KINETICS OF TWO-QUANTUM SENSITIZED EXCITATION IN THE SINGLET AND SINGLET-TRIPLET CHANNELS

V. A. Markel and M. I. Stockman

We consider theoretically the kinetics of two-quantum sensitized excitation (TSE), that is, the excitation of chromophore acceptors by nonradiative energy transfer from the higher singlet and triplet levels of an impurity donor chromophore. We consider the intensities of exciting radiation that saturate the first singlet level of the donor. It is shown that, as the radiation intensity increases, quenching of the lower triplet level and a corresponding decrease of the phosphorescence intensity (relative to that of the fluorescence) take place. For the realistic values of parameters that characterize the donors and acceptors, the singlet channel of TSE dominates over the singlet-triplet channel under the conditions that the excitation pulses are sufficiently short and the first excited singlet is saturated. The cause of the decrease of phosphorescence and of the suppression of the singlet-triplet channel of TSE, which take place as the excitation radiation intensity increases, is the depletion of the triplet subsystem of levels that occurs as a result of TSE.

(Translated from Russian by V.A.Markel)

room temperature of the liquid solution the lowest excited level is $^1A_g^*$, then in the solid solution it is ^1B_u. Such an inversion obviously is not due to configuration relaxation, which is excluded in solid solution, but to a greater long-wavelength shift of the intense transition as to the refractive index of the solvent increases when the temperature decreases.

$^{1)}$ Our measured value of absorption at $\lambda = 694$ nm from the excited singlet state and calculated high population of the S_1^{II} state [Fig. 1(b)] for the DPB solution in cyclohexane is in good agreement with the value of the cross section σ_{in}^{694} measured in Ref. 5.

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Kinetics of two-quantum sensitized excitation in the singlet and singlet–triplet channels

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A theoretical description is given of the kinetics of two-quantum sensitized excitation (TSE), i.e., excitation of acceptors by nonradiative energy transfer from higher singlet and triplet levels of an impurity donor chromophore. Exciting radiation intensities saturating the first singlet of the donor are examined. It is shown that as the radiation intensity increases, there take place an emptying of the lower triplet level of the donor and a corresponding decrease in phosphorescence in comparison with fluorescence. At realistic values of the parameters characterizing the donor and acceptors, the singlet channel of TSE predominates over the singlet–triplet channel when the durations of the exciting pulse are not too long, and also in the presence of high saturation of the first excited singlet. The cause of the decrease in phosphorescence and depression of the singlet–triplet channel of TSE as the exciting radiation intensity increases is the abandonment of the triplet subsystem of levels as a result of TSE.

INTRODUCTION

Nonradiative energy transfer from highly excited levels of organic chromophore molecules to the surrounding acceptors is a universal phenomenon encountered in many systems and eliciting considerable interest.

Energy transfer from high-lying singlet levels of an impurity chromophore, excited by stepwise absorption of two radiation quanta, to impurity acceptors in solution,[1] to a crystalline matrix,[2] to a solvent,[3,4] and to macromolecules[5] has been observed. In Ref. 5, a nonlinear photochemical modification of macromolecules was discovered. The studies of Refs. 1–5 were carried out with the aid of laser sources in the presence of appreciable saturation of the first singlet level of the chromophore.

Such processes of excitation of acceptors by transfer of two-quantum excitation energy from the donors will be referred to as two-quantum sensitized excitation (TSE). These processes are induced by stepwise excitation of the donors in singlet levels (in the singlet channel). A theory of singlet TSE is given in Ref. 6.

Two-quantum sensitized excitation makes it possible to localize photoexcitation in an area of the order of a nanometer around an impurity chromophore.[7] Two-quantum sensitized excitation underlies the method of photomodifi-

cation of macromolecules, proposed in Ref. 7; it is selective with respect to both their type[8,9] and location in the primary structure of the macromolecule.[10] In Ref. 10 addressed TSE was carried out, as a result of which damage was induced in the macromolecule within a radius of several angstroms from a given location in its primary structure.

Previously, ordinary (not laser) sources were used to observe the process of TSE in a singlet–triplet channel (see the survey of Ref. 11), a process based on the following sequence of events. After a quantum is absorbed, the chromophore goes into the first excited singlet state S_1, and this is followed by internal conversion to a lower triplet level T_1, from which absorption of a second quantum takes place which promotes the chromophore to a higher triplet state T_2. The excitation is then transferred to the acceptor by a resonance exchange mechanism, and the donor returns to the ground electronic state.

Two-quantum sensitized excitation in the singlet–triplet channel has been studied for different donor–acceptor pairs and under different conditions[12-16] (see also Ref. 11). Chemical photomodification of acceptors as a result of TSE has been observed.[15-17] The same mechanism can be used to account for the two-quantum photoreactions taking place via the lower triplet level.[18-20]

The theory of singlet–triplet TSE was developed[13-14]

64

only for the case of low radiation intensities, when the S_1 level is not saturated, i.e., its population is proportional to the radiation intensity. The singlet channel was not significant and not considered.

The object of the present work was to develop a theory of TSE for the case of low saturation of the intermediate singlet level S_1, a saturation characteristic of exciting laser radiation. Both the singlet and singlet–triplet TSE channels are significant and considered. It is shown, in particular, that the relative yield of TSE in the singlet–triplet channel decreases as the radiation intensity increases.

The theory presented below makes it possible to determine which of the TSE channels (singlet or singlet–triplet) makes the chief contribution to the excitation (modification) of acceptors under specified irradiation conditions. The answer to this problem is important, since TSE leads to different states of the acceptor (singlet or triplet) depending on which channel is effective. Although these states are close in energy, the acceptors present in them differ in reactivities, lifetimes, excitation migration rates, etc.

FORMULATION OF THE PROBLEM AND FUNDAMENTAL EQUATIONS

Figure 1 shows combining levels of the donor [coupled by radiative (wavy arrows) and nonradiative transitions (straight arrows)]. Also shown are symbols for the constants determining the rates of the transitions: σ_{ij}—cross section of the $S_j \to S_i$ transition (for $i < j$, σ_{ij} is the stimulated-emission cross section); σ_{ij}^T are the analogous cross sections for transitions between triplet levels; the superscript T always denotes a quantity pertaining to the triplet levels; $\Gamma_{ij}, \Gamma_{ij}^T$ are partial rates of relaxation of the populations of electronic levels with $S_j \to S_i$ and $T_j \to T_i$ transitions, respectively; the total rates of relaxation are $\Gamma_j = \Sigma_i \, \Gamma_{ij}, \Gamma_j^T = \Sigma_i \, \Gamma_{ij}^T$; $\Gamma_{iv}, \Gamma_{iv}^T$ are the rates of relaxation for vibrational sublevels in the S_i and T_i electronic states; W is the rate of the nonradiative transition from S_1 to T_1 (rate of internal conversion).

We shall assume that the donors are sufficiently distant from one another and shall neglect the excitation exchange between them (TSE in the singlet channel with allowance made for the summation of excitation of different donors was discussed in Ref. 21). Excitation transfer to the acceptors will be taken into account by renormalizing the relaxation constants Γ_{02} and Γ_{02}^T (see below).

Following Ref. 6, we separate out the significant small parameters. The latter include the rates of change in the pop-

FIG. 1. Energy level diagram of the chromophore.

ulation of lower excited electronic levels S_1 and T_1 as compared to the analogous rates for the higher levels S_2 and T_2, and to the rates $\Gamma_{iv}, \Gamma_{iv}^T$ of relaxation with respect to the vibrational sublevels of all the states

$$\Gamma_2, \; \Gamma_2^T, \; \Gamma_{iv}, \; \Gamma_{iv}^T \gg \Gamma_1, \; \Gamma_1^T, \; \sigma_{ij}I, \; W, \; \frac{1}{I}\frac{dI}{dt}, \qquad (1)$$

where I is the intensity of the exciting radiation. It follows from Eq. (1) that the transitions take place from the vibrational equilibrium states S_i and T_i, i.e., practically from their ground vibrational sublevels. The populations of the higher levels S_2 and T_2 are small, although the first excited levels of S_1 and T_1 may be saturated. As a consequence of Eq. (1), transitions to higher states can be neglected, and the discussion can be confined to the scheme of levels and transitions presented in Fig. 1.

We shall also allow for the fact that the polarization relaxation rates on transitions to electronically excited states of organic chromophores (at temperatures above the nitrogen temperature) substantially exceed the rates of other relaxation processes. Therefore, to describe TSE, we shall use below the balance kinetic equations for the populations n_i ($i = 0,1,2$) and n_i^T ($i = 1,2$) of the S_i and T_i levels:

The indicated relationships between relaxation constants for organic dyes are based on a large number of experimental data (see, for example, a discussion of this question in Ref. 6 and the references cited there). At ordinary values of the parameters, the values of intensity I saturating the S_1 level and satisfying Eq. (1) lie in the range from fractions to hundreds of megawatts per square centimeter.

On the basis of the balance of the processes shown in Fig. 1, we write the system of kinetic equations

$$\dot{n}_0 = -\sigma_{10}In_0 + \Gamma_1 n_1 + \Gamma_1^T n_1^T + \Gamma_{02}n_2 + \Gamma_{02}^T n_2^T, \qquad (2)$$

$$\dot{n}_1 = -(\Gamma_1 + \sigma_{21}I + W)\,n_1 + \sigma_{10}In_0 + \Gamma_{12}n_2, \qquad (3)$$

$$\dot{n}_1^T = -(\Gamma_1^T + \sigma_{21}^T I)\,n_1^T + Wn_1 + \Gamma_{12}n_2^T, \qquad (4)$$

$$\dot{n}_2 = -\Gamma_2 n_2 + \sigma_{21}In_1, \qquad (5)$$

$$\dot{n}_2^T = -\Gamma_2^T n_2^T + \sigma_{21}^T In_1^T. \qquad (6)$$

It was assumed in the derivation of Eqs. (2)–(6) that the higher states S_2 and T_2 are populated only in the cascade processes $S_0 \to S_1 \to S_2$ and $S_0 \to S_1 \to T_1 \to T_2$. Direct population (bypassing the cascade) of S_2 is excluded if the radiation has a sufficiently long wavelength: its frequency is below the frequency of the 0–0 transition $S_0 \to S_2$; direct population of T_2 is forbidden by the selection rules.

In the system (2)–(6), the processes of excitation transfer from higher levels S_2 and T_2 in TSE are taken into account by means of the relaxation constants Γ_{02} and Γ_{02}^T (the indicated excitation transfers are accompanied in the donor by the transitions $S_2 \to S_0$ and $T_2 \to S_0$). This approach is based on Ref. 6, which showed that inclusion of energy transfer from higher levels to the acceptors, energy migration through the acceptor medium, and possible return to the donor leads to a renormalization of the relaxation constants of the kinetic equations: The renormalized (resultant) rate of excitation transfer is added to the rate of the transition from the donor state to S_0.

In the absence of excitation transfer from higher levels, the relaxation rates Γ_{02} and Γ_{02}^T are low. Thus the branching ratios
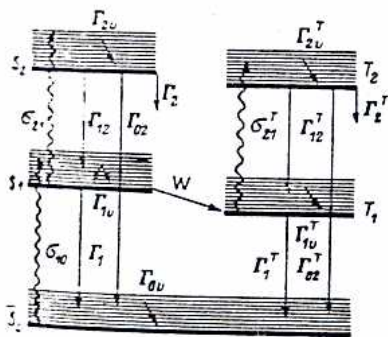
$$\beta=\frac{\Gamma_{12}}{\Gamma_2}, \quad \beta^T=\frac{\Gamma_{02}^T}{\Gamma_2^T} \tag{7}$$

are approximately equal to the efficiencies of excitation transfer from the S_2 and T_2 levels (β^T is identical to the parameter β from Refs. 11 and 14).

Conditions (1) make it possible to eliminate the fast relaxation variables $n_2(t)$ and $n_2^T(t)$ and obtain a closed reduced system of equations for $n_0(t)$, $n_1(t)$, and $n_1^T(t)$ (see the analogous procedure in Ref. 6). Considering the kinetics in terms of times $t \gg \Gamma_2^{-1}, (\Gamma_2^T)^{-1}$, we neglect the time derivatives in the left-hand sides of Eqs. (5) and (6) and find

$$n_2(t)=\frac{\sigma_{21}I}{\Gamma_2}n_1(t), \quad n_2^T(t)=\frac{\sigma_{21}^TI}{\Gamma_2^T}n_1^T(t). \tag{8}$$

Substituting Eq. (8) into Eqs. (2)–(4), we obtain the desired reduced system

$$\dot{n}_0=-\sigma_{10}In_0+(\Gamma_1+\beta\sigma_{21}I)n_1+(\Gamma_1^T+\beta^T\sigma_{21}^TI)n_1^T, \tag{9}$$
$$\dot{n}_1=-(\Gamma_1+\beta\sigma_{21}I+W)n_1+\sigma_{10}In_0, \tag{10}$$
$$\dot{n}_1^T=-(\Gamma_1^T+\beta^T\sigma_{21}^TI)n_1^T+Wn_1. \tag{11}$$

The sum of the populations

$$n_0+n_1+n_1^T\approx1 \tag{12}$$

is, of course, the integral of the system (9)–(11).

KINETICS OF TSE

For simplicity we shall consider a rectangular light pulse $I(t)$ starting at time $t=0$. We assume the layer to be optically thin.

The steady-state solution of the system (9)–(11) (which is obtained with large times) is

$$\bar{n}_1=\frac{\gamma_1^T\sigma_{10}I}{W\sigma_{10}I+\gamma_1^T(\gamma_1+\sigma_{10}I+W)}, \tag{13}$$

$$\bar{n}_1^T=\frac{W\sigma_{10}I}{W\sigma_{10}I+\gamma_1^T(\gamma_1+\sigma_{10}I+W)}, \tag{14}$$

where

$$\gamma_1=\Gamma_1+\beta\sigma_{21}I, \quad \gamma_1^T=\Gamma_1^T+\beta^T\sigma_{21}^TI. \tag{15}$$

As is evident from Eqs. (13) and (14), in the presence of TSE in the singlet–triplet channel (i.e., when $\beta^T\neq0$), the ratio $\bar{n}_1^T/\bar{n}_1=W/\gamma_1^T$ decreases monotonically to zero as I increases. The steady-state population $\bar{n}_1^T$ initially increases with I, then reaches a maximum, and finally decreases $\infty 1/I$ (nonlinear quenching of the T_1 level) as I increases. This behavior with changing intensity is explained as follows. The chromophores in the T_1 state are excited to T_2 at a rate proportional to I, whence they go rapidly [in a time of the order of $(\Gamma_2^T)^{-1}$] into S_0 with probability β^T. Thus the rate of abandonment of T_1 is proportional to I; however, the rate of arrival in T_1 is limited (no higher than W), which leads to nonlinear quenching of T_1.

Consequently, the ratio of phosphorescence intensity to fluorescence intensity is proportional to n_1^T/n_1, and hence, as I increases, it decreases as W/γ_1^T. Donor phosphorescence quenching due to TSE was observed in the experiment of Ref. 12.

Let us consider the excitation dynamics of the chromophore. Solving the linear system (9)–(11) with initial condi-

tions $n_0(0)=1$, we obtain

$$n_1(t)=\bar{n}_1\left[1+\frac{\lambda_-(1+\lambda_+/\gamma_1^T)e^{\lambda_+t}-\lambda_+(1+\lambda_-/\gamma_1^T)e^{\lambda_-t}}{\lambda_+-\lambda_-}\right], \tag{16}$$

$$n_1^T(t)=\bar{n}_1^T\left[1+\frac{\lambda_-e^{\lambda_+t}-\lambda_+e^{\lambda_-t}}{\lambda_+-\lambda_-}\right], \tag{17}$$

where $\lambda_\pm$ are the nonzero eigenvalues of the system (9)–(11),

$$\lambda_\pm=-\frac{1}{2}\{\gamma_1+\gamma_1^T+W+\sigma_{10}I\pm[(\gamma_1-\gamma_1^T+\sigma_{10}I+W)^2$$
$$-4W\sigma_{10}I]^{1/2}\}. \tag{18}$$

The eigenvalues $\lambda_\pm$ can be both real and complex. In the latter case, the solutions λ_+ and λ_+ are formally vibrational; this is explained by the presence of a closed cycle in which excitation of the chromophore levels takes place: $S_0\to S_1\to T_1\to T_2\to S_0$. However, the oscillation period is always greater than or of the order of the time of establishment of the steady state. In addition, one maximum of the function $n_1(t)$ (i.e., one vibration) gives a biexponential solution (16) for purely real $\lambda_\pm$. Therefore, the shape of the $n_1(t)$ and $n_1^T(t)$ curves does not change appreciably in going from real $\lambda_\pm$ to complex ones (see below).

As is evident from Eqs. (16)–(18), as the saturation increases, there is not only quenching of the T_1 level, but also a reduction of the time required to reach the steady-state solutions (13) and (14). In the asymptotics of large I it follows from Eq. (18) that

$$\lambda_+=-(\sigma_{10}+\beta\sigma_{21})I, \quad \lambda_-=-\beta^T\sigma_{21}^TI, \tag{19}$$

i.e., both times $\tau_+=1/\lambda_+$ and $\tau_-=-1/\lambda_-$, which determine the kinetics (16) and (18), decrease as $1/I$.

The number of events of TSE of acceptors in the singlet channel (i.e., events of excitation transfer from the S_2 level) during the time τ of action of the exciting pulse is

$$N=\Gamma_{02}\int_0^\tau n_2(t)\,dt=\beta\sigma_{21}I\int_0^\tau n_1(t)\,dt. \tag{20}$$

Similarly the number of TSE events in the singlet–triplet channel is

$$N^T=\Gamma_{02}^T\int_0^\tau n_2^T(t)\,dt=\beta^T\sigma_{21}^TI\int_0^\tau n_1^T(t)\,dt. \tag{21}$$

We shall illustrate the qualitative characteristics of the solutions obtained by means of the curves shown in Figs. 2 and 3, which were calculated for realistic values of the parameters. Namely, the efficiency of transfer from S_2 is $\beta\sim0.1$ (Refs. 13, 14, and 16); according to the estimates of Ref. 6, the efficiency of transfer from T_2, β^T, is of the same order. The quantum yield of the transition to the triplets (internal conversion) $\Phi=W/(\Gamma_1+W)$ is assumed to be high ($\Phi>0.3$), in order to emphasize the role of the singlet–triplet TSE channel.

Figure 2 shows the $n_1(t)$ and $n_1^T(t)$ curves in the case of real eigenvalues for different saturations of the S_1 level (saturation parameter $\chi=\sigma_{10}I/\Gamma_1$) in the presence of singlet and singlet–triplet TSE (excitation transfer efficiencies $\beta=0.1$, $\beta^T=0.1$). It is evident that for short times [compared to the lifetime of the first singlet $\tau_1=1/(\Gamma_1+W\chi)$] $n_1>n_1^T$, and n_1^T increases with saturation. Dif-

66   Opt. Spectrosc. (USSR) 67 (1), July 1989
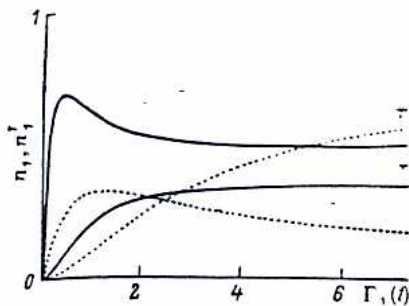
V. A. Markel and M. I. Shtokman   66

FIG. 2. The populations $n_1(t)$, $n_1^T(t)$ as functions of time after the pulse is turned on. Case of real eigenvalues. Parameter values: $\sigma_{10}/\sigma_{21} = 1$, $\beta = 0.1$, $W/\Gamma_1 = 0.5$, $\sigma_{21}^T/\sigma_{10} = 1$, $\Gamma_1^T/\Gamma_1 = 0.01$, $\beta^T = 0.1$; $x = 1$ (dashed line), $x = 7$ (continuous line). The superscript T indicates the population of the triplet level T_1.

FIG. 4. Ratio N^T/N as a function of pulse duration τ on the double log scale. Curves 1–4 were plotted for $x = 0.1, 1, 12, 100$. Parameter values: $\sigma_{21}/\sigma_{10} = 1$, $\beta = 0.1$, $W/\Gamma_1 = 0.5$, $\sigma_{21}^T/\sigma_{10} = 1$, $\Gamma_1^T/\Gamma_1 = 0.01$, $\beta T = 0.1$.

ferent curves are observed for long times. At low saturations, as t increase, n_1^T begins to exceed n_1. However, as saturation increases, n_1^T decreases and becomes smaller than n_1. This characteristic reflects the previously noted [see the discussion following Eq. (14)] nonlinear quenching of the T_1 level, caused by TSE in the singlet–triplet channel.

The $n_1(t)$ and $n_1^T(t)$ curves in the case of complex eigenvalues are shown in Fig. 3. This case can be realized [see Eq. (18)] if the probability of energy transfer from the higher triplet β^T is sufficiently high. As is evident from Fig. 3, in this case the population of the singlet n_1, after reaching its maximum value, decreases much more slowly with time (cf. Fig. 2). This figure, like Fig. 2, clearly shows a reduction of the time taken by the populations to reach steady-state values as I increases, as was mentioned earlier [see the discussion of Eqs. (19)].

Finally, we shall consider the relative efficiency of the singlet and triplet–singlet TSE channels. Figure 4 shows graphs of the ratios of TSE based on the indicated mechanisms, calculated according to Eqs. (20) and (21) as functions of pulse duration for different values of x. It is obvious that when the durations of the exciting pulse τ are not too long compared to the lifetime of the first singlet ($\tau < \tau_1$), the singlet channel is more efficient. This fact is understandable, since under the indicated conditions the triplet level T_1 has not sufficient time to be populated. The singlet–triplet channel also loses to the singlet one at low saturations ($x > 10$), and does so for all pulse durations. The latter, less obvious characteristic is due to nonlinear quenching of the T_1 triplet level, which was discussed earlier.
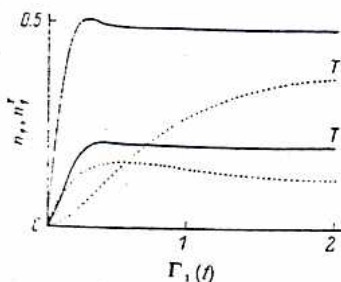

FIG. 3. The populations $n_1(t)$, $n_1^T(t)$ as functions of the time elapsed after the pulse was turned on in the case of complex eigenvalues. Parameter values: $\sigma_{21}/\sigma_{10} = 1$, $\beta = 0.1$, $W/\Gamma_1 = 3$, $\sigma_{21}^T/\sigma_{10} = 1$, $\Gamma_1^T/\Gamma_1 = 0.01$, $\beta^T = 0.9$; $x = 1$ (dashed line), $x = 8$ (continuous line). The superscript T indicates the population of the triplet level T_1.
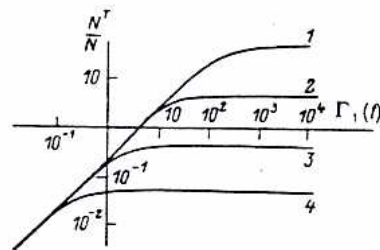
DISCUSSION

We shall briefly discuss certain applications of the theory developed here. In our view, TSE processes are of greatest interest from the standpoint of selective induction of photo-transformations of acceptors, particularly macromolecules.[7,8,10] Of particular importance in this connection is the answer to the question at the beginning of the article: Which of the TSE channels, the singlet or singlet–triplet one, makes the determining contribution to the observed modification of the acceptors? In addition to the above, dependences of the transfer probability as a function of the distance R between the donor and acceptor are distinguished in these channels. For the singlet–triplet channel, this dependence is exponential (resonance exchange mechanism of energy transfer). For the singlet channel, the resonance induction mechanism is additionally included, and the dependence on R becomes an exponential and power superposition, i.e., it generally decreases more slowly with R, and this may lead to a certain delocalization of damage in directed modification of macromolecules with the aid of TSE.

In the absence of saturation in the case of long pulses (or continuous irradiation), the ratio of TSE yields in the channels discussed is calculated according to Eqs. (13), (14), (20), and (21)

$$\frac{N}{N^T} = \frac{\beta \sigma_{21} \Gamma_1^T}{\beta^T \sigma_{21}^T W}. \tag{22}$$

Since it is reasonable to expect that $\beta \sim \beta^T$, $\sigma_{21} \sim \sigma_{21}^T$, the ratio (22) is small in the parameter Γ_1^T/W. Usually $\Gamma_1^T \lesssim 10^6$ sec^{-1}, $W \gtrsim 10^9$ sec^{-1}; hence, $N/N^T \lesssim 10^{-3}$. The indicated conditions are characteristic of the experiments of Refs. 12–21. It is clear from the above estimates that in these studies, the main contribution to the excitation and modification was from the singlet–triplet channel in accordance with the data and interpretations given there.

A different situation takes place when laser sources with a significant optical saturation are used. As an example, we shall analyze the relative role of two TSE channels in experiments on selective modification of DNA.[8,10] Specifically, we shall consider acridine orange dye as the donor of two-quantum excitation, a nitrogen laser being used as the source [pulse time $\tau = 8$ nsec, $I = 150$ MW/cm^2 $= 2.5 \times 10^{26}$ photons/(cm^2 sec)]. The parameters of this dye are as follows: $\sigma_{10} = 5.1 \times 10^{-18}$ cm^2, $\sigma_{21} = 5.7 \times 10^{-17}$ cm^2, $\tau_1 = 5$ nsec (see Ref. 8 and the references cited there); $\Phi = 0.02$.[22] The energy transferred to the acceptor is ~ 6 eV, which is appreciably higher than the energy of its lower excited levels (~ 4 eV). This means that

67   Opt. Spectrosc. (USSR) 67 (1), July 1989

V. A. Markel and M. I. Shtokman   67

the transfer proceeds with the liberation of vibrational energy (it is exothermic), and according to the experimental data of Ref. 11, one should expect $\beta^T \sim 0.1$; according to the estimates, β is of the same order.[6] We shall therefore assume that, as before in the calculations, $\beta = 0.1$, $\beta^T = 0.1$.

Calculation with the indicated parameters, in accordance with Eqs. (17)–(21), gives the following results. The maximum population of the intermediate states is $n_1 = 0.4$, and $n_1^T = 1.3 \times 10^{-3}$, i.e., the T_1 level is emptied as a result of nonlinear quenching caused by TSE. The ratio of the yield of the singlet–triplet channel to the yield of the singlet channel is $N^T/N = 2.6 \times 10^{-2}$. Thus the singlet TSE channel predominates. Comparison with Fig. 4 (where the yield of the singlet–triplet channel is known to be too high, since the efficiency of internal conversion was assumed to be very high) shows that the singlet channel in the experiments of Refs. 8 and 10 predominates at all intensities. This was due to the fact that the duration of the exciting pulses was not too long.

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Interference of a physical radiation field and of vacuum fluctuations at a light-source output

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We have studied the causal and statistical relationships of two contributions to the light-field strength at a light-source output: the physical field issuing from the source cavity through the coupling mirror, and the wideband field of vacuum fluctuations which interferes with this physical field and is reflected from the mirror. We have found a procedure for averaging the experimentally observed quantities if they are expressed in terms of Heisenberg field operators at the light-source output. The results can be used in problems involving transformation of light-field quantum statistics for propagation through parametrically active nonlinear media, when parametric-scattering-type wideband radiation stimulated by vacuum fluctuations can arise.

GENERAL STATEMENT

Let us consider a light wave issuing from a light source (specifically, a cavity source) through a mirror with amplitude transmission $\tau, |\tau| \ll 1$. The strength E (which quantum-mechanically is understood to be an operator) of the light field in the traveling wave issuing from the source has a dual physical nature.

On the one hand, we have, excited in the source, a light field that emerges to the outside through a mirror, enters into certain interactions in the outer space, and finally reaches a detector. In many physical cases, observation will reveal in the light only the frequencies, spectral widths, etc., characteristic of the source (with allowance made for subsequent interactions in the outer space). These cases can be described if one relates the light field strength in the source and outside it (behind the mirror) by multiplying by the transmittance τ, as is done in classical electrodynamics.

68

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