Separate detection of ionizing radiation with different specific energy losses by organic heterostructured scintillators

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Molecular organic scintillation materials are the most effective objects for creating systems that detect various kinds of ionizing radiation, that the most harmful to humans (alpha particles, fast neutrons, etc.). In addition, organic crystals and liquids are capable to separate these types of radiation from photons of background gamma radiation. In these scintillators, ionizing radiation generates two types of luminescent response—prompt and delayed radioluminescence. Ionizing radiation with a high specific energy loss $dE/dx$, i.e. energy loss $E$ per unit path length $x$, generates a scintillation pulse in these media with a high proportion of the slow component. Recently, new types of scintillators have been developed, namely, heterogeneous organic scintillators containing single-crystal scintillation grains that can be combined by hot pressing sintering (polycrystals or Van der Waals ceramics) or can be incorporated into a transparent gel composition (composite scintillators). The ability of heterogeneous organic scintillators to separate signals from radiation with different $dE/dx$ and the physical basis of this process in heterogeneous scintillation materials remain one of the urgent, unexplored problems.

This work presents the results of the study of the form of scintillation pulse shapes for the samples of organic single crystals, polycrystals and compositional scintillators based on stilbene in comparison with the same results obtained for $p$-terphenyl and anthracene for various types of ionizing radiation excitations. The peculiarities of the influence of the triplet-triplet annihilation process on the formation of a slow component of the radioluminescence pulse in these systems have being studied. We found that the ability of new types of organic heterogeneous materials (polycrystals and composite scintillators) to the separate registration of ionizing radiation in the shape of the scintillation pulse is close to the corresponding values that characterize this ability of structurally perfect single crystals.

Keywords: form of scintillation pulse, anthracene, stilbene, $p$-terphenyl, single crystal, polycrystal, composite scintillator.
Особливістю впливу процесу триплет-триплетної анігіляції на формування у цих системах повільного компонента радіолюмінесценційного імпульсу є те, що здатність нових типів органічних гетероструктурованих матеріалів (полікристалів і композиційних сцинтилляторів) до розбідної реєстрації іонізуючого випромінювання за формою сцинтилляційного імпульсу близька до відповідних значень, що характеризують цю здатність для структурно досконалих монокристалів.

Ключові слова: форма імпульсу радіолюмінесценції, стильбен, n-терфеніл, антрацен, монокристал, полікристал, композиційний сцинтиллятор.

Роздільна реєстрація іонізуючого ізлучення з різними удельними потерями енергії з гетероструктурованими сцинтилляторами

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Molecular organic scintillation materials are the most effective objects for creating systems that detect the kinds of radiation, that the most harmful to humans (alpha particles, fast neutrons, etc.). In addition, organic crystals and liquids are capable to separate these types of radiation from photons of background gamma radiation. In these scintillators, ionizing radiation generates two types of luminescent response - prompt and delayed radioluminescence Ionizing radiation with a high specific energy loss dE/dx, i.e. energy loss E per unit path length x, generate a scintillation pulse in these media with a high proportion of the slow component. As an example of such ionizing radiation, one can cite recoil nuclei, alpha particles, low energy electrons, neutrons (as an example of indirectly ionizing radiation). Ionizing radiation with low dE/dx values (such as medium and high-energy electrons and photons of gamma radiation), in turn, generate scintillation pulses with a small portion of a slow component. In organic crystals, the slow component of the radioluminescence pulse occurs during triplet-triplet (hereinafter abbreviated T-T) annihilation of localized triplet molecular excitons (hereinafter T-states). If there is an effective diffusion transport of these triplet states, then they are able to localize on neighbouring molecules and, therefore, approach each other to such a distance when the exchange-resonance mechanism of their interaction becomes possible. In the case of a long-range inductive-resonance mechanism of energy transfer of electronic excitation, the quantum mechanical spin forbidding for transitions between energy states with different spins requires that the spins of each of the interacting molecules remain unchanged before and after T-T annihilation. These selection rules for the conditions of the exchange-resonance mechanism of electronic excitation energy transfer require only the conservation of the total value of the spins for both interacting molecules before and after T-T annihilation. The exchange-resonance mechanism of electronic excitation energy transfer becomes effective
only when the molecular orbitals of interacting molecules overlap, i.e. at extremely short distances between adjacent molecules. Such effects have been proven for organic single crystals and liquids [1 - 3].

Recently, new types of scintillators have been developed - heterogeneous organic scintillators containing single-crystal scintillation grains that can be combined by hot pressing sintering (polycrystals or Van der Waals ceramics) or can be incorporated into a transparent gel composition (composite scintillators) [4]. Previously, the features of the formation of the slow component of the scintillation pulse and its presence for these heterogeneous organic scintillators were not studied, but were given only as an experimental fact [5 - 8]. Therefore, the ability of heterogeneous organic scintillators to separate signals from radiation with different dE/dx and the physical basis of this process in heterogeneous scintillation materials remain one of the urgent, unexplored problems.

**Theory**

The appearance of electronically excited states can precede molecular luminescence not only as a result of optical excitation (photoluminescence), but, e.g., in the case of radioluminescence, i.e., as a result of excitation by ionizing radiation. In the latter case, under the action of ionizing radiation, charge pairs arise, the recombination of which precedes the formation of the luminescent signal [2, 3]. Eq. (1) describes the recombination process for such pairs (both homogeneous and heterogeneous):

\[
S_1^* + e \rightarrow S_1^* + S_1
\]

where \(S_1^*\), or \(T_1^*\), and \(S_1\), or \(T_1\) are highly excited energy states, and the lower excited states (singlet or triplet), and \(h\) and \(e\) are molecules with an uncompensated negative charge and with an excess electron, respectively.

The generation of singlet states leads to the appearance of prompt radioluminescence arising because of the allowed (according to the spin selection rules) optical transition:

\[
S_1 \rightarrow S_0 + \nu
\]

In equation (2), \(\nu\) is the frequency of the prompt radioluminescence photon and \(h\) is Planck constant. The appearance of the prompt radioluminescence leads to the formation of the fast component of the scintillation pulse. Its decay time \(t\) for effective organic scintillators is in the range from 0.4 to 30 ns [1, 4].

The formation of the slow component occurs by another mechanism for the exchange of excitation energy. At small distances between triplet-excited molecules, when molecular orbitals overlap, an exchange interaction between two \(T\)-states (3) becomes possible. As it mentioned above, it is the case when the sum of the spins of both molecules before and after the interaction can change as a result. The following reactions become possible [1 - 4]:

\[
T_1 + T_1 \rightarrow Q + S_0
\]

Reactions that result in formation of quintet states (\(Q\)), as well as states with higher multiplicities, require the simultaneous change in the wave functions of more than two electrons. In such a situation, ionization becomes energetically more likely. For this reason, the appearance of quintet states, as well as states with higher multiplicity, for the above systems is not energetically favorable [3].

In the process (3), the emission of scintillation photons is delayed by the time required for two \(T\)-states to meet each other. Therefore, this type of luminescence is called "delayed luminescence." A slow component of the radioluminescence pulse is forming, lasting from hundreds of nanoseconds to microseconds. From the above estimates, it becomes obvious that at the initial moments of time \(t\) after excitation, the intensity of fast component determines the shape of the scintillation pulse and masks the luminescence that forms it the slow component. For large times \(t\) after excitation \((t > r)\), the contribution of fast luminescence to the total luminescence should be negligible.

According to expression (3), the following system of kinetic equations describes the change in the concentration of \(T\) and \(S\) states [4, 5]:

\[
\begin{align*}
\frac{dC_T(r,t)}{dt} &= D_T \Delta C_T(r,t) - \\
&- \beta_T C_T(r,t) - F_{rT}(r,t); \\
\frac{dC_S(r,t)}{dt} &= D_S \Delta C_S(r,t) - \\
&- \beta_S C_S(r,t) + (f / 2) F_{rT}(r,t)
\end{align*}
\]

where \(C_T(r,t)\) and \(C_S(r,t)\) are the concentrations of \(T_1\) and \(S_1\) states, respectively, which arise at a distance \(r\) from the trajectory of the particle at time \(t\) after its passage. In system of equations (4) \(\beta_T\) and \(\beta_S\) are the probabilities of the monomolecular decay of \(T_1\) and \(S_1\) states, \(D_T\) and \(D_S\) functions.
are the diffusion coefficients of these states, respectively. The third term in the first equation of system (4) is the collision integral:

$$F_T(r, t) = \int \frac{w(R)N_g(t)dR}{2}.$$  \hfill (5)

where \(w(R)\) is the probability of bimolecular quenching of \(T_1\) states Eq. (3) that are at a distance \(R\) from each other; \(N_g(t)\) is the number of such pairs per unit of volume. The concentration of \(T_1\) states determines the average distance between them and the type of their interaction. For large values of the concentration \(C_T(r, t)\) Eq. (5) describes its rapid decrease in time. Such type of \(T-T\) annihilation is the concentration-controlled non-radiative process. Due to such intense primary blanking, a further change in CT \((r, t)\) as a result of the T-T annihilation process is significantly slowing down. From some time \(t_f\) after excitation, the process (3) of quenching of \(T_1\) states becomes slow, and from \(t > t_f\), we have:

$$F_T(r, t) \int_{-\infty}^{0} \gamma C_T^2(r, t)$$ \hfill (6)

where \(\gamma\) is the time-independent effective kinetic coefficient that determines the disappearance of \(T_1\) states after their collision. In the situation when (6) holds, then the change in the concentration of \(T_1\) states determines the first term of the first equation in (4). It determines the rate of diffusion expansion of the region where the \(T_1\) states are concentrated. \(T-T\) annihilation becomes a diffusion-controlled process. The solution (4) if (6) in the approximation of the so-called “given” diffusion is described in detail in [2].

If we denote the characteristic time of the process of diffusion displacement by the distance \(r_0\) as:

$$t_p = r_0^2 / 4D_T.$$  \hfill (7)

then according to [2] for the time range \(t_f < t < t_{ph}\) (where \(t_{ph}\) is the time of phosphorescence, i.e. direct transition \(T_1 \rightarrow S_0 + h\nu_{ph}\)), we obtain that for the time \(t\) after excitation the number of emitting photons of delayed radioluminescence is equal to [1 - 3]:

$$N(t) = N_0 \exp \left[ -2\beta_T t \right] \left(1 + t / t_D\right)^{-1/2}.$$  \hfill (8)

where \(N_0\) is the initial number of \(T_1\)-states (in real approximation plays the role of the normalizing factor), \(\beta_T\) is the same value as in the first equation of system (4), \(l\) is dimension of \(T_1\)-states diffusion. Eq. (7) describes \(t_p\). When the value of \(\beta_T\) for a given sample is fixed in time, instead of (8) we obtain [1, 3, 4]:

$$N(t) = (1 + 4Dt / t_D^2)^{-1/2}.$$  \hfill (9)

According to (9), the shape and intensity of the slow component of the scintillation pulse should depend significantly on the specific energy losses of the \(dE/dx\) ionizing particle. Indeed, the quantities \(l\), \(D_T\), and \(r_0\) determine the shape of the slow component according to (9). The \(T\)-state diffusion coefficient of \(D_T\) and the dimension of this diffusion \(l\) depend on the characteristics of the object. At the same time, both the parameter \(r_0\) and the above-mentioned dimension of this diffusion \(l\) will be determined not only by the properties of the object, but also by the conditions of excitation, i.e. \(dE/dx\) of the ionizing particle. Comparing (8) and (9), we can conclude that the factor \(N_0\), which is not taken into account in (9), is proportional to the number of initial \(T\)-states (for small \(\beta_T\)) which will determine the intensity of the slow component. It also depends on the values of \(dE/dx\).

Experimental

The samples of single crystals and polycrystals had a cylindrical (diameter \(D\) and height \(h\)) or cubic form. We also investigated composite scintillators of size \(30 \times 30 \times 20 \text{mm}^3\). We used the optimal fraction of grain sizes (from 1.7 to 2.2 mm) to obtain heterogeneous organic scintillators with high light output (for more information, see [9]).

Fig. 1 shows a block diagram of a simple installation for measuring the kinetics of radioluminescence by a single-photon method. It can be used, e.g., to the study of the slow component of the scintillation flare, when high temporal resolution is not required. An ionizing particle of a radionuclide source of ionizing radiation (SIR), entering the test sample (S), ionizes and excites its molecules, causing the appearance of a pulse of radioluminescence. The sample is in optical contact with a photoelectron multiplier, which we will call “start” photomultiplier tube (PEM 1). The signal at the output of the starting photomultiplier tube gives the information about the time of arrival of the particle. Photons of radioluminescence through the diaphragm D get to the photocathode of another photomultiplier tube. It is so-called “stop” photomultiplier tube (PEM 2). The time-to-amplitude converter (T-A) generates signals of constant duration, the amplitude of which is proportional to the time interval between the arrival of signals in the “start” and “stop” channels. The multichannel amplitude analyser (MAA) analyses the amplitude spectrum of the signals at the output of the T-A converter. The single photon method allows determining the time parameters of a radioluminescence pulse. According to this method, the time intervals between the excitation of the scintillator
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(“start” signal) and the moment of detection of a random single photon by the “stop” photomultiplier tube [10].

Fig. 1. The block diagram of the set up for measuring the parameters of the kinetics of radioluminescence by single-photon method: D is diaphragm, S is sample that is in optical contact with the “start” photomultiplier tube (PMT 1), PMT is the “stop” photomultiplier tube, IRS - ionizing radiation source, CF is constant fraction discriminator that analyzes the signal from an anode of a photomultiplier tube, T-A is time-amplitude converter, MAA is multi-channel amplitude analyzer, CU is coincidence unit, DL is delay line, which compensates for the start pulse delay time and allows us to shift the radioluminescence kinetics curve on the screen of MAA.

To separate a signal from one type of excitation, e.g., neutrons in the presence of background gamma radiation, it is necessary to use special electronic units, which separate the signals from different types of ionizing radiation. Fig. 2 shows a block diagram of the set-up that we used to separate radioluminescence signals excited by radiation with different specific energy losses $dE/dx$. The separation of signals that are excited by ionizing radiation with large and small $dE/dx$ is based on a comparison of the relative contributions of the slow and fast components of the radioluminescence pulse, i.e., the value that increases with increasing $dE/dx$. The spectrometric signal was accumulated in the memory of the analyzing device depending on what determined the formation of the digitized signal at the control outputs. If a signal from radiation with small values of $dE/dx$ is recorded (for gamma-ray photons $dE/dx \sim 10^{-1} - 10^{-2}$ MeV / cm), then the contribution of the slow component of the pulse is small, and the control signal was formed at the control output "$\gamma$". If radiation with large $dE/dx$ values is recorded (for recoil protons generated by fast neutrons $dE/dx \sim 10^{1} - 10^{2}$ MeV / cm, and for alpha particles $dE/dx \sim 10^{3}$ MeV/cm), a control signal was generated at the control output "$n$". Details of the operation of the set-up see in [11].

Fig. 2. The block diagram of the experimental set up for separate detection of the signals from radiations with different $dE/dx$.

As a MAA (Fig. 1), can be also used a personal computer that analyzes and memorizes the signal from the amplitude-to-digit converter. A delay line is required to select the most convenient location of the recorded curve on the analyzer screen. Changing its length by joining additional calibrated delay lines allows you to shift the signal on the abscissa scale and thereby calibrate this scale as a timeline.

The experimental points of the curves of the kinetics of radioluminescence were approximated by the following method. It was initially taken into account that the value of the curve rise time constant is practically determined by the increase in the momentum of instantaneous radioluminescence (the fast component of the scintillation pulse), as well as the fact that the decay of the fast component is much less than the characteristic decay duration of the slow component. Therefore, the fast component was described as a convolution of the exponent describing the growth of the fast component with a constant time $\tau_1$, and the exponent describing the attenuation of the fast component with a constant time $\tau_2$. For this, the experimental points of increasing the experimental curve and its initial part of the attenuation, which satisfy the exponential approximation (10), were performed. That is, the fast component was approximated by the formula:

$$N(t) \mid_{t=\tau} \sim N_0 \left\{ \exp(-t/\tau_2) - \exp(-t/\tau_1) \right\}$$

(10)

The value of $t = t_k$ we determined by the linear approximation of the initial damping plot of the experimental curve by the least-squares method, as a boundary value satisfying the equation of the line:

$$\ln N(t) = a + bt.$$ 

(11)
The time distribution of the experimental points of the slow component we obtained because of subtracting the values of the fast component from the experimental values. Fig. 3 illustrates the above procedure.

![Fig. 3](image)

**Results and discussion**

Fig. 4 - Fig. 6 demonstrate the results of studies of the radioluminescence pulse shape of some samples of organic scintillators. Each of the figures shows the results obtained for the above three types of radiation excitation. For a clear demonstration of the ratio of components to the overall pulse shape, each curve we normalized to its maximum.

![Fig. 4](image)

Table 2 shows the \( \beta_i \) values. These values are equal to the ratio \( \rho_i / \rho_{\gamma} \), where \( \rho_i \) are the \( \rho \) values obtained for excitation by gamma-excitation photons.

The calculation of the areas under the curve for various components of the scintillation pulse led to the ratio of the contributions of the slow \( N_S \) and fast \( N_F \) components (12) of the scintillation pulse:

\[
\rho = N_S / N_F.
\]

(12)

Table 1 presents the calculation data of \( \rho \) - values (12).
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Table 1.

| Sample                     | $\rho$ value depending on the type of excitation | $^{239}$Pu | $^{239}$Pu-Be | $^{152}$Eu |
|----------------------------|-----------------------------------------------|-----------|--------------|-----------|
| Stilbene single crystal    |                                               | 0.46      | 0.29         | 0.14      |
| Stilbene polycrystal       |                                               | 0.36      | 0.22         | 0.11      |
| Stilbene composite scintillator |                                         | 0.47      | 0.23         | 0.19      |
| p-Terphenyl single crystal |                                               | 0.36      | 0.17         | 0.13      |
| p-Terphenyl composite scintillator |                                         | 0.34      | 0.12         | 0.09      |
| Anthracene composite scintillator |                                         | 0.36      | 0.1          | 0.16      |

Table 2.

| Sample                     | $\beta$ value depending on the type of excitation | $^{239}$Pu | $^{239}$Pu-Be | $^{152}$Eu |
|----------------------------|-----------------------------------------------|-----------|--------------|-----------|
| Stilbene single crystal    |                                               | 3.3       | 2.1          | 1         |
| Stilbene polycrystal       |                                               | 3.5       | 2            | 1         |
| Stilbene composite scintillator |                                         | 2.5       | 1.2          | 1         |
| p-Terphenyl single crystal |                                               | 2.7       | 1.3          | 1         |
| p-Terphenyl composite scintillator |                                         | 3.7       | 1.3          | 1         |
| Anthracene composite scintillator |                                         | 2.3       | 0.6          | 1         |

Conclusions.

The main results of the work are the following.

1. Heterogeneous scintillators have significant potential in terms of their use for the separation of ionizing radiation. The data obtained for these systems are close to those obtained for single-crystal samples.

2. Stilbene-based scintillators have the highest separation capability.

3. $p$-Terphenyl based scintillators are promising for separation problems.

4. Anthracene-based scintillators, given their high light output [1, 2], are perhaps best to use for detecting alpha particles.

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