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# DEPOLARIZATION OF THE FLUORESCENCE IN DONOR-ACCEPTOR PAIR UNDER PERIODIC ELECTRIC FIELD

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## Introduction

Kinetics of the transfer of excitation between donor and acceptor groups in nanostructures and supramolecular complexes and elaboration of the theoretical model for describing of the features of such type of the transfer are actual problems of optoelectronics, molecular, sensor electronics and biophysics. The given theoretical investigation is devoted to elaboration of the two-level semi-phenomenological model featuring the kinetics of the transfer of the excitation between the donor and acceptor in the molecular complex in the external periodic electric field.

The given investigation is theoretical result, however has also practical value. First, the given investigation is showing how in dependence from the relation of the basic parameters of the system it is possible to model and to control processes of the transfer of excitation during biochemical processes with the participation of the biomacromolecules. Secondly, supramolecular complexes and nanostructures with the donor-acceptor groups are the functional elements of the devices of the optoelectronics and the molecular electronics and parametric guidance of the processes of the transfer is extremely important.

Now existing time-resolved experimental techniques which allow to detect superposition of the quantum states in the different biochemical molecular systems. In addition, these states are the functional states in the applications of the bioinformatics, quantum computers, molecular electronics and the molecular engineering [1].

Time evolution of the superposition of the quantum states of the molecular complexes and nanostructures can have experimentally observable physical quantities. Among the observable effects is the depolarization of the fluorescence. Evolution of the superposition of the quantum states which take place in the molecular complexes by means of the observation of the time dependence of the depolarization of fluorescence is theoretically explored in this article.

The system of the non-interacting molecules with donor and acceptor groups is under investigation. For the analysis we shall take the donor and the acceptor groups are identical. The molecular system is excited by the short impulse of polarized light, and the electronic excitation is initially localized on the donor and interacts only with full symmetrical vibration of ligand environments, thus the vibrational subsystem forms the package in the form of the coherent type of the state. The excited state of acceptor group of the pair is resonant for the excited state of the donor because of the complete equivalence of the donor and acceptor groups. Account of the interaction with vibrational degrees of freedom essentially modifies the dynamics of the transport of the excitation from the donor to the acceptor.

Since the donor and acceptor are identical molecules the fluorescence is not affected but depolarization of the fluorescence will be affected, because the “memory” of the initial polarization is lost. For simplicity we assume that both dipole moments on the donor’s and acceptor’s molecules to be coplanar and mutually perpendicular. Creating the excitation of the donor-acceptor pair which is localized on the donor molecule by the light polarized in the direction of the dipole moment on that molecule. If the intensities of the parallel fluorescence and perpendicular fluorescence to the direction of the polarization of the incident light are $I_{\mathrm{II}}$ , $I_{\perp}$ then degree of the depolarization of the fluorescence is

$$f = (I_{\mathrm{II}} - I_{\perp})/(I_{\mathrm{II}} + I_{\perp}) \qquad (1)$$

For the investigation of the excitation transfer within the pair this is convenient observable value. It is clear, that the intensity of the fluorescence in the direction of the unit vector $e_{\eta}$ is given by [2, 3]

$$I_{\eta} = \sum_{m,n} \rho_{mn} (\mu_m e_{\eta})(\mu_n e_{\eta}) \qquad (2)$$

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$\mu_m$ are dipole moments in excited states of the donor and acceptor, $\rho_{mn}$ are components of the density matrix. In the basis of the local states indexes m and n may be 1 or 2.

If the angle between the polarization of the incident light and transition dipole moment of the donor's excited state-1 and acceptor excited state- 2 is φ we can write (see fig. 1)

$$\mu_1 e_{II} = \mu_2 e_{\perp} = \cos\varphi, \quad \mu_1 e_{\perp} = -\mu_2 e_{II} = -\sin\varphi \tag{3}$$

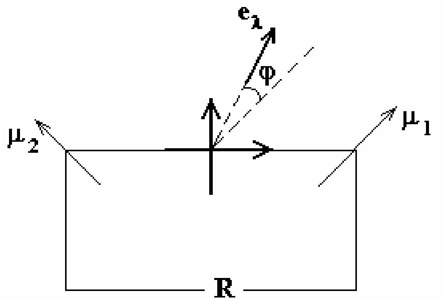


*Fig. 1. Geometry of the particular planar dipole moment of the donor-acceptor pair. Vectors $\mu_1, \mu_2$ are perpendicular and equal in length. The unit vector $e_\lambda$ lies along the polarization vector of exciting light, and the angle $\varphi$ is measured from the direction of $\mu_1$*

### Semi-phenomenological model

The excitation transfer process in the donor-acceptor pair under the action of the sinusoidal electric field which interacts only with the dilatational component of the dipole moment of the donor and acceptor groups is proposed.

In this paper we have calculated some factors of the theory of the depolarization of the fluorescence for the excitation transfer process in the donor-acceptor pair under the action of the sinusoidal electric field. It is assumed that for the donor-acceptor pair takes place the resonance of the energy of the lower excited levels. Other excited levels are essentially removed from this pair of the levels so the interaction with them is not considered. The approach of the two-level system is taken unto accounts. It is assumed, that the excitation which is localized on the donor or on the acceptor group interacts only with full-symmetrical vibration of the ligands of this group. Introduction of the new normal coordinates allow exclude one of the new normal coordinates as the full-symmetrical increased on the unit electronic matrix.

Using for the calculations the two-level model Hamiltonian from [4] and assuming that the vibrational subsystem is in the coherent type of the state we realize the plan of the calculation of the time dependence of the average values of the physical quantities grounded on use of the canonical equations of Hamilton and the approximation for the time wave function in the form of the Davydov's type of the soliton [5].

The Hamiltonian of the considered system is:

$$H(t) = \frac{1}{2}\left(p^2 + \omega_0^2 q^2\right) + v(a_1^+ a_2 + a_1 a_2^+) + gq(a_1^+ a_1 - a_2^+ a_2) + \mu_{II}\varepsilon_0 \cos(\Omega t)(a_1^+ a_1 - a_2^+ a_2) \tag{4}$$

Here – $p, q$ are the momentum and coordinate of the vibrational mode $q$ with frequency $\omega_0$; $a_i^+, a_i$ – are the operators of the creation and annihilation of the excitation on the donor – 1 and acceptor – 2 groups correspondently; $v, g$ are the resonance electronic constant and constant of the electron-vibrational interaction; – $\varepsilon_0$, Ω are the magnitude and the frequency of the sinusoidal electric field, $\mu_{II}$ is the longitudinal component of the dipole moment of the excited state of the donor group, induced by the short-time polarized light.

In this work the quasi-classical approximation was used. Davydov's type of the time-dependent wave function in Hamilton canonical equation of the motion for the description of the time evolution of the depolarization of the fluorescence was applied

$$\psi(t) = \exp(-i(\beta(t)p - \pi(t)q)\sum_{j=1}^{2} \alpha_j a_j^{+} \left|0\right\rangle . \qquad (5)$$

The system of the linkage differential equations for the amplitudes was obtained:

$$i\frac{d\alpha_1}{dt} = v\alpha_2 + g\beta\alpha_1 - \mu_{II}\varepsilon_0\alpha_1 \cos(\Omega t) - i\frac{\alpha_1}{\tau_1}$$

$$i\frac{d\alpha_2}{dt} = v\alpha_1 - g\beta\alpha_2 + \mu_{II}\varepsilon_0\alpha_2 \cos(\Omega t) - i\frac{\alpha_2}{\tau_2}$$

$$\frac{d\pi}{dt} = -\omega_0\beta + g\left[\left|\alpha_1\right|^2 - \left|\alpha_2\right|^2\right] . \qquad (6)$$

$$\frac{d\beta}{dt} = \pi$$

To consider the excitation lifetime on the donor and on the acceptor the relaxation times are phenomenologically entered. The dilatational excitation lifetime is characterizing the relaxation of the diagonal density matrix elements caused by the spontaneous transitions between the levels. The traversal relaxation time for the non-diagonal matrix elements is characterizing the time of the infringement of the phase relations between the states - «time of phase memory». In the formula (6) are phenomenologically entered $\tau_1, \tau_2$ as the dilatational relaxation times characterizing the excitation lifetime on the donor and on the acceptor groups accordingly. As the donor and acceptor group are accepted identical, so $\tau_1 = \tau_2$ and the time of the traversal relaxation in such approach will be spotted as $\frac{1}{T_\perp} = \frac{2}{\tau}$ .

Here $\alpha_j(t),\ j = 1,2\ ;\ \beta(t), \pi(t)$ are the time-dependent amplitudes of the probability of the electron's detection on the excitation state of the donor or on the acceptor excitation state and the average values of the coordinate and momentum of the vibrational mode, correspondently.

Time dependence of the fluorescence of the depolarization through the solutions of the system (6) can be spotted as follows using the reasons presented above

$$f = \left(\left|\alpha_1(t)\right|^2 - \left|\alpha_2(t)\right|^2\right)\cos(2\varphi) + \ (\alpha_1(t)\alpha_2^{*}(t) + \alpha_1^{*}(t)\alpha_2(t))\sin(2\varphi) . \qquad (7)$$

**Results and conclusion**

The main results of the given consideration, which follow from the numerical solution of (6) are presented on the fig. 2 – 4.

On the figures 2–4 the time dependence of the depolarization of the fluorescence for the some values of the parameters of the system is presented. For reasoning some values of the parameters of the system which brightly show features of the transfer in the model system in the two extreme cases of the strong and weak electron-vibrational interaction are chosen.

The analysis of the numerical solution (6) presented by the time dependence of the depolarization of the fluorescence of the donor-acceptor pair on fig. 2–4 allows to make following conclusions. The cases presented on the fig. 2-3 correspond to the case of the weak electron-vibrational interaction.

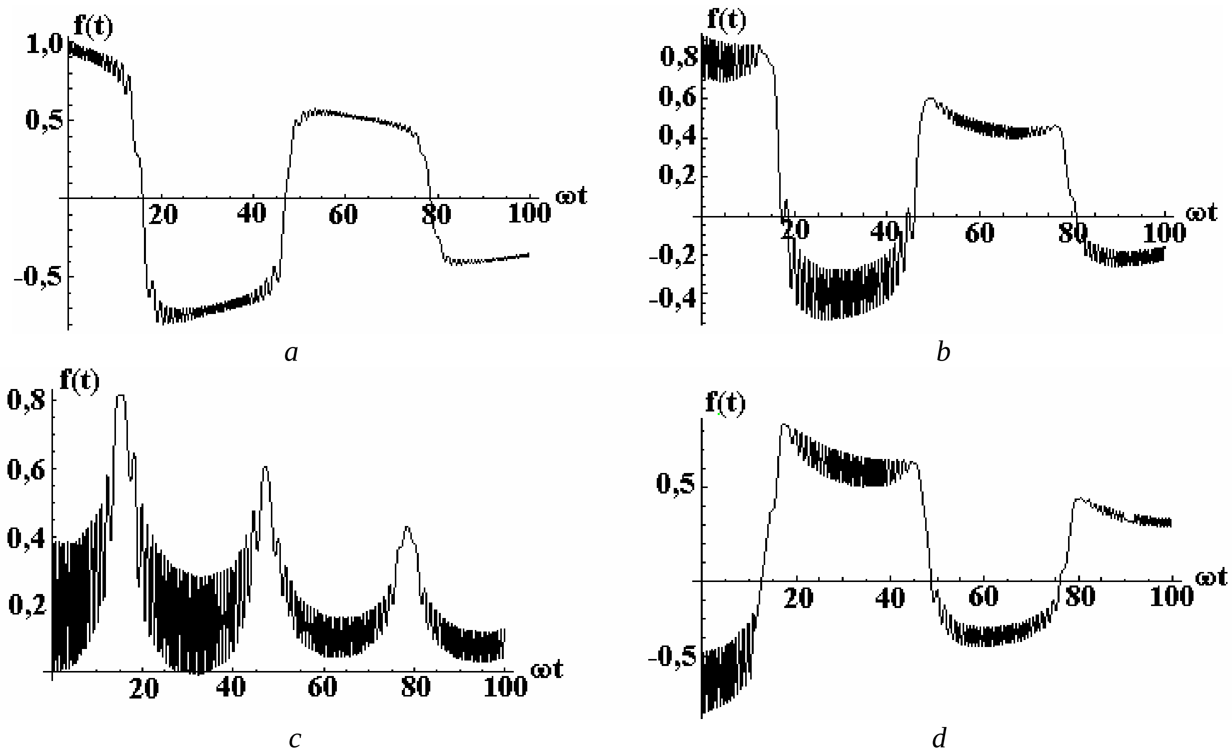


*Fig. 2. Time dependence of the depolarization of the fluorescence for the next parameters of the system:* $v = 1,\ g = 0.1,\ \mu_{II}\varepsilon = 5,\ \omega_0 = 1,\ \Omega = 1,\ \ \tau = 0.005\omega_0,\ \varphi = 0,\ \pi/4,\ \pi/2,\ 3\pi/2,\ (a) - d))$

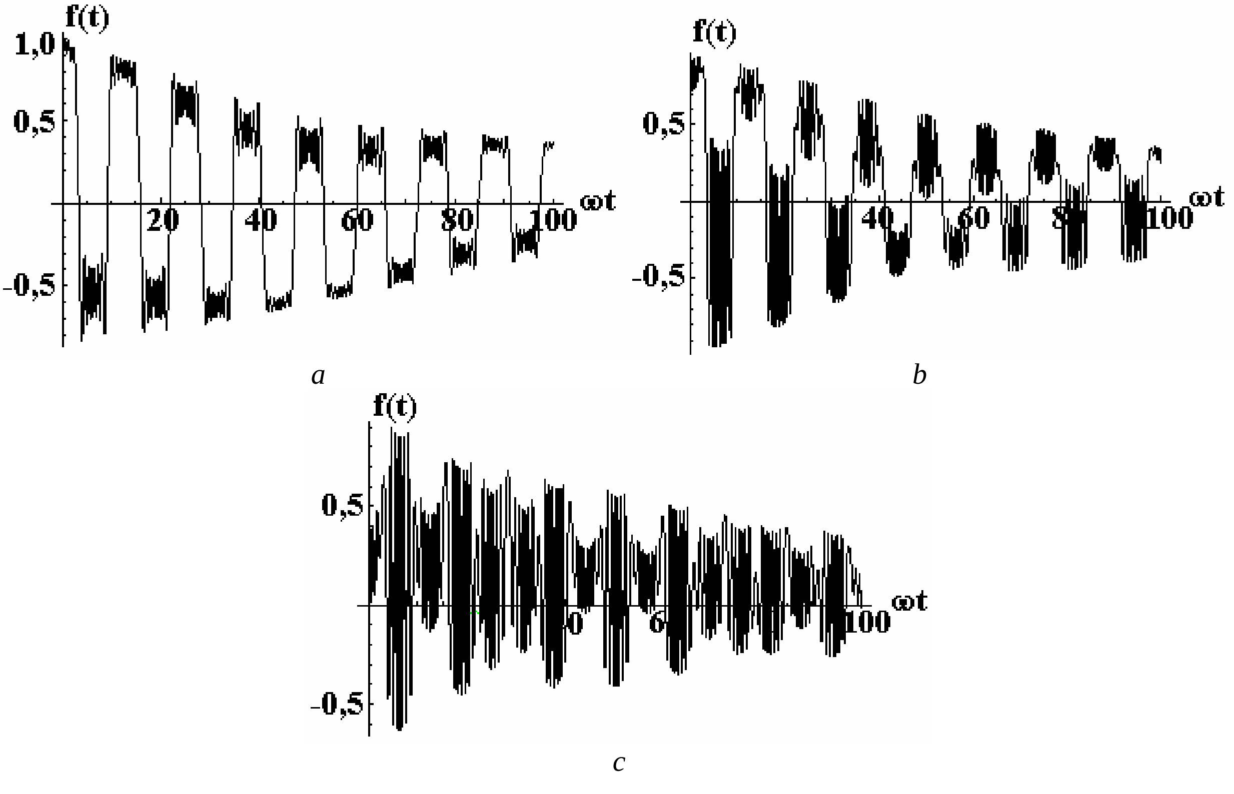
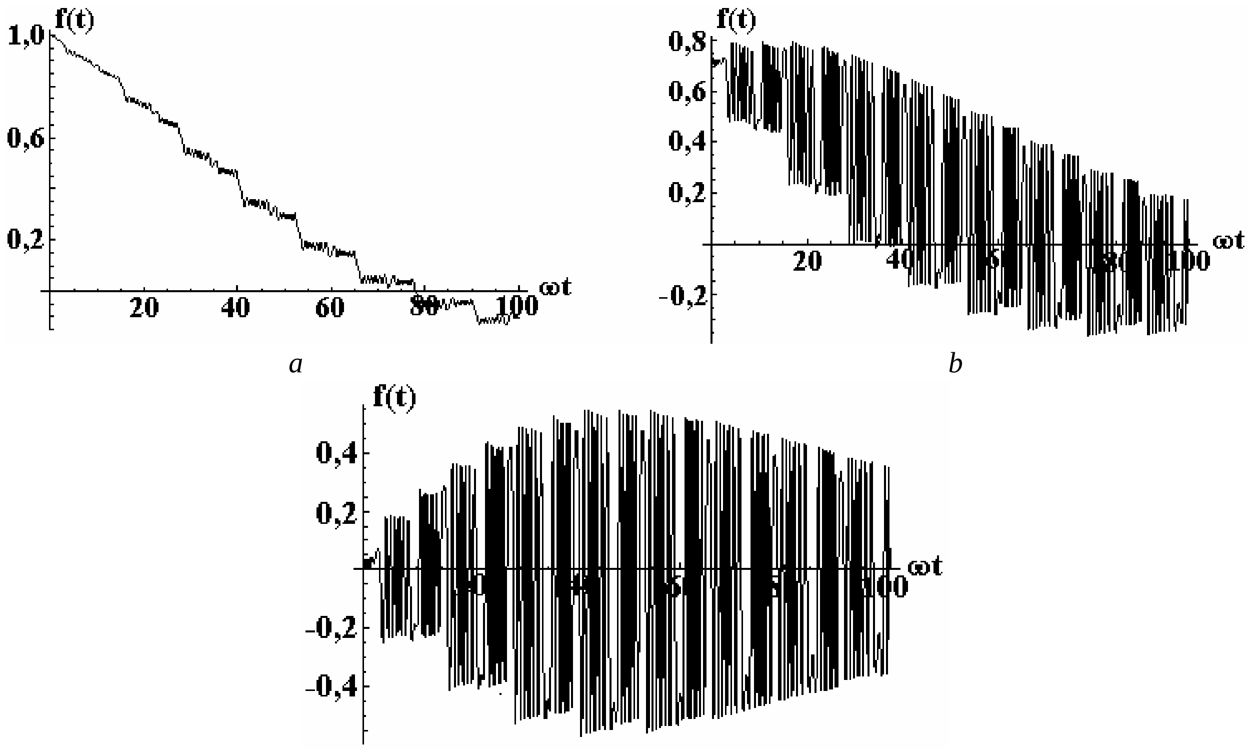


*Fig. 3. Time dependence of the depolarization of the fluorescence for the next parameters of the system:* $v = 1,\ g = 0.1,\ \mu_{II}\varepsilon = 5,\ \omega_0 = 1,\ \Omega = 5,\ \ \tau = 0.005\omega_0,\ \varphi = 0,\ \pi/4,\ \pi/2,\ (a) - c))$

Non-linear effects taking place for the case of the strong electron-vibrational interaction in this case may be neglected. Quantum beats of the time dependence of the depolarization of the fluorescence are the consequence of the interference of the excited states of the donor and acceptor of the donor-acceptor pair.



*a* *b*

*c*

*Fig.4. Time dependence of the depolarization of the fluorescence for the next parameters of the system:* $v = 0.1,\ g = 1,\ \mu_{II}\varepsilon = 5,\ \omega_0 = 1,\ \Omega = 5,\ \tau = 0.005\omega_0,\ \varphi = 0,\ \pi/4,\ \pi/2,$ *(a)–(c)*

On the fig. 4 the case of the strong electron-vibrational interaction when it is important to consider non-linear effects is presented.

Let's analyze the case a) fig. 4, when the corner between the dipole moment of the system and the vector of polarization of radiation $\varphi = 0$. In this case influence of the interference addends may be neglected.

The strong electron-vibrational interaction interferes in the transport of the excitation from the excited state of the donor to the excited state of the acceptor and essentially influences on the character of the fluorescence of the donor-acceptor pair. The time dependence of the depolarization of the fluorescence varies monotonously. Whereas for the cases b) and c) fig. 4. ($\varphi = \pi/4,\ \pi/2$) the contribution from the interference addends is essentially the monotonous time dependence of the depolarization of the fluorescence is modified by the quantum beats.

Thus, for the donor-acceptor pair interacting with exterior periodic electric field and being in the excited state in the form of superposition of quantum states in the two-level approach were detected the features of the time behavior of the depolarization of fluorescence. This model allows to consider non-linear properties of the system, and also to consider the role of the interference of the quantum states on the dynamics of the transfer of the excitation from the donor to the acceptor in the molecular complex under external electric field.

The cases of the strong and weak electron-vibrational coupling were analyzed. The essential role of the interference of the quantum states is specified in the processes of the energy transfer in this system. This consideration has doubtless interest from the point of view of the studying of the functional devices of the optoelectronics, bioinformatics, molecular and sensor electronics and quantum computers.

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## Summary

The donor-acceptor pair in the external periodic electric field is under studying. The molecular system is excited by the short impulse of the polarized light, and the electronic excitation initially localized on the donor and interacts only with full symmetrical vibration of the ligand environments, thus the vibrational subsystem forms the package in the form of the coherent state. Donor and acceptor molecules are assumed as identical type of the molecules. The time dependence of the depolarization of the fluorescence is numerically calculated on the basis of the semi-phenomenological model. Numerical estimates are given for cases of the strong and weak electron-vibrational interaction. Transfer of the excitation in the system is defined by the non-linear properties of the system, especially in the case of strong electron-vibrational interaction. The depolarization of the fluorescence is consequence of the such transport and contains the interference addends which conduct to the quantum beats in the time dependence.