FORMATION OF A COMPLEX NONLINEAR RESPONSE IN BICHROMOPHORE SOLUTIONS

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A theoretical investigation of the dynamics of the stimulated emission of solutions of bichromophores consisting of a donor with a high intersystem crossing probability and an acceptor between which a radiationless inductive-resonant energy transfer is possible is carried out. The complex dynamics of the behavior of the system is demonstrated, which makes it possible to use these chromophore ensembles as multistable devices with a memory of order of the triplet state lifetime.

Key words: stimulated emission, bichromophores, optical information processing.

One of directions of the development of methods of optical information processing which makes it possible to achieve a high parallelism is the development of spatial light modulators based on media with a complex controllable nonlinear response (NR). To date, phenomena of optical bistability and optical control of light fluxes have been demonstrated for a rather wide class of materials with an NR (see, e.g., [1]), but little attention has been paid to media based on complex molecules, although they seem to be very promising, since complex molecules have considerable absorption cross-sections and can convert to long-lived states. Earlier, Gorbatschevich et al. [2, 3] investigated the possibility of employing bichromophore ensembles as controlling media. However, the common approach based on the use of luminescence of solutions restricts substantially the possibilities of NR control, which is primarily connected with the complex character of interaction of molecules with their environment in a solution. On the other hand, the method of the pump-and-probe spectroscopy [4], which consists in creating a nonlinear perturbation in the medium by one or several powerful light fluxes which is then investigated by a weak probing wave, has been developed in nonlinear spectroscopy. In this case, the powerful exciting radiation can be used as a factor controlling the NR.

In the present work, we consider the formation of a complex NR in a solution of bichromophores which is scanned by a relatively weak probing wave with a frequency differing from that of the powerful exciting radiation.

Let us consider a solution of bichromophores that consists of molecules of two types between which radiationless inductive-resonant electronic excitation transfer (REET) is possible. We assume that spectra of molecules constituting the bichromophore allow these molecules to be excited independently. Due to the spectral difference of the molecules, we consider the energy transfer to be directed from molecule 1 to molecule 2, and molecule 1 in what follows will be referred to as the donor and molecule 2 will be referred to as the acceptor. We also assume that the donor molecule has a high probability of intersystem crossing to the triplet state \( T_1 \). The spectra of acceptor absorption and donor emission are strongly overlapped. Figure 1 presents a diagram of electronic energy levels of a bichromophore of this type. Here \( k_1, k_2, \) and \( k_{ph} \) are rate constants of spontaneous deactivation of excited states of the molecules, \( k_z \) and \( k_e \) are rate constants of intersystem crossing, \( k_{REET} \) is the rate constant of the REET;

\[
\begin{align*}
    b_1(2) &= \frac{\sigma_1(2)f_1(2)}{hv_1(2)}; \\
    a_1(2) &= \frac{\sigma_3(4)f_3(4)}{hv_3(4)}.
\end{align*}
\]

where $\sigma_1(2)$ and $\sigma_3(4)$ are absorption cross-sections of the molecules, and $I_1(2)$ and $I_3(4)$ are power densities of the exciting radiation at the absorption (emission) frequency of the donor (acceptor) molecules. In what follows, we will express the quantities $b_1(2)$ and $a_1(2)$ in units of $k_f$, and time $t$ in units of $1/k_f$. Let us assume for definiteness that $k_f = k_f$, $k_g = 0.01k_f$, $k_{ph} = 10^{-4}k_f$, and $k_e = 0$.

In agreement with the conditions of the investigation, we will excite the given bichromophore solution by two light fluxes at frequencies $\nu_1$ and $\nu_4$. Here frequency $\nu_1$ corresponds to the absorption band of the donor molecule and, in what follows, we will refer to this light flux $I_1$ as the exciting one, and the light flux $I_4$ at the frequency $\nu_4$ corresponding to the acceptor emission band will be referred to as probing.

In the system under consideration, the rate constant of the REET between the donor and acceptor molecules is much greater than the rate constants of the spontaneous deactivation of the excited state of the donor molecule ($k_{\text{REET}} >> k_{f1}$, $k_f$) due to the small distance separating these molecules. Therefore, the acceptor determines the possibility of REET and affects substantially the population of donor molecules. The probability of population of the $S_1$ state of the donor molecule in the bichromophore will be extremely low if the acceptor is in the ground state, and will be considerable upon promoting the acceptor to the excited state.

We will denote possible states of the bichromophore by a set of the three indices $\{i, j, k\}$ that characterize the corresponding $S_1$ and $T_1$ states of the donor $(i, j)$ and $S_1$ state of the acceptor $(k)$. Indices $i$, $j$, and $k$ can take values of 0 or 1, and the value 1 means that the system is in the corresponding state. Populations of these states will be denoted as $Y_{lik}$. Owing to the large value of the REET rate constant, the state $\{1, 0, 0\}$ when the donor is in the $S_1$ state and the acceptor is in the ground state has a low probability and therefore can be excluded from further consideration. Thus, to describe the given bichromophore (under the normalization condition $Y_{000} + Y_{001} + Y_{010} + Y_{011} + Y_{101} = 1$), one can write the system of balance equations

$$
\frac{dY_{001}}{dt} = \left(1 - Y_{001} - Y_{010} - Y_{011} - Y_{101}\right) b_1 - Y_{001} \left(k_f + b_2 + a_2 + a_1 + k_g\right) + Y_{101} k_e,
$$

$$
\frac{dY_{010}}{dt} = -Y_{010} \left(k_{ph} + k_f + k_e + a_2\right) - Y_{011} k_f + Y_{101} \left(k_f + a_1 + k_f + a_2\right),
$$

$$
\frac{dY_{011}}{dt} = -Y_{011} \left(k_{ph} + k_f + k_e + a_2\right) + Y_{011} k_e + Y_{101} k_e,
$$

$$
\frac{dY_{101}}{dt} = Y_{010} b_2 - Y_{011} \left(a_2 + k_{ph} + k_f + k_f\right) + Y_{101} k_e.
$$

(2)

The following equations can be written for populations $X_{1d}$ and $X_{1a}$ of the $S_1$ state of donor and acceptor molecules and the population $X_T$ of the $T_1$ state of donor molecules:

$$
X_{1d} = Y_{101}, \quad X_{1a} = Y_{001} + Y_{011} + Y_{101}, \quad X_T = Y_{011} + Y_{010}.
$$

(3)