

Some aspects of scintillation mechanism in organic molecular dielectrics

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Abstract - Aspects of the scintillation mechanism in organic systems obtained on the base of precise measurements of the radioluminescence pulse shape are discussed. It shown that the process of scintillation light pulse formation is mainly determined by initial conditions of excited states generation.

Key words : *Scintillation, excited states, triplet-triplet annihilation, particle track.*

INTRODUCTION

The foundations theory of the scintillation process in organic materials was laid in the early 60th [1-3]. It was grounded on a series of assumptions accounting only in part the radioluminescence specific features. The theory of formation of slow component had it own problems. It was used the diffusion approach without checking of limits of its applicability for description of the process of energy exchange of triplet excitations in the regions of a high activation density (tracks, blobs, spurs). This approach was based on the model of diffusion - controlled triplet - triplet (*T-T*) annihilation, which is right when concentration of triplet states (*T*-states) is low and their interaction is defined by diffusion process. This process as well as process of high activation density region formation has to be caused by specific energy losses dE/dx of initial ionising particle. This relationship was unknown and neglected by the theory of 70th - 80th [1-5]. It results in three orders of a magnitude difference of the values of diffusion constant D_T of *T*-states had been obtained from radioluminescence experiment on base of these assumptions and the same D_T been known from photoluminescence measurements [2].

THEORY

A heavy ionising particle initiates ionization and excitation of molecules of substance by direct Coulomb interactions on distances up to several molecular diameters (see Figure 1). Secondary high-energy electrons create short tracks. Particles with high specific energy losses dE/dx form the regions of high activation density whose symmetry is close to cylindrical one, and particles with low dE/dx form such regions with spherical symmetry in the mean. An increase of dE/dx results in a rise of that part of energy of a particle, which is lost in the region of such a track. In high activation density regions, triplet (*T*) excited states are mainly generated, while in low activation density regions, singlet (*S*) ones are dominating. The ratio between the number of *T*-states and *S*-states for high activation density regions is 3:1, and for low activation density regions $10^{-6}:1$ [5]. Therefore, the processes in the regions of a particle track determine the mechanism of delayed radioluminescence pulse formation; whereas ones outside of a track determine the mechanism of the prompt radioluminescence.

The delayed radioluminescence is formed in the regions of high activation density where

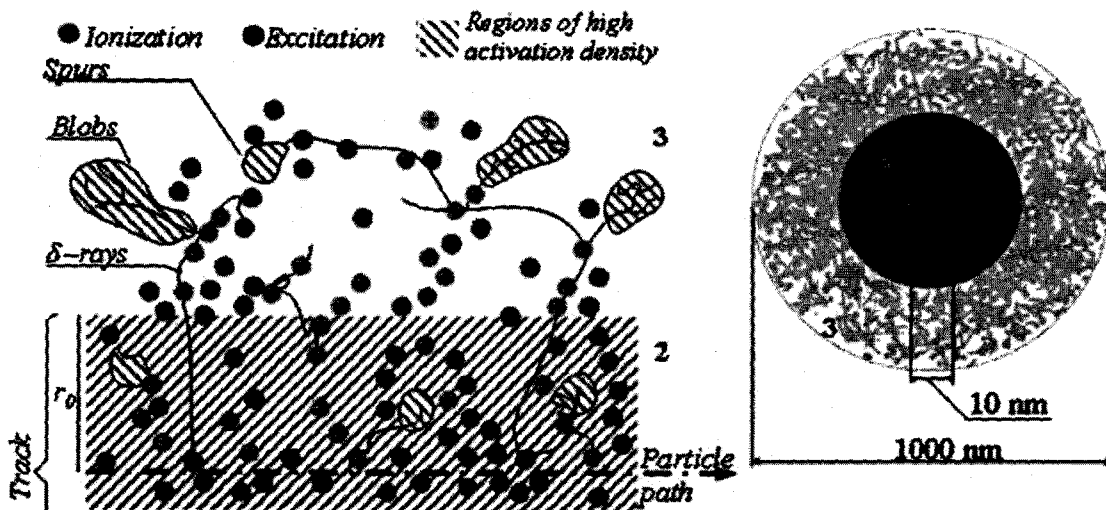
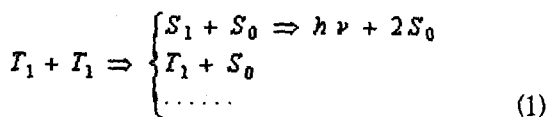


Fig. 1. Schematics presentation of initial excitation processes in a substance caused by ionizing particle with high specific energy losses: 1 is the "core" of track; 2 is the regions of high density of activation ("halo" of track); 3 is the regions of low density of activation, $r_0 = 50-100$ nm for $dE/dx = 10^4 - 10^2$ MeV/cm (see Table 1); values of cross section diameters were taken from [6].

the concentration of triplet-excited states is large and therefore the process of $T-T$ annihilation (1) has a large probability. It can result in energy quenching, when the concentration of T -states is too high, or can result in delay luminescence (with light photon energy $h\nu$ (see first equation in (1))) when the concentration of T -states decrease so that the process of $T-T$ annihilation is defined by diffusion of T -excited states:



Process of delay radioluminescence can be describe by system of kinetic equations

$$\begin{cases} \frac{\partial C_T(r,t)}{\partial t} = D_T \Delta C_T(r,t) - \beta_T C_T(r,t) - F_{TT}(r,t) \\ \frac{\partial C_S(r,t)}{\partial t} = D_S \Delta C_S(r,t) - \beta_S C_S(r,t) + \frac{F_{TT}(r,t)}{2} \end{cases} \quad (2)$$

In system (2) $C_T(r, t)$ and $C_S(r, t)$ are concentrations of T_1 and S_1 states, D_T and D_S

are their diffusion constants; b_T and b_S are probabilities of monomolecular losses of T_1 and S_1 states, respectively. Collision integral $F_{TT}(r,t)$ describes a probability of bimolecular quenching of T -states. So, when the third term in the right part of the first equation of system (2) is of primary importance (concentration-controlled $T-T$ annihilation) then the specific quenching defines the process (1), when the second term is of primary importance then the exponential decay luminescence can take place, and when the first term will be of primary importance (diffusion-controlled $T-T$ annihilation) a delayed radioluminescence takes place [5, 7].

It was shown [8] that due to intensive concentration-controlled $T-T$ annihilation process for the times $0 < t < t_i = 50$ ns after excitation the concentration C_T of T -excited states in tracks falls appreciably and approach based on the model of diffusion-controlled triplet-triplet ($T-T$) annihilation becomes real. E.g., for alpha particles (dE/dx is about 10^4 MeV/cm) C_T decreases from 10^{18} cm^{-3} to 10^{16} cm^{-3} . Really, for relatively weak bimolecular quenching (when $C_T = 10^{16}$ cm^{-3}) [7] the collision integral is described as:

$$F_{IT}(t) = \int W(r) N_r dr \approx \gamma C_T^2(t), \quad (3)$$

where $W(r)$ is the probability of bimolecular quenching of T -excitons separated by the distance r , N_r is the number of pairs of such T -excitons per unit of volume, γ is the constant.

Solving the system of kinetic equations (2) for the case of condition (3), i.e. for the process of delayed radioluminescence [3, 4], one can obtain the shape of the scintillation pulse slow component in a form [5, 6]:

$$I(t) \approx \text{const} \cdot \left(1 + \frac{t}{t_D}\right)^{-k}, \quad (4)$$

with

$$t_D = \frac{r_0^2}{4D_T}, \quad (5)$$

where t_D is an approximation constant describing characteristic time of diffusive track expansion, k is a constant, which is equal to 1 for cylindrical symmetry (high dE/dx), and equal to 3/2 for the regions of spherical symmetry (low dE/dx), e.g. for average spur. For $C_T < 10^{14} \text{ cm}^{-3}$ ($t > 2 \mu\text{s}$) the process of delayed radioluminescence pulse formation does not correspond to the conditions of the diffusion approach and the pulse shape is described by time exponential function [8].

Experiments and discussion

The radionuclide source ^{137}Cs (conversion electrons with the energy $E_r = 0.622 \text{ MeV}$) were used for light yield measurements. The radionuclide sources of particles (^{241}Am , dE/dx is about 10^4 MeV/cm), neutron (^{252}Cf , Pu-Be, dE/dx is about $10^1 - 10^2 \text{ MeV/cm}$) and photons of radiation (^{60}Co , dE/dx is about 10^2 MeV/cm) were used for the measurements of the delayed radioluminescence pulse shape.

Table 1 shows results of investigation the delayed radioluminescence of organic single crystals irradiated by different types of ionising radiations. The calculation of parameter t_D (5) has been carried out as follows. Parameter k is determined by approximation of experimental curves (see e.g. Figure 2) with linearized relationship (4):

$$J_k(t) = \{I(t)\}^{-1/k} \approx At + B, \quad (6)$$

where A, B are approximation constants. After that, a value of parameter t_f was varied. It has been obtained, that parameter k can be approximated as a constant since the moment of time $t > t_f = 50 \text{ ns}$ for all samples under investigation.

Difference between $k = 1$ and values k obtained in experiments for particles (^{241}Am),

Table 1. Values k , r_0 and t_D for anthracene single crystal for different types of ionising radiation obtained from results of scintillation pulse shape measurements.

Radiation*	k	r_0 , nm	t_D , ns
α particles (^{241}Am)	1.05	50	30
neutrons (^{252}Cf)	1.06	65	50
γ photons (^{60}Co)	1.44	100	120

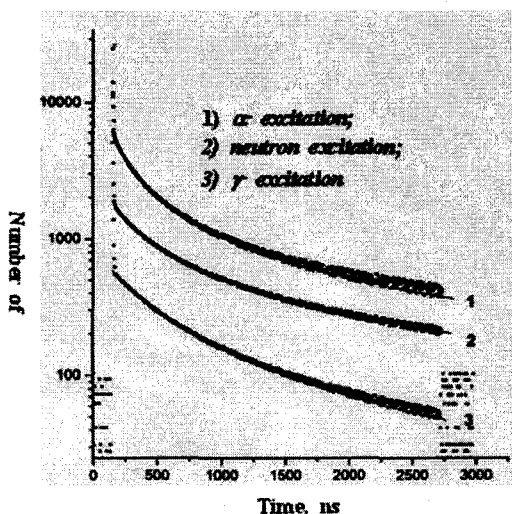


Fig. 2. Delayed radioluminescence pulse curves for stilbene single crystal and their approximation by Eq.(4).

neutrons (^{252}Cf), as well between $k = 1.5$ and k obtained in experiments for photons of gamma radiation (^{60}Co) gives the error of in definition of symmetry of high activation density regions for the cases under discussion. So, these results confirm cylindrical symmetry of tracks for ionising radiations with high dE/dx ($>10^1$ MeV/cm) and spherical one for radiations with low dE/dx ($<10^1$ MeV/cm). After that, using calculated values k one could determine characteristic time of diffusive track expansion t_D .

Having the values of t_D and taking the diffusion constant D_T of triplet excitons from the photoluminescence data, one can determine the mean values of cross-section radius r_0 of high activation density regions from equation (5). Let us calculate r_0 for anthracene single crystal irradiated normally to the ab plane (along the axis c). For such a situation, D_T is well known to be equal to $2\text{-}104$ cm²/s [7].

Using equation (5) one can obtain r_0 for different types of radiation. Table 1 presents the values of parameters k , r_0 and t_D for anthracene single crystal depending on the type of ionising radiation. Values of r_0 , in contrast to that of $r_0 = 10\text{nm}$ used in the theory of 70th-80th, are in a good agreement with the results of the studies of organic track detectors [6].

Conclusions

For times $0 < t < 50$ ns after excitation concentration-controlled $T\text{-}T$ annihilation reduces the concentration of T -states C_T . Since $t > 50$ ns the process of $T\text{-}T$ annihilation becomes quasi-stationary. Diffusion of T -states defines formation of slow component of scintillation pulse since $t > 50$ ns (i.e. when in our experiments $C_T < 10^{16}\text{cm}^{-3}$). For times $t > 2$ μs when ($C_T < 10^{13}\text{-}10^{14}\text{cm}^{-3}$) the non-radiative monomolecular quenching of T -states becomes one of the main process.

Figure 3 illustrates the time scale of the processes discussed. The knowledge of

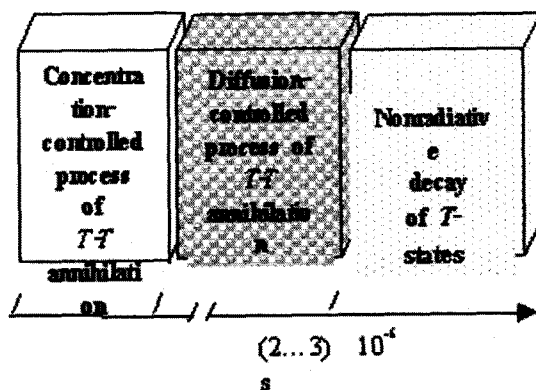


Fig. 3. Processes of triplet excitations energy exchange in the regions of high activation density.

parameters of diffusion-controlled $T\text{-}T$ annihilation process is useful for design measuring systems for neutron-gamma discrimination technique (see e.g. [9]).

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