv} is the rate of relaxation over vibrational sublevels of the state S_i, and the superscript M labels acceptor levels as before (see Fig. 1).

Since the ratio Γ_1/Γ_2 is small, the exciting intensity I can be chosen to lie in the range

$$\Gamma_1/\sigma_{10} \lesssim I \ll \Gamma_2/\sigma_{21}, \tag{2}$$

where σ_{ij} is the $S_j \rightarrow S_i$ absorption cross section. Inequality (2) indicates that the level S_1 can be saturated for a low population of S_2. Transitions from S_2 to higher-lying singlets can, of course, be neglected under these conditions. By virtue of (1) and (2), the $S_1 \rightarrow S_2$ transition occurs from the state S_1 thermalized over the vibrational sublevels, i.e., practically from the ground vibrational sublevel S_1. Transitions to the triplet state can also be ignored when the light pulses are short enough. Finally, assuming that

$$\Gamma_1 \ll \Gamma_1^M, \tag{1a}$$

we can also neglect transitions to higher-lying singlet states of the acceptors. Henceforth, we shall assume that (1), (2), and (1a) are satisfied, and this will enable us to confine our attention to five levels and the transition scheme shown in Fig. 1.

We shall suppose that the donor and acceptor polarizations relax instantaneously on the scale of the above lifetimes. This is assured by the strong adiabatic broadening of the levels of large molecules, and the broad spectrum of the exciting radiation. As a result, we are able to use the balance equations for the populations.

Let us illustrate the above relationships between the various relaxation lifetimes by considering the following examples. For coumarin dyes (such as were used in a number of experiments[10] with DNA), $\sigma_{10} = 3 \times 10^{-17}$ cm^2,

$\sigma_{21} = 5.5\times 10^{-17}$ cm^2 ($\lambda = 337$ nm); $\Gamma_1 = 3.2\times 10^8$ s^{-1} (Ref. 5), $\Gamma_{0v} = 8\times 10^{11}$ s^{-1} ($T = 295$ K) (Ref. 13); for phthalocyanine dyes $\Gamma_1 \simeq 10^8$ s^{-1}, $\Gamma_{1v} \sim \Gamma_{0v} \simeq 2\times 10^{11}$ s^{-1} (Ref. 14); for rhodamine 6G, $\Gamma_1 = 1.1\times 10^8$ s^{-1} (Ref. 5), $\Gamma_{1v} = 1.7\times 10^{11}$ s^{-1} (Refs. 15 and 16); and for rhodamine B, $\Gamma_1 = 2.7\times 10^8$ s^{-1} (Ref. 5), $\Gamma_{1v} > 5\times 10^{11}$ s^{-1} (Ref. 16). The polarization relaxation rate $\Gamma_\perp$ for the electronically excited states of organic molecules is so high that it has been measured in only very few cases. For example, for azulene, the rate constant for the $S_0 \rightarrow S_1$ transition is $\Gamma_\perp = 3\times 10^{12}$ s^{-1} at $T = 30$ K and increases rapidly with increasing temperature.[17] The presence of well-defined hot fluoresence from nonthermalized vibrational sublevels at excitation energies of 5–6 eV shows that $\Gamma_2 \gtrsim \Gamma_{2v}$. It may be expected on the basis of the data reported in Ref. 6 that the magnitude of Γ_1^M for acceptors at high excitation energies (5–7 eV) will lie in the range 10^{11}–10^{12} s^{-1}.

Generalizing the above and other experimental data (see, in particular, Ref. 12 and the references cited therein), we may conclude that typical values of the above parameters are

$$\begin{gathered}\sigma_{10},\ \sigma_{21} \sim 10^{-16}-10^{-17}\ \text{cm}^2,\quad \Gamma_1 \sim 10^8-10^9\ \text{s}^{-1},\\ \Gamma_2,\ \Gamma_{0v},\ \Gamma_{1v},\ \Gamma_{2v},\ \Gamma_1{}^M \sim 10^{11}-10^{12}\ \text{s}^{-1},\quad \Gamma_\perp \geqslant 10^{13}\ \text{s}^{-1}.\end{gathered} \tag{3}$$

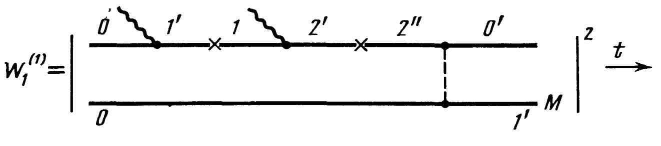
These values show that the inequalities adopted above were realistic. In particular, (2) can now be rewritten in the numerical form (in units of power)

$$10\ \text{MW/cm}^2 \leqslant I \ll 10\ \text{GW/cm}^2. \tag{2a}$$

Such intensities are readily attainable if we use pulsed nano- and picosecond lasers.

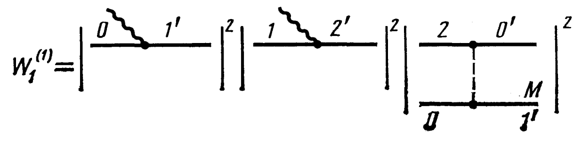
In addition to the "useful" process shown in Fig. 1, other two-photon transitions proceeding through virtual levels of the acceptor are possible in this level scheme. In particular, direct two-photon excitation of the acceptor without the dissipation of the donor is obviously a parasitic effect (which disturbs selectivity). We must now estimate the probability per unit time W_1 of the primary excitation of the acceptor for different processes, assuming optically nonsaturating excitation and using the usual perturbation theory for the S-matrix.

In the useful process



(4)

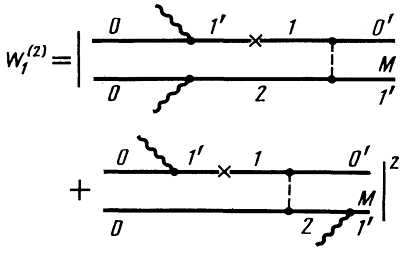
where the upper line corresponds to the donor and the lower (with index M) to the acceptor, we show the number of each state, the primes designate the vibrationally excited states over which summation is implied, the wavy lines represent the external field due to the exciting radiation (assumed to be quasistationary in approximate estimates), the broken line represents the matrix element of the interaction responsible for the excitation transfer (dipole-dipole, to be specific), and a cross represents the amplitude for relaxation over vibrational sublevels. Since this relaxation leads to the loss of phase memory, the probability (4) splits into a product of probabilities:



$$= \frac{\sigma_{10}I}{\Gamma_1}\,\frac{\sigma_{21}I}{\Gamma_2}\,v_e, \tag{5}$$

where v_e is the probability of energy transfer from the donor state S_2. In introducing the second factor in (5), we assumed that the amplitude for excitation transfer was independent of the particular vibrational sublevel, which is not fundamental but produces a substantial simplification in calculations and will be used henceforth. In the process described by (5), the energy received by the acceptor is $E_{a0} = E_1 + \hbar\omega$, where ω is the frequency of the exciting radiation and E_1 is the energy of the thermalized level S_1 (in practice, the ground vibrational sublevel).

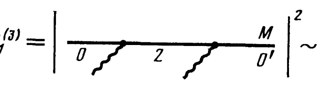
There is another possible process of two-photon excitation of the acceptor through its virtual state in which the role of one of the two photons is played by excitation transferred radiationlessly from the donor level S_1 while the donor level S_2 takes no part in this process at all [cf. the transition from (4) to (5)]:



$$\sim \frac{\sigma_{10}I}{\Gamma_1}\,\frac{|d_{20}{}^M|^2 I}{\hbar c}\,\frac{\omega}{(\Delta\omega)^2}\,v_e, \tag{6}$$

where the nonresonant inner line 2 corresponds to the virtual intermediate state S_2^M of the acceptor, d_{20}^M is the matrix element of the dipole transition to this state, and $\Delta\omega$ is the detuning of ω from the acceptor state S_2^M. The process represented by (6) is not, strictly speaking, parasitic (it does not lead to the delocalization of excitation over the acceptor medium), since $W_1^{(2)}$ in (6) and $W_1^{(1)}$ in (5) have the same dependence on the distance r between the donor and acceptor, which determines the transfer probability v_e [$v_e(r) \propto r^{-6}$, according to Foerster]. The energies transferred in (5) and (6) are equal. However,the probability of process (6) is very small in comparison with (5); see below.

For the direct two-photon excitation of the acceptor without the participation of the donor (such processes have been examined in detail in the literature; see the review,[4] which is parasitic in this problem, we have



$$\sim \left|\frac{d_{12}{}^M d_{20}{}^M I}{\hbar c}\right|^2 \left(\frac{\omega}{\Delta\omega}\right)^2 \frac{1}{\gamma^M} \tag{7}$$

where γ^M is the spectral width of the $S_0^M \rightarrow S_1^M$ transition.

Let us compare the probabilities (5)–(7). Assuming that all the corresponding optical dipole matrix elements d are of the same order of magnitude, and that the spectral width γ of the different transitions is also of the same order, and recalling that $\sigma \sim |d|^2\omega/(\hbar c\gamma)$, we find that

$$\frac{W_1^{(1)}}{W_1^{(2)}} \sim \frac{(\Delta\omega)^2}{\Gamma_2\gamma} \gtrsim 10^4, \quad \frac{W_1^{(1)}}{W_1^{(3)}} \sim \frac{v_e(\Delta\omega)^2}{\Gamma_1\Gamma_2\gamma} \gtrsim 10^6. \tag{8}$$

The numerical estimates in (8) were obtained for the following realistic parameter values: $\omega \sim 10^{16}$ s^{-1} (near-UV), $\Delta\omega/\omega \approx 0.5$, $\Gamma_2 \lesssim 10^{12}$ s^{-1}, $\Gamma_1 \lesssim 10^{10}$ s^{-1}, and $\gamma/\omega \sim 0.1$; $v_e \sim |d|^2/\hbar^4\gamma r^6$ was estimated in Ref. 7 as being $v_e \sim \Gamma_2 \sim 10^{12}$ s^{-1} for $r \sim 5$ Å. We note that processes of the form of (4) and (6) but without relaxation of the populations of the vibrational sublevels of S_1 have the small factor $\Gamma_1/\Gamma_{1v} \sim 10^{-3}$ in the probability W_1, whereas those proceeding without relaxation of polarization via the $S_0 \rightarrow S_1$ transition contain the factor $\Gamma_1/\Gamma_\perp \ll 10^{-3}$ as compared with the corresponding processes$^{1)}$ (4) and (6).

Thus, process (4) [or (5), which amounts to the same thing][7] that proceeds through the two levels S_1 and S_2 of the donor is the dominant process and we shall confine our attention to it.

Let n_i be the population of the i-th electron level of the donor, where $n = n_0 + n_1 + n_2$. It follows from (2) that

$$n_2 \ll n, \tag{9}$$

so that the kinetic equations for the populations can be written in the form

$$\partial n_1/\partial t = -\Gamma_1 n_1 + \Gamma_{12} n_2 - (\sigma_{10} + \sigma_{01} + \sigma_{21}) I n_1 + \sigma_{10} I n; \tag{10}$$

$$\partial n_2/\partial t = -\Gamma_2 n_2 + \sigma_{21} I n_1 - F, \quad F \equiv \int f(\mathbf{r})\, d\mathbf{r}; \tag{11}$$

$$\partial n/\partial t = -W_1^* n_1 - W_2^* n_2, \tag{12}$$

where t is the time, W_i^* is the donor photodegradation rate for the level S_i, σ_{01} is the stimulated emission cross section for the level S_1 at frequency ω, Γ_{12} is the $S_2 \rightarrow S_1$ spontaneous transmission rate, F is the excitation exchange integral for the acceptor medium, and $\mathbf{r}$ is the acceptor position vector measured from the donor.

The rate of exchange of excitation between the donor and the medium is

$$f(\mathbf{r}) = n_2 w_e(\mathbf{r}) - n_1^M(\mathbf{r}) w_d(\mathbf{r}), \tag{13}$$

where $n_1^M(\mathbf{r})$ is the population of the acceptor level S_1^M at the point $\mathbf{r}$, $w_e(\mathbf{r})$ is the probability density for the transfer of excitation from the donor to this particular acceptor, and $w_d(\mathbf{r})$ is the probability density for the reverse process. When the energy-transfer rate is independent of the vibrational sublevels participating in the process (which is assumed), we have $w_e(\mathbf{r})/w_d(\mathbf{r}) = \text{const}$. The value of this constant depends on the ratio of Γ_{2v} and v_e. When $\Gamma_{2v} \ll v_e$, exchange will, clearly, occur between excited vibrational sublevels that are in resonance with one another ($S_{2'}$ and $S_{1'}^M$, as shown in Fig. 1) and

$$w_d(\mathbf{r}) = w_e(\mathbf{r}). \tag{14}$$

In the other limiting case, the first stage is thermalization over the vibrational sublevels of S_2 *and* S_1^M, followed by excitation transfer, and

$$w_d(\mathbf{r}) = \exp(-\Delta E/T) w_e(\mathbf{r}), \tag{15}$$

where T is the temperature and ΔE is the effective (averaged over vibrational sublevels) difference between the energies of the conjugate $S_{2'} \rightarrow S_{0'}$ and $S_{0'}^M \rightarrow S_{1'}^M$ transitions. We note that the linearity of (13) in the population numbers ensures that the latter are small in accordance with (1), (2), (1a), and (9). The specific form of $w_e(\mathbf{r})$ for different types of interaction is well known.[2,9] For example, for the Foerster (dipole-dipole) transfer

$$w_e(\mathbf{r}) = \rho(\mathbf{r}) \Gamma_2 (R_F/r)^6,$$

where $\rho(\mathbf{r})$ is the acceptor density at the point $\mathbf{r}$.

The general form of the continuity equation for the excitation of the acceptor medium is

$$[\partial/\partial t + \Gamma_1^M(\mathbf{r}) + \operatorname{div} \mathbf{j}]\, \rho(\mathbf{r})\, n_1^M(\mathbf{r}) = f(\mathbf{r}), \tag{16}$$

where j is the linear (in general, integro-differential) operator for the excitation current and $\Gamma_1^M(\mathbf{r})$ is the rate of relaxation of the acceptor state S_1^M at the point $\mathbf{r}$. The range of validity of the continuous-medium approximation [for which $\rho(\mathbf{r})$ is a continuous function] and of the diffusion approximation for the excitation current

$$\mathbf{j} = -\mathbf{D}\nabla, \tag{17}$$

where $\mathbf{D}$ is the diffusion coefficient, is known in the case of ordered systems. We note that the possibility of the diffusion description of excitation migration in unordered media is highly nontrivial, and has frequently been examined. It was reliably established for (quasi)stationary migration (see the review by Burshteĭn.[19] The solution of (16) will be examined below in relation to this particular case. Hopping migration,[20] which we hope to investigate in the future, is an alternative and more realistic mechanism.

Let us consider acceptor media [and problems for (16)] of different dimensions. In particular, let us examine quasi-one-dimensional chains (for example, linear macromolecules such as DNA and RNA), quasi-two-dimensional systems (for example, thin films, planar macromolecular structures such as the protein β-layer, crystals with a special plane of fast diffusion$^{1)}$), and three-dimensional media. To avoid unimportant complications, we shall consider that the acceptor media are homogeneous (Γ_1^M, D and ρ independent of $\mathbf{r}$) and isotropic (the diffusion coefficient $\mathbf{D}$ will be assumed to be a scalar).

We turn now to the radiation transfer equation. It will be convenient to work in terms of macroscopic coordinates X, Y, Z (not to be confused with the microscopic coordinates $\mathbf{r}$, measured locally from the position of each of the donors). Suppose that the exciting radiation propagates in the direction of the Z axis. We shall neglect reabsorption of the fluorescence, assuming that the Stokes shift of the fluorescence and absorption frequencies due to the $S_1 \rightarrow S_2$ transition is sufficiently large and the cross section of the exciting beam is sufficiently small. We shall also assume that superfluorescence is absent. This is usually assured by the absorption of fluorescence photons in the $S_1 \rightarrow S_2$ transition, or it can be achieved by introducing an impurity that absorbs at the fluorescence frequency. Neglecting retarded effects, we can write the continuity equation for the intensity I of exciting radiation as a function of Z in the form (C is the volume density of donors)

$$\frac{1}{C}\frac{\partial I}{\partial Z}=-(\sigma_{21}-\sigma_{10}-\sigma_{01})In_1-\sigma_{10}In. \tag{18}$$

Equations (10)–(12), (16), and (18) form a closed system for the populations $n(t,Z)$, $n_1(t,Z)$, $n_2(t,Z)$, $n_1^M(\mathbf{r},t,Z)$ and the intensity $I(t,Z)$. The system is nonlinear and does not split into independent subsystems, which means that all these quantities must be determined in a self-consistent manner (cf. the Introduction).

3. ELIMINATION OF RAPIDLY-RELAXING VARIABLES

We shall suppose that the exciting radiation is a pulse whose duration τ_p must be smaller than, or of the order of, the lifetime of the state S_1, so that we can avoid large excitation losses through the relaxation of the donor from this state. By virtue of (1) and (1a), τ_p may, however, be much longer than the S_2 and S_1^M relaxation times:

$$1/\Gamma_2,\ 1/\Gamma_1{}^M\ll\tau_p\lesssim1/\Gamma_1. \tag{19}$$

Assuming that (19) is valid and neglecting the time derivatives in (11) and (16), let us solve them and thus eliminate the variables $n_1^M(\mathbf{r})$ and n_2. We note that the condition of stability of the donor against single-photon degradation, $W_1^*\ll\Gamma_1$, is assumed satisfied and, by virtue of (19), enables us to neglect this degradation and take $W_1^*=0$ in (12).

Under the above conditions, the solution of (16) has the form

$$\rho n_1{}^M(\mathbf{r})=n_2\int G^L(\mathbf{r},\mathbf{r}')w_e(\mathbf{r}')d\mathbf{r}', \tag{20}$$

where G^L is the Green function of the operator

$$L=\mathrm{div}\,\mathbf{j}+\Gamma_1{}^M+v_d(\mathbf{r}),\qquad v_d(\mathbf{r})\equiv w_d(\mathbf{r})/\rho. \tag{21}$$

We now integrate (16) term by term with respect to $\mathbf{r}$. The contribution of the term containing div $\mathbf{j}$ is then found to vanish, so that, using (21), we obtain

$$F=n_2W^t,\qquad W^t=\Gamma_1{}^M\int g^L(\mathbf{r})w_e(\mathbf{r})d\mathbf{r}, \tag{22}$$

where W^t = const has the significance of the renormalized (due to the return of excitation to the donor) probability of transfer of the excitation to the acceptor medium (in the terminology of Ref. 19, W^t is the rate of migrationally-accelerated stationary quenching of S_2) and the function $G^L(\mathbf{r})$ is given by

$$g^L(\mathbf{r})\equiv\int G^L(\mathbf{r},\mathbf{r}')d\mathbf{r}', \tag{23}$$

and satisfies the equation

$$Lg^L(\mathbf{r})=1. \tag{24}$$

In deriving (22)–(24), we used the symmetry property of the Green function of the Hermitian $G^L(\mathbf{r},\mathbf{r}')=G^L(\mathbf{r}',\mathbf{r})$. It is precisely this property that has enabled us to reduce our migration problem, in which the source and sink densities $w_e(\mathbf{r})$ and $e_d(\mathbf{r})$ have the same shape, to Eq. (24) with a constant source density (unity on the right-hand side).

When the current is taken in the form given by (17), Eq. (24) assumes the form

$$[-D\Delta+\Gamma_1{}^M+v_d(\mathbf{r})]g^L(\mathbf{r})=1, \tag{24a}$$

which is well-known from the diffusion theory of the capture of excitons by traps.[21] However, in our problem, we have to deal with the integral of $g^L(\mathbf{r})$ in (22), whereas the zero-order moment of this function was considered in Ref. 21.

Let us now eliminate n_2 from the above equations. It follows from (11) and (22) that

$$n_2=I\sigma_{21}n_1/(\Gamma_2+W^t). \tag{25}$$

Substituting this in (10) and (12), we obtain a set of equations for the populations n and n_1 in the final form:

$$\partial n_1/\partial t=-\Gamma_1n_1+\sigma_{10}In-(\sigma_{10}+\bar\sigma_1)In_1; \tag{26}$$

$$\partial n/\partial t=-\sigma_{21}{}^*In, \tag{27}$$

where

$$\begin{gathered}\bar\sigma_1\equiv\sigma_{01}+\bar\sigma_{21}+\sigma_{21}{}^t,\qquad\bar\sigma_{21}\equiv\sigma_{21}(\Gamma_2-\Gamma_{12})/(\Gamma_2+W^t),\\ \sigma_{21}{}^*\equiv\sigma_{21}W_2{}^*/(\Gamma_2+W^t),\qquad\sigma_{21}{}^t\equiv\sigma_{21}W^t/(\Gamma_2+W^t).\end{gathered} \tag{28}$$

The quantities defined by (28) can be interpreted as the cross sections for absorption (through the $S_1\rightarrow S_2$ transition) accompanied by the following processes: $\bar\sigma_1$—depopulation of the state S_1, $\bar\sigma_{21}$—transition to S_0, σ_{21}^*—photochemical degradation of the donor, and σ_{21}^t—transfer of excitation to the medium (return of excitation to the donor is taken into account and eliminated). We note that Eqs. (26) and (27) have the same form as in the absence of exchange of excitation with the medium. However, the last process renormalizes [according to (22) and (28)] the coefficients of these equations. When degradation is neglected ($n=1$), Eq. (26) has the same form as the previously known equation[5] for the stepwise two-photon excitation of an isolated chromophore.

Let us now examine the main observed quantities (per donor per pulse). The number of events in which excitation is transferred to the medium and is not returned to the donor, $N_1^t=\int Fdt$, can be transformed to the following form with the aid of (22) and (25):

$$N_1{}^t=\sigma_{21}{}^t\int n_1Idt. \tag{29}$$

Since the state S_2 is short-lived, the entire fluorescence of the donor is emitted from the level S_1. The total number of fluorescence photons is

$$N_1{}^f=Q_0{}^f\Gamma_1\int n_1dt, \tag{30}$$

where Q_0^f is the quantum yield of unsaturated fluorescence. Finally, the number of photons absorbed by the donor can be written in the form [see (18)]

$$N_1{}^a=(\sigma_{21}-\sigma_{10}-\sigma_{01})\int In_1dt+\sigma_{10}\int Indt. \tag{31}$$

The quantities given by (29)–(31) are not independent. In fact, integrating (26) term by term and using the condition that $n_1=0$ for $t=-\infty$ and $t=\infty$, we find that the relationship between them is

$$Q^f/Q_0{}^f+Q^t/Q_s{}^t=1,\qquad Q^f\equiv N_1{}^f/N_1{}^a,\qquad Q^t\equiv N_1{}^t/N_1{}^a, \tag{32}$$

where Q^f and Q^t are, respectively, the quantum yield of fluorescence and of excitation of the medium, and the constant

$$Q_s{}^t=\sigma_{21}{}^t/(\sigma_{21}+\bar\sigma_1-\sigma_{01})\equiv W^t/[2(\Gamma_2+W^t)-\Gamma_{12}] \tag{33}$$

has the significance of the limiting (for saturating radiation intensities) excitation quantum yield of the medium. From (32) and (33) we obtain the rigorous inequalities $Q' < Q_s^t < 1/2$, the second of which is obvious *a priori*: at least two absorbed photons are lost in each medium-excitation event. Equation (32) reflects the fact that the transfer of excitation to the medium is accompanied in the donor by the transition $S_2 \rightarrow S_0$ and, consequently, the depopulation of S_1, as well as a proportional reduction in fluorescence.

To conclude this section, let us consider the renormalized probability W^t of excitation transfer, given by (22). When the migration of excitation over the medium is unimportant, we may omit the div **j** term from (22) and use (22) and (24) to show that

$$W^t = \Gamma_1^M \int w_e(\mathbf{r}) [\Gamma_1^M + v_d(\mathbf{r})]^{-1} d\mathbf{r}. \tag{34}$$

When the rate of return of excitation is small $\Gamma_1^M \gg v_d$, we find from (21) and (24) that $g^L(\mathbf{r}) = 1/\Gamma_1^M = \text{const}$, and the renormalized transfer probability is equal to the original probability, as expected:

$$W^t = W_e, \quad W_e \equiv \int w_e(\mathbf{r})\, d\mathbf{r}. \tag{35}$$

When migration and return of excitation ($\Gamma_1^M \lesssim v_d$) are important, we must provide the specific form of the current operator **j**. Henceforth, we shall use the diffusion approximation (17). We shall examine the case of strong exchange ($\Gamma_1^M \ll v_d$) and simultaneous strong diffusion [$(D/\Gamma_1^M)^{1/2} \gg a$, where a is the radius at which excitation exchange occurs; $a \sim R_F$ for the Foerster transfer]. It is then reasonable to assume that the scale of the solution is much greater than the radius a, so that the shape of the functions $w_e(\mathbf{r})$ and $w_d(\mathbf{r})$ is unimportant and can be represented by the δ-function:

$$w_e(\mathbf{r}) = W_e \delta(\mathbf{r}), \quad v_d(\mathbf{r}) = W_d \rho^{-1} \delta(\mathbf{r}), \quad W_d \equiv \int w_d(\mathbf{r})\, d\mathbf{r}. \tag{36}$$

Taking the Fourier transform of (24a), we find from (22) that

$$W^t = W_e \left[1 + W_d \rho^{-1} \int (\Gamma_1^M + \mathbf{k}^2 D)^{-1} (2\pi)^{-N} d\mathbf{k}\right]^{-1}, \tag{37}$$

where N is the dimensionality of the diffusion problem.

For a linear medium, it follows from (37) that

$$W^t = W_e [1 + W_d (2\Gamma_1^M H_1)^{-1/2}]^{-1}, \tag{38}$$

where $H_1 = 2D\rho^2$ is the average hopping frequency (in the case of diffusion transfer) between neighboring acceptors for $N = 1$.

For $N = 2$, the integral in (37) diverges logarithmically as $k \rightarrow \infty$. Since the approximation defined by (36) ceases to be valid for $r \lesssim a$, integration must be cut off at $k \sim 1/a$ and [see (38)]

$$W^t = W_e [1 + {}^1/_4 W_d H_2^{-1} \ln (H_2 / \nu_a \Gamma_1^M)]^{-1}, \tag{39}$$

where $H_2 = \pi D \rho^2$ is the mean hopping frequency in the two-dimensional case and

$$\nu_a = \int\limits_{r \leqslant a} \rho\, d\mathbf{r}$$

is the mean number of acceptors within the exchange radius. It is clear from (39) that, when $N = 2$, the renormalization ratio W^t / W_e is largely determined by the ratio W_d / H_2, and the dependence on the rate of loss of excitation Γ_1^M in the medium is only logarithmic.

In the three-dimensional case, we have an essential divergence in (37). Consequently, the assumption that all the characteristic scales of the diffusion solution are much greater than the exchange radius a for $N = 3$, which was used in justifying (36) (and, strictly speaking, for $N = 2$, as well), is not self-consistent.

To determine W^t in a closed form for all N, let us replace $v_d(\mathbf{r})$ with a rectangle of radius a and equivalent power: $v_d(\mathbf{r}) = v_0 \theta(a - r)$, $v_0 \equiv W_d / \nu_a$. From (22) and (24a), we then have

$$W^t = W_e \Gamma_1^M (\Gamma_1^M + v_0)^{-1} [1 + v_0 (\varkappa_1 \Gamma_1^M)^{-1} \Phi_N], \tag{40}$$

where Φ_N for $N = 1$, 2, and 3 is respectively given by

$$\Phi_1 = \varkappa_2 [\varkappa_1 + \varkappa_2 \operatorname{cth} \varkappa_1]^{-1}; \tag{40a}$$

$$\Phi_2 = 2\varkappa_2 [\varkappa_2 I_0(\varkappa_1)/I_1(\varkappa_1) + \varkappa_1 K_0(\varkappa_2)/K_1(\varkappa_2)]^{-1} \tag{40b}$$

$$\Phi_3 = 3(1 + \varkappa_2)(\varkappa_1 \operatorname{cth} \varkappa_1 - 1)[\varkappa_1 (\varkappa_1 + \varkappa_2 \operatorname{cth} \varkappa_1)]^{-1}, \tag{40c}$$

where

$$\varkappa_1 \equiv a[(\Gamma_1^M + v_0)/D]^{1/2}, \quad \varkappa_2 \equiv a(\Gamma_1^M / D)^{1/2},$$

and $I_m(x)$, $K_m(x)$ are the modified cylinder functions of order m.

We now proceed in (40) to the limit of strong diffusion ($\varkappa_2 \ll 1$) and strong exchange ($v_0 \gg \Gamma_1^M$) at constant total probability W_d of return of excitation, i.e., to the limit in (36). From (40) and (40a) ($N = 1$), we then obtain the exact expression given by (38), which is independent of a. From (40) and (40b) with $N = 2$, we then have

$$W^t = W_e 2 [\varkappa_1 I_0(\varkappa_1)/I_1(\varkappa_1) + \varkappa_1^2 \ln (2/\gamma_E \varkappa_2)]^{-1}$$

($\gamma_E \approx 1.78$ is the Euler-Mascheroni constant), which is asymptotically identical with (39). For $N = 3$, we find from (40) and (40c) that [see (38) and (39)]

$$W^t = (W_e / W_d)\, 4\pi\rho a D,$$

i.e., the normalized probability W^t is independent of Γ_1^M or the primary transfer probability W_e [it depends only on the ratio W_e / W_d which is equal to unity and $e^{\Delta E/T}$ for (14) and (15), respectively], and W^t is determined by $4\pi\rho a D$ which, according to the Smoluchowski formula, is the rate of diffusion-controlled trapping by black spheres of radius a.

4. KINETICS OF EXCITATION BY A SHORT PULSE

Let us now consider the most interesting case $\tau_p \ll \Gamma_1^{-1}$ [see (19)] in which the loss of excitation by relaxation in the donor is, of course, at a minimum. We may then neglect the term $\Gamma_1 n_1$ in (26) and obtain the solution of (26) and (27) subject to the initial conditions $n_1(0) = 0$ and $n(0) = 1$:

$$n_1(J) = \sigma_{10} (\sigma_+ - \sigma_-)^{-1} [\exp(-\sigma_- J) - \exp(-\sigma_+ J)], \tag{41}$$

$$n(J) = (\sigma_+ - \sigma_-)^{-1} [\sigma_+ \exp(-\sigma_- J) - \sigma_- \exp(-\sigma_+ J)], \tag{42}$$

where J is the photon number density in the pulse (integrated "power"):

$$J = \int\limits_{-\infty}^{t} I(t')\, dt'; \tag{43}$$

$$\sigma_\pm \equiv {}^1/_2 (\sigma_{10} + \bar{\sigma}_1) \pm [{}^1/_4 (\sigma_{10} + \bar{\sigma}_1)^2 - \sigma_{21}^* \sigma_{10}]^{1/2}. \tag{44}$$

We note that, for a donor that is stable against two-photon photochemical degradation,

$$\sigma_{21}{}^{*}\ll\sigma_{10},\ \sigma_{21} \tag{45}$$

and as a consequence

$$\sigma_{-}\ll\sigma_{+},\quad \sigma_{+}\approx\sigma_{10}+\bar{\sigma}_{1},\quad \sigma_{-}\approx\sigma_{21}{}^{*}\sigma_{10}/(\sigma_{10}+\bar{\sigma}_{1}). \tag{46}$$

To solve this space problem, we transform in (18) to the variable J and hence obtain

$$\begin{gathered} C^{-1}(\partial J/\partial Z)=-N_1{}^a(J),\\ N_1{}^a(J)=[1-n(J)]\,(\sigma_{21}+\bar{\sigma}_1-\sigma_{01})/\sigma_{21}{}^{*}+n_1(J), \end{gathered} \tag{47}$$

where $n_1(J)$ and $n(J)$ are given by (41) and (42) and $N_1^a(J)$ is given by (31). The variables in (47) are separable, and the required solution $J_z\equiv J(Z)$ can be found from

$$CZ=\int_{J_Z}^{J_0} dJ/N_1{}^a(J),\qquad J_0\equiv J(0). \tag{48}$$

Using (41) and (42), the number of excitation events (29) can be written in the form

$$N_1{}^t=\sigma_{21}{}^t\int_0^J n_1 dJ=[1-n(J)]\sigma_{21}{}^t/\sigma_{21}{}^{*}. \tag{49}$$

From (48) and (49), we find that the number of excitation events and the excitation quantum yield Q^t in the entire volume V are respectively given by:

$$N^t=C\int N_1{}^t dV=S\int_{J_Z}^{J_0} N_1{}^t(J)/N_1{}^a(J)\,dJ, \tag{50}$$

$$Q^t=(J_0-J_Z)^{-1}\int_{J_Z}^{J_0} N_1{}^t(J)/N_1{}^a(J)\,dJ\ , \tag{51}$$

where S is the cross section of the irradiated volume. The case of an optically thick layer corresponds to $J_z=0$ in (50) and (51).

The integrals encountered in (48), (50), and (51) cannot in general be expressed in terms of tabulated functions. We must therefore begin by considering limiting cases, and then numerical results. In the absence of optical saturation ($\sigma_{10}J_0\ll1$), and if we use (32), we obtain

$$J_Z=J_0\exp(-C\sigma_{10}Z), \tag{52}$$

$$Q^t={}^1/_4\sigma_{21}{}^t(J_0+J_Z),\quad Q^f=Q_0{}^f[1-{}^1/_4(\sigma_{21}+\bar{\sigma}_1-\sigma_{01})(J_0+J_Z)]. \tag{53}$$

It is clear that, as the pulse power J_0 increases, the quantum yield Q^t grows in direct proportion to it, whereas Q^f falls linearly.

In the case of saturation ($\sigma_{10}J_Z\gg1$), we find from (47) and (48) that

$$J_Z=\sigma_{-}{}^{-1}\ln\{1+\exp(C\sigma_s Z)[\exp(\sigma_{-}J)-1]\}, \tag{54}$$

where the saturated absorption cross section is given by

$$\sigma_s=\sigma_{10}(\sigma_{21}+\bar{\sigma}_1-\sigma_{01})/(\sigma_{10}+\bar{\sigma}_1). \tag{55}$$

For photostable donors [i.e., when (45) is satisfied], and when the layer thickness is not too large, there is a range of moderate pulse power

$$J_Z\gg1/\sigma_{10},\quad J_0\ll1/\sigma_{21}{}^{*}, \tag{56}$$

for which saturation is present but photodegradation is still relatively unimportant. Equation (54) then assumes the simpler form

$$J_Z=J_0\exp(-C\sigma_s Z), \tag{57}$$

but with the cross sections σ_s instead of the σ_{10} of (52). We also note that σ_s in (55) can be either greater or smaller than σ_{10}. For the range defined by (56), it follows from (51) and (32) that

$$Q^t\approx Q_s{}^t,\quad Q^f\approx Q_0{}^f l[(1-e^{-l})J_0(\sigma_{21}+\bar{\sigma}_1-\sigma_{01})]^{-1}, \tag{58}$$

where the saturated optical density is $l=C\sigma_s R$, and R is the geometric thickness of the system. According to (58), Q^t eventually reaches its limiting value, whereas Q^f is inversely proportional to J_0.

Finally, complete degradation of donors throughout the volume occurs in the limit of high power and finite thickness of the optical layer (for $J_Z\gg1/\sigma_{21}^{*}$). We then have $Q^t\approx Q_s^t$, as before, but the total yield N^t given by (50) remains finite and is determined by the total number of effective donor excitation cycles prior to donor degradation:

$$N^t=Sl\sigma_{21}{}^t/\sigma_{21}{}^{*}\sigma_s. \tag{59}$$

Figures 2–4 show the results of numerical calculations for $\sigma_{-}/\sigma_{+}=0.01$, where

$$\alpha\equiv\sigma_{10}/\sigma_s,\quad \zeta_0\equiv\sigma_+J_0,\quad \zeta_Z\equiv\sigma_+J_Z.$$

Figure 2 shows the transmitted pulse power J_Z as a function of the incident power J_0, obtained by numerical solution of (48) for four sets of parameter values. These calculations have confirmed that the absorption law given by (51), valid at low power, takes the form given by (57) for moderate power. Finally, in accordance with (54), photodegradation eventually produces complete transmission. When the optical thickness is large ($l=3$), the difference between these absorption regimes is not very clearly defined because they coexist in different parts of the system.

Figure 3 shows calculations of the excitation and fluorescence quantum yields Q^t and Q^f obtained from (51) and (32). These calculations confirm the formulas given by (53) and (58) for limiting cases, and describe intermediate regions as well. The behavior of Q^t and Q^f as functions of J_0 for layers of different optical thickness is in general similar, but

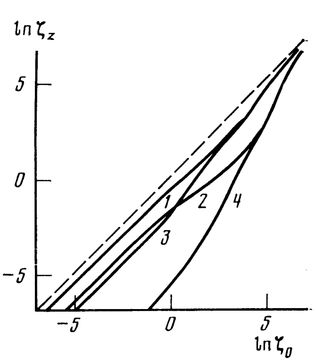


FIG. 2. Transmitted pulse power as a function of the incident pulse power (on a double logarithmic scale). Dashed line corresponds to zero absorption. The parameter values are: 1—$\alpha=0.5$, $l=1$; 2—$\alpha=0.5$, $l=3$; 3—$\alpha=2$, $l=1$; 4—$\alpha=2$, $l=3$.

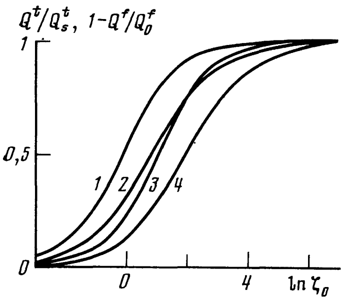


FIG. 3. Transfer and fluorescence quantum yields as functions of the incident pulse power. The parameter values are: 1—$\alpha = 0.5$, $l \ll 1$; 2—$\alpha = 0.5$, $l \gg 1$; 3—$\alpha = 2$, $l \ll 1$; 4—$\alpha = 2$, $l \gg 1$.

for a thin layer saturation sets in much more rapidly, as expected.

In contrast to Q^t and Q^f, the absolute excitation yield of the medium, N^t (Fig. 4), calculated from (50) for an optically thin layer, is found to reach a constant for $J_0 \to \infty$ as a result of the nonlinear photodegradation of donors, in accordance with (59). At the same time, for an optically thick layer with $J_0 \to \infty$, the yield N^t grows without limit because the region of effectively absorbing molecules moves inward into the system without limit.

5. CONCLUDING DISCUSSION

Let us now briefly summarize the main results of this paper. We have succeeded in finding the exact (for $\tau_p \ll \Gamma_1^{-1}$) solution of the nonlinear set of equations given by (18), (26), and (27) for the populations [Eqs. (41) and (43)] and by (48) for the intensity. The solution is expressed in terms of the resultant pulse "intensity area" by analogy with the "amplitude area" used in the case of coherent pulses, for example, in self-induced transparency. Equations (50) and (51) [together with the general relation given by (32)] provide us with formulas for the main observed quantities.

The basic parameter that has enabled us to eliminate medium variables, and then solve exactly the nonlinear set of equations for the populations and intensity, is the rate of relaxation from the first electronic level of the donor, which is small compared with the other relaxation rates. When organic dyes are used as donors, the relative difference between these rates amounts to three orders of magnitude [see (3)], so that we are dealing with a satisfactory parameter.

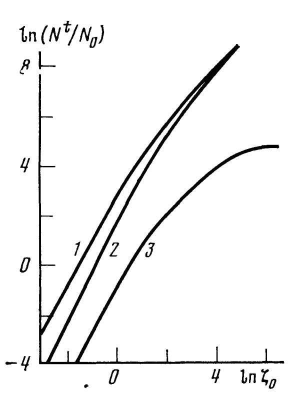


FIG. 4. Absolute yield of excitation of the acceptor medium as a function of the incident pulse power. The normalizing constant N_0 was taken to be SQ^t_s/σ_+. The parameter values are: 1—$\alpha = 0.5$, $l \gg 1$; 2—$\alpha = 2$, $l \gg 1$; 3—$l \ll 1$ (independent of α).

The least expected feature of the problem is that the transitions to the second excited donor singlet S_2 has an important influence on the kinetics of the process, despite the low population of this level [see (9) and (25)]. In fact, transitions to S_2 give rise to the transfer of excitation to the medium, a change in the absorption of the radiation, a reduction in the population of S_1, and a corresponding fall in fluorescence, as well as the photochemical degradation of donors (even when they are absolutely stable in S_1; see Ref. 22). These effects are deterined by the corresponding cross sections given by (28), and the main quantities (41), (42), (48), and (51) [see also (32)] are expressed in terms of these cross sections.

The transfer of excitation to acceptors is reflected in the nonzero value of the probability W^t given by (22). This effect reduces to an essential renormalization of the cross sections in (28), and influences the solution through them (see above). Migration of excitation over the acceptors has an important effect on W^t and, consequently, on the transfer of energy to the acceptor medium [see (33) and (51)]. The effect of migration has a radical dependence on the dimensionality of the medium [cf. the values of W^t given by (40)–(40c), and their asymptotic behavior].

Let us now consider some applications. The processes examined above must be taken into account in the description of powerful dye lasers. In fact, the working medium in such lasers is the dye in the so-called neutral solvents (i.e., solvents that do not absorb the laser or the exciting radiation). These solvents can, however, act as acceptors of two-photon excitation which appears as a result of the absorption of a photon of either the laser or the exciting radiation by the dye molecule in the working laser level S_1. As indicated above, energy transfer to the solvent leads to the depletion of the level S_1 [see (41)], i.e., to reduced inversion and hence reduced laser power.

The chemical modification resulting from absorption of energy transferred by the donors ensures that the acceptor subsystem becomes a medium that records transfer events, and this can be exploited in studies of donor excitation kinetics, optical information storage, and so on.

We now return (see also the Introduction) to one of the most interesting (from our point of view) areas of application of the above theory, namely, the photomodification of the molecules of nucleic acids at a particular point in their primary structure (to be specific, we shall speak of DNA although our discussion will also apply to RNA). It is important to note that there are no direct experimental data on excitation exchange with DNA or on the relaxation of highly-excited states of DNA chromophores at energies of 5–7 eV. The estimates given below are therefore based on analogies and are tentative in character. We also note that energy transfer from the higher-lying electronically-excited singlets of dyes to surrounding acceptors do not appear to have been observed directly (see Refs. 1, 2, and 9), so that experiments with DNA[10–11] may be regarded as the first indirect confirmation of this type of transfer.

DNA-breaking experiments both with addressing[11] and the earlier experiments without addressing[10] made use of the so-called interacting dyes, i.e., planar chromophoric molecules capable of inserting themselves (intercalating) between the planes of neighboring DNA-base pairs of the Watson-Crick double helix. It is clear from the geometry of the intercalation complexes[23] that the overlap of π-electron shells of the dye molecule and the neighboring DNA bases is quite considerable in these complexes. It is therefore probable that we are dealing with strong exchange ($W_e \gg \Gamma_1^M$) and that excitation transfer to the two nearest base pairs occurs by resonant exchange or by the inductive mechanism.[9] By virtue of (3), it is also probable that W_e exceeds the rate of vibrational relaxation. If this is so, then (14) is valid and $W_e = W_d$. We note that, according to the estimates given in Ref. 7, the dipole-dipole mechanism will also ensure strong exchange at distances $r \sim 5$ Å: $W_e \sim 10^{12}\ \mathrm{s}^{-1}$.

For the migration hopping frequency H_1, we shall take the usual value for singlet excitations in molecular crystals,[1,9] i.e., $H_1 \sim 10^{11} - 10^{13}\ \mathrm{s}^{-1}$, which in DNA corresponds to reasonable values of the excitation diffusion coefficient: $D \sim 10^{-4} - 10^{-2}\ \mathrm{cm}^2/\mathrm{s}$. Comparison of Γ_1^M [see (3)] with H_1 leads to the conclusion that in the case of strong exchange in DNA we can have both weak ($H_1 \ll \Gamma_1^M$) and strong ($H_1 \gg \Gamma_1^M$) migration. Combining (34) with (38), we obtain the following universal (in migration rate) estimate for strong excitation exchange:

$$W^t = [\Gamma_1{}^M \cdot \max\,(2H_1,\ \nu_a{}^2\Gamma_1{}^M)]^{1/2} \sim 4\cdot 10^{11} - 3\cdot 10^{12}\ \mathrm{s}^{-1}, \tag{60}$$

where $\nu_a = 4$ (two base pairs). We note that the renormalized probability W^t (60) does not depend on the primary probability W_e (saturated sink[2]). From (33), we then obtain the following expression for the saturated excitation quantum yield (as usual,[5] we assume that $\Gamma_2 \approx \Gamma_{12}$):

$$Q_s{}^t \approx {}^1/_2(1 + {}^1/_2\Gamma_2/W^t]^{-1} \approx 0{,}2 - 0{,}4. \tag{61}$$

This numerical estimate has been made for the least favorable value $\Gamma_2 \sim 10^{12}\ \mathrm{s}^{-1}$. Consequently, the magnitude of Q_s^t will be more than sufficient for the observation and utilization of excitation in DNA. The above estimates favor the interpretation[10,11] in which the observed DNA chain breaks are a consequence of sensitized two-photon excitation.

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