

## DELAYED LUMINESCENCE FROM BIOLOGICAL SYSTEMS WITHIN THE DAVYDOV SOLITON MODEL

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We report on the application of Davydov solitons to explain delayed luminescence (DL) arising from simple biological systems. The soliton model describes self-trapped localized electron or exciton states in biological quasi-one-dimensional macromolecules and provides support for charge and energy transport for macroscopic distances. We have chosen alga *Acetabularia acetabulum* (A. a.) for the experimental and theoretical study as a model system due to the fact that this is a unicellular organism in which the cytoskeleton contains macromolecular structures (actin filaments, microtubules, etc.) of a length of several hundreds of angstroms and more. Namely in these structures, many-soliton coherent states can exist. We studied DL in the presence of an external source of light at a relatively high intensity of illumination. Kinetics and quantum yields of the DL from the system after its exposition for a finite time to a light source were calculated. It was found that the total number of photons emitted, is a non-linear function of the irradiation intensity, time of exposition, and dose of illumination. The quantum yield of DL first increases with the dose and then reaches saturation. The analytical results provide good fit of the experimental data obtained for A. a. in a large range of incident dose, up to saturation. We retain that further investigations, taking into account inhibition of the photosystem at a very high intensity or a dose of illumination, are necessary.

### Introduction

The phenomenon of DL consists of photo-induced light emission for a long time (seconds and more) after illumination of a sample and was proved to exist not only in conventional solid state systems but also in biological ones [1]. A big amount of experimental data has been accumulated in the last twenty years [2-12] from which it emerges that DL possesses a number of characteristic properties which are sensitive to the chemical, physical, and physiological state of a system, and can give the global information on the organism. Among these, we recall the main:

a) the correspondence of the DL kinetics in a long time interval to the phenomenological Becquerel law, given by the hyperbolic time dependence:

$$I(t) = \frac{I_0}{(1 + t/\tau)^a}, \quad (1)$$

which becomes linear on a long-log scale;

b) the same time trend of the different components of the DL emission spectrum;

c) the non-linear dependence of the initial intensity of DL from the intensity of impinging light.

In literature, there are two basic historical hypotheses about the origin of DL.

The first one [13] retains that DL arises from some minor imperfections in the photochemical mechanism of primary charge separation, generated by charge recombination. The second one [14, 15] assumes that DL in biological systems is connected to the key property of coherence of states and fields in living matter. However, neither of the two hypotheses provides the correct trend given by (1) and no previsions are made about properties b) and c).

Besides these hypotheses, a new model [16, 17] based on the Davydov soliton concept was proposed in the last two years, which seems to provide explanation of properties a) through c) and a good fitting of the experimental data. Indeed, the long duration of DL from biological systems appears as a property strictly connected with the existence of states much more stable than conventional excitons. The model assumes that DL is connected with the formation of autolocalized exciton and electron states created by the pre-illumination of the sample. In particular, in a biological cell, according to A. Davydov [18, 19], such autolocalized (self-trapped) states can be formed in low-dimensional macromolecular structures due to the electron-phonon interaction in polypeptide chains. They are described by systems of nonlinear differential equations, which admit soliton-like solutions, and, therefore, such autolocalized electron states are called solitons or electrosolitons [18, 19] or, after A. Scott, Davydov solitons. It has been first suggested in [16] that these self-trapped electron states can participate in the process of delayed luminescence of biological systems.

Similarly, another model for DL was developed in [17] which is valid for systems with strong correlation between electrosolitons, e.g., at their high concentration. For the experimental and theoretical study, the alga A.a. was chosen as a model system due to the fact that it is a unicellular organism that contains a photosystem, and whose cytoskeleton

contains macromolecular structures (actin filaments, microtubules, etc.) of a length of several hundreds of angstroms and more.

Both the non-correlated and correlated models describe the kinetics of the DL after the external irradiating light source is switched off. In order to study the DL at a high intensity and a dose of illumination, it is necessary to generalize the model in such a way that the process is observed from the very beginning, when the external light source is switched on. In the present paper, we have developed such a model.

### 1. The Model

It is known [20] that, from the point of view of electron structure, proteins possess the semiconductor-like energy band structure with a filled valence band and an empty conduction band. Solitonic states in biological macromolecular structures like the ones in algae A.a., which are energetically favoured as compared with the conduction band electron states, are characterized by an energy level in the conventional forbidden band. Moreover, the process of charge separation due to external illumination takes place in specific protein complexes, the reaction centers, which have also energy states in the forbidden band. Electrons released at the ionized reaction centers are excited in the conduction band and, with a certain probability, are self-trapped in macromolecules. The luminescence arises from the decay of these localized states into the conduction electron band with a following fast transition to the ionized reaction centers. A comparison of the experimentally measured fluorescence and DL emission spectra [22] reveals no energy shift, therefore the probability of direct transition of electrons from the self-trapped state to the reaction centers is neglected. The spatial arguments support this model as well: a soliton localizes within a few lattice sites and can transit to a distant reaction center via the conduction band by the back reaction.

According to the above, the electron-hole recombination determines the intensity of DL

$$I = - \frac{dn}{dt}, \quad (2)$$

and the kinetics of DL is described by the following system of equations:

$$\frac{dn}{dt} = - p_r N n + Y, \quad (3)$$

$$\frac{dN}{dt} = p_d v - p_r N n - p_l N (v_0 - v) + Y, \quad (4)$$

$$\frac{dv}{dt} = - p_d v + p_l N (v_0 - v). \quad (5)$$

Here,  $n$  is the number of ionized reaction centers,  $N$  is the number of (excess) electrons in the conduction band,  $v$  is the number of localized electrons;  $p_l$ ,  $p_d$ ,  $p_r$  are the probabilities per unit time (or equivalently the rates) of electron localization, soliton dissociation, and electron-hole recombination, respectively. Furthermore, the condition for neutrality is expressed by the equation

$$n = N + v, \quad (6)$$

and the probability of electron localization  $p_l$  is proportional (with the coefficient  $\alpha$ ) to the energy of the localized states, which is split from the energy of the conducting band bottom by the value  $E_s$ , and, generally, depends on the number of localized states  $v$ :

$$p_l(v) = \frac{\alpha E_s(v)}{\hbar}. \quad (7)$$

When solitons are non-correlated (at very small concentrations, in not long enough macromolecules, etc.), electrons localize in the independent (bi)soliton states, and the probability of localization is independent of the soliton concentration [15]. On the contrary, when the soliton correlation is essential, the energy of localized states depends on the soliton concentration, that is restricted by the maximum available value  $\delta_0$ , above which solitons do not exist [21]. Therefore, in this case, the probability of localization, which is proportional to the energy of localization (7), has the form [21]

$$p_l = p_0 \left( 1 - \frac{v}{v_0} \right), \quad (8)$$

where

$$p_0 = \frac{\alpha J g_0^2}{3 \hbar}, \quad v = 2\delta. \quad (9)$$

In the above relations,  $g$  and  $J$  are the dimensionless electron-phonon coupling constant and the resonance interchange parameter of the polypeptide chain, respectively, and  $v_0 = 2\delta_0$ . Finally, the parameter  $Y$  is the yield of illumination and represents the number of ionized reaction centers (the number of excess electrons generated per unit time by illumination). We remark that  $Y$  is, in general, a non-linear function of the intensity of illumination  $I_{ill}$  and the number of ionized reaction centers. However, we study linear pumping here and set

$$Y = Y_0, \quad (10)$$

where  $Y_0$  is a constant proportional to  $I_{ill}$ .

In the following, it is convenient to introduce dimensionless variables as follows:

$$\tau = p_d t, \tag{11}$$

$$x = \frac{v}{v_0}, \quad y = \frac{N}{N_0}, \quad z = \frac{n}{n_0}, \tag{12}$$

$$\gamma = \frac{P_0}{P_r}. \tag{13}$$

In this system of units, Eqs. (2) - (6) take the form:

$$I(\tau) = - \frac{dz}{d\tau}, \tag{14}$$

$$\frac{dz}{d\tau} = - a y z + P(z), \tag{15}$$

$$\frac{dy}{d\tau} = x - a y z - a \gamma y (1 - x)^2 + P(z), \tag{16}$$

$$\frac{dx}{d\tau} = - x + a \gamma y (1 - x)^2, \tag{17}$$

$$z = x + y,$$

where:

$$a = \frac{P_r v_0}{P_d}, \tag{19}$$

and, according to (10), we have to put:

$$P(z) = P_0. \tag{20}$$

### 2. Steady State Regime

It is possible to assume that, due to the fact that the probability of (bi)soliton dissociation is much less than the probability of electron decay from the conduction band [23], the quasi-stationary (steady state) regime is valid:

$$\frac{dy}{d\tau} \ll \frac{dx}{d\tau}. \tag{21}$$

Under this approximation, we get from Eq. (16) taking into account Eq. (19):

$$y = \frac{z + P_0}{a [z + \gamma (1 - z)^2]}, \tag{22}$$

and, substituting Eq. (22) into Eq. (15), we obtain

$$\frac{dz}{d\tau} = \frac{P_0 - 2zP_0 + \left(P_0 - \frac{1}{\gamma}\right) z^2}{1 + \left(\frac{1}{\gamma} - 2\right) z + z^2}. \tag{23}$$

The latter equation together with Eq. (14) describe the whole process of light emission from the sample, both during the illumination by the external source ( $P_0 > 0$ ) between the times  $\tau = 0$  and  $\tau = \tau_{\text{ill}}$  and during the process of DL, after the source is switched off ( $P_0 = 0$ ), for  $\tau > \tau_{\text{ill}}$ . Integration of Eq. (23) between  $\tau = 0$  and  $\tau = \tau_{\text{ill}}$  gives the total quantum yield, that is, the total number of photons emitted by the sample. It is easy to obtain the explicit relation for  $z(\tau)$ :

$$\tau = \frac{\gamma}{P_0 \gamma - 1} z + A \log [R(z)] + B \log [S(z)], \tag{24}$$

where  $A$  and  $B$  are constants which depend on the parameters of kinetic rate  $\gamma$  and pumping  $P_0$ :

$$A(P_0, \gamma) = \frac{\gamma(2 + P_0) - 1}{2(P_0 \gamma - 1)^2},$$

$$B(P_0, \gamma) = \sqrt{\frac{\gamma}{P_0}} \frac{P_0 \gamma (1 + P_0) - P_0 + 1}{2(P_0 \gamma - 1)^2}, \tag{25}$$

and  $R(z)$  and  $S(z)$  are the polynomials:

$$R(z) = 1 - 2z + \left(1 - \frac{1}{P_0 \gamma}\right) z^2, \tag{26}$$

$$S(z) = \frac{1 - \sqrt{P_0 \gamma} \sqrt{P_0 \gamma + P_0 \gamma - (P_0 \gamma - 1) z}}{1 + \sqrt{P_0 \gamma} \sqrt{P_0 \gamma - P_0 \gamma + (P_0 \gamma - 1) z}}. \tag{27}$$

Analysis of Eq. (24) can be performed by inverting it numerically, both as a function of pumping  $P_0$  and dose  $D = P_0 \tau_{\text{ill}}$ . It is worth mentioning that, in the limit  $P_0 \rightarrow 0$ , Eq. (24) coincides with the corresponding relation of the correlated soliton model of DL [17].

### 3. Results and Comparison with Experimental Data

Analysis of the function  $z = z(D)$  has been performed numerically. It appears that, on fixing the value of parameter  $\gamma$ , the quantum yield first increases as the dose increases, then, for relatively large values of  $D$ , it reaches the saturation. Some results are showed in Fig. 1 for  $\gamma = 1, \gamma = 50$ , and different values of pumping:  $P_0 = 0.01, P_0 = 0.2$  and  $P_0 = 5$ .

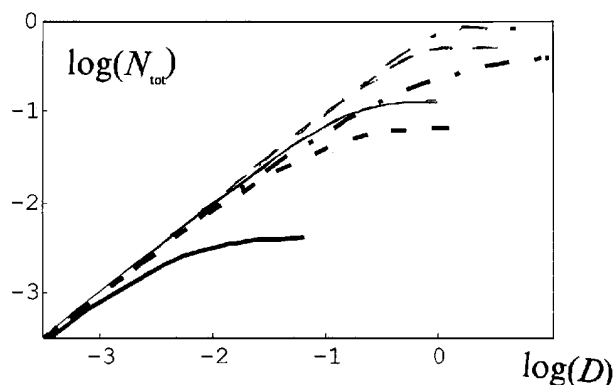


Fig. 1. Dependence of the quantum yield of DL on dose at various intensities of illumination:  $P_0 = 0.01$  (solid line),  $P_0 = 0.3$  (dashed line),  $P_0 = 5$  (dot-dashed line). Thick lines are plotted for  $\gamma = 1$ , normal lines for  $\gamma = 50$

The experiments consisted in illuminating the sample, composed of an A.a. cell placed in a plastic Petri dish filled with artificial sea water, with a pulse of selected wavelength and measuring the time dependence of the number of photons emitted. In the results reported below, we used a stimulating light of 565 and 585 nm produced by LEDs (Oshino OLUY153, OLUG153) that were fed by current from a stabilized power supply (Hewlett-Packard 6216A). The incident fluxes were:  $0.8 \cdot 10^{12}$ ,  $5.8 \cdot 10^{12}$ , and  $1.9 \cdot 10^{13}$  photon/(s  $\cdot$  cm<sup>2</sup>). The illumination times varied from 1 to 1000 s [24].

Fig. 2 represents the experimental data for algae A.a. and the theoretical fit for different values of pumping:  $P_0 = 0.05$ ,  $P_0 = 0.36$ ,  $P_0 = 6.75$ , and  $\gamma = 10$ . This value of the kinetic rate corresponds to the best fit obtained for the experimental data on the DL kinetics from algae A.a. [17]. The experimental results are indicated by different markers for different values of the intensity of illumination. By comparing the experimental data with theoretical results, we conclude that the correlated soliton model for DL in the presence of pumping explains not only the time behaviour of DL [16, 17], but also the non-linear dependence of the total quantum yield of DL on the intensity and dose of illuminating light for relatively high values of impinging dose up to saturation.

## Conclusion

The model developed in the present paper, takes into account the process of illumination. It provides both the qualitative and quantitative explanations of the main characteristics of DL from alga A.a.: the non-linear dependence of the intensity of DL on the intensity of the impinging light, the hyperbolic behaviour of the time decay, and the same time trend

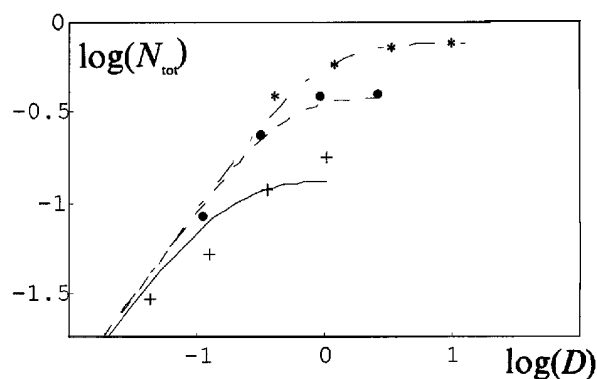


Fig. 2. Fitting of experimental data for algae A.a. on log-log scale. Theoretical results (lines) are plotted for  $\gamma = 10$  and different values of  $P_0$ :  $P_0 = 0.05$  (solid line),  $P_0 = 0.36$  (dashed line) e  $P_0 = 6.75$  (dot-dashed line). Markers correspond to experimental data (in arbitrary units) for different values of the intensity of illuminating light  $I_{ill}$ :  $I_{ill} = 0.08$  (+),  $I_{ill} = 0.58$  (•),  $I_{ill} = 1.87$  (\*)  $\times 10^{13}$  photon/(cm<sup>2</sup>  $\cdot$  s)

for different spectral components. Moreover, the model shows, in good agreement with the experimental results, the non-linear dependence of the total quantum yield on the dose and intensity of illumination. The quantum yield first increases as the dose increases and then, for relatively high values of dose, it reaches some saturation. However, experimental results show a decreasing of the quantum yield for very high values of impinging dose. To explain this behaviour, we retain that further investigations are necessary, taking into account the inhibition of photosystems [26 - 28]. In particular, we suggest (this work is in progress) to consider the process of illumination as a non-linear function of the number of ionized reaction centers.

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