Scintillation primary quenching in organic condensed media revisited

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The revised model of the scintillation process in organic condensed media takes into account the fundamental influence of the polarization effects on the processes proceeding in a track of ionizing particle. A very fast process of the primary quenching of the hot polaron pairs is the first "step" of "specific quenching". It defines the future processes of formation both fast and slow components of a scintillation pulse. The secondary quenching is the second "step" of "specific quenching". It takes place after track formation and thermalization. It results in decrease of the number of charge states and excited molecules. The influence of the primary quenching on "specific quenching" process is much stronger than the influence of the secondary quenching.

Уточненная модель сцинтилляционного процесса в органических конденсированных средах учитывает определяющее влияние поляризационных эффектов, протекающих в треке ионизирующей частицы. Очень быстрый процесс первичного тушения горячих поляронных пар — это первый "этап" "специфического тушения". Он определяет последующие процессы формирования как быстрой, так и медленной компонент сцинтилляционного импульса. Вторичное тушение является вторым "этапом" "специфического тушения". Этот процесс протекает после формирования и термализации трека. Влияние первичного тушения на "специфическое тушение" гораздо сильнее, чем влияние вторичного тушения.

The so-called effect of "specific quenching" for organic scintillators is well known from the 1960's [1]. Heavy particles (even such as protons or alpha particles) or electrons of low energies (i.e. energies $E \leq 120$ keV) i.e. ionizing radiations those have specific energy losses dE/dx about and higher than 10^1 MeV/cm produce scintillation pulses with lower energy efficiency in comparison with photons of gamma radiation of middle energies [2, 3]. The process that causes such additional losses, which growth with dE/dx increase, is called as "specific quenching". For the case when "specific quenching" takes place, the light yield (LY) of an organic molecular scintillator increases non-linearly with the particle energy E growth and decreases with dE/dx

increase [2]. Many scientists have studied this fundamental problem of scintillation technique, but until now, there are more questions than answers. This paper presents the brief analysis of results obtained in this field up to quite a recent time was done in this paper to refine the model of scintillation process in organic molecular scintillators.

One aspect of this problem is the following. If a high concentration of primary states causes the effect of "specific quenching" [1] and results in non-linearity of scintillation response, then this concentration can decrease for one of the following two reasons. They are i) the exchange interaction between charge states (the recombination of charge states), and ii) diffusion ex-

pansion of particle track. The influence of luminescence, the excitation energy transfer, trapping of the charge states at some distance from the track, etc. has to be the same for excitations when track is formed (e.g. recoil protons, alpha particles) and for excitations when track is not formed (e.g. excitation be photons of gamma radiation of middle energies E_γ). To estimate the direct influence of the processes in track on non-linearly of scintillation response we introduced the following value [3]:

$$\zeta_{i,\gamma} = \left(\frac{M_i}{E_i}\right) \Big/ \left(\frac{M_\gamma}{E_\gamma}\right) = \frac{E_\gamma}{E_i}\bigg|_{M_i=M_\gamma}, \qquad (1)$$

where M_i and M_γ are the number of scintillation photons those are generated by ionizing radiation of i-type (when track is formed) and by photons of gamma radiation with energies of E_i and E_γ, respectively. E.g., for the case of alpha excitation the $\zeta_{\alpha,\gamma}$-value (1) gives the ration between the energy E_γ, which is necessary to produce M scintillation photons in a given scintillator, and the energy E_α, which is necessary to produce the same number M of scintillation photons in the same scintillator as well as to compensate the energy losses in track of alpha particle of energy E_α. Therefore, value (1) has to be always less than one and decreases with quenching effect increase. Such a value shows the ratio between the excitation energy that is necessary to produce M scintillation photons in the scintillator and the total energy losses of excitation in the scintillator those are necessary when ionizing radiation forms the track. The values of $\zeta_{i,\gamma}$ (1) allow us to study the influence of recombination of primary states and the diffusion expansion of a track on "specific quenching". Let us suppose that we used the scintillators constructed from the same scintillation material but with greatly different structural ordering. In different experiments, ionizing radiations, which have the different specific energy losses in the scintillation material, irradiate such the scintillator. All other measuring conditions are the same in such a series of light yield measurements. If the primary quenching is an extremely fast process that takes place mainly over a short distance then the results obtained for the same type of excitation but for scintillators
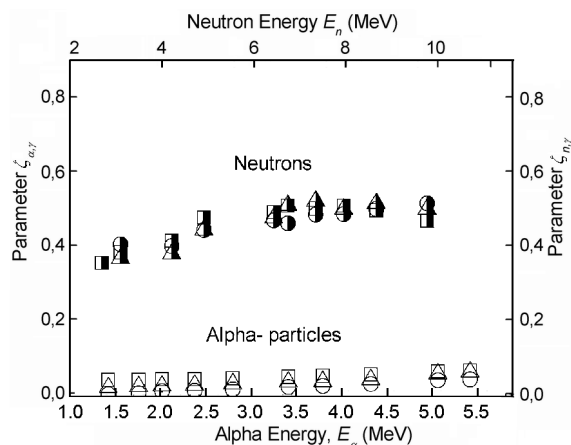

Fig. 1. The $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values (lower and upper family of curves) as a function of the energy of excitation. Squares, triangles and circles represent the $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values for single crystal, hot-pressed polycrystal and composite (1.7 to 2.0 mm grain size) stilbene scintillator, respectively. Half-filled symbols are from neutron excitation while open symbols are from alpha excitation.

with different structure ordering (i.e. the structurally perfect single crystal and scintillator with reduced transport of charge states inside the track) have to be very similar. If the primary quenching is weak and slow process then it influences on the decrease of primary charge states concentration (and therefore on light yield) and the influence of the diffusion expansion of track are comparable or even the influence of the last process is more important. In such a case, the difference in scintillation signals obtained for scintillators with different structural ordering has to be compared with the difference in signals obtained for one scintillator irradiated by different radiation, or has even to be higher.

In addition to organic single crystals with controlled structural perfection as highly ordering scintillation materials, we proposed the technology of production hot-pressed polycrystals, cold-pressed polycrystals, and composite materials made using the same scintillation materials [4]. Polycrystals and composite scintillators were made using grains of single crystals. Grains of a required size were obtained by grinding a single crystal with high structural perfection at a low temperature, followed by sieving. A solid recrystallization process took place in hot-pressed polycrystals, and the real size of the grains increased slightly
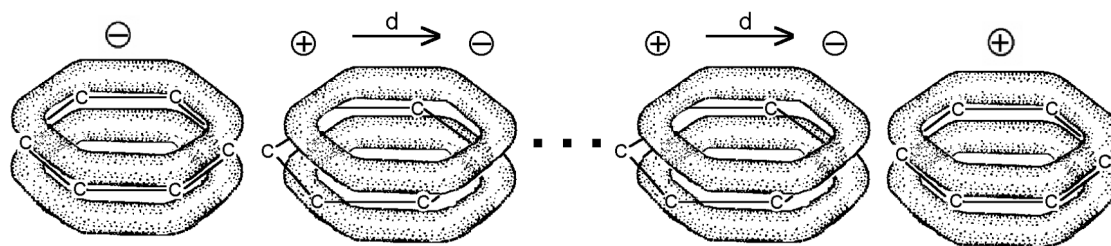
Fig. 2. Schematic diagram of polaron pair formation in a hypothetic molecular crystal that consists of benzene molecules.

compared to initial sizes. Composite scintillators were prepared by adding specific grain size fractions of a scintillation crystal to optically transparent glue. In our experiments, we used scintillators based on the same material (stilbene or *p*-terphenyl). Fig. 1 shows the $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values obtained for the scintillators on the base of stilbene. One can see that the difference of $\zeta_{i,\gamma}$-values for an organic single crystal, a polycrystal and a composite scintillator is negligible in comparison with the difference between $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values those were obtained for the same one scintillator. It means that the primary quenching in a particle track has to be a very fast and effective process that runs faster than a particle track size changes.

The polarization effects have the prime influence on the process of charge state formation, transport and recombination in organic molecular crystals [5]. The average time that is necessary for charge carriers to jump from one molecule to other in organic crystals τ_j is about 10^{-12} s. This time is necessary for a random jump of charge carrier to the next molecule. Therefore, value of τ_j gives the lower limit of a time for the diffusion expansion of a particle track on one molecular layer. The time τ_p that is necessary for electronic polarization of neighbouring molecules varies from 10^{-16} to 10^{-15} s. If in such an organic molecular dielectric some molecule loses an electron (i.e. the M_{p+} state is forming) then this electron has to localize onto some other molecule. This results in the formation of an M_{p-} state. Such a molecular quasi-ion polarizes about 7000 molecules around it [5]. A polaron pair (M_{p+}, M_{p-}) arises because molecular π-orbitals of neighbouring molecules have a negative charge and are attracted to the molecular quasi-ion for the case of M_{p+} state or are repelled from the molecular quasi-ion for M_{p-} state (see Fig. 2). Up to a distance r_C, which for organic crystals is about 13–16 nm, these two so-called CP-

states ([5]) behave like a bipolaron, i.e. the state that precedes and promotes the recombination, which results in molecular excitation or quenching. The time of molecular polaron formation is 10^{-15} to 10^{-14} s. The characteristic energy of such a polarization interaction is about 10^{-1} eV. It is greater by two orders of magnitude than the energy of Van der Waals' interaction that holds molecules in the lattice of a molecular single crystal [3, 5, 6].

The charge state transport between molecules of an organic crystal can be described as the intermolecular barrier tunnelling [5, 6]. Applied electrostatic field increases the charge transport with the field. For field strengths $E \leq 10^5$ V/cm, an effective mass of a charge carrier decreases with E-value increase. In a very strong field when $E \sim 10^6$ V/cm, which is comparable with the local field strength inside the polaron pair, the time of charge carrier scattering τ becomes an extremely small value and can be estimated as 10^{-14} s. E.g. the direct calculation of drift velocity for anthracene made on the base of experimental data gives τ = $8 \cdot 10^{-14}$ s that is comparable with the time of molecular polaron formation [5]. The charge carrier, that moves in an electric field with drift velocity higher than mean thermal velocity does not thermalize [5, 7]. According to [7] for time about 10^{-13} s after generation a charge carrier does not thermalize and is still a hot-carrier.

Recently [8, 9], we obtained the semi-empirical description of quenching processes in a track of an ionizing particle for organic crystalline scintillators. We proceed on the assumption that the quenching in track is a very fast process and runs faster than a particle track size changes. It was the first time when the influence of polarization interactions on polaron states recombination in the particle track was taken into account. The approximation of experimental results showed a good agreement with theoretical assumptions.

Let us rate above information under the aspect of description of the scintillation
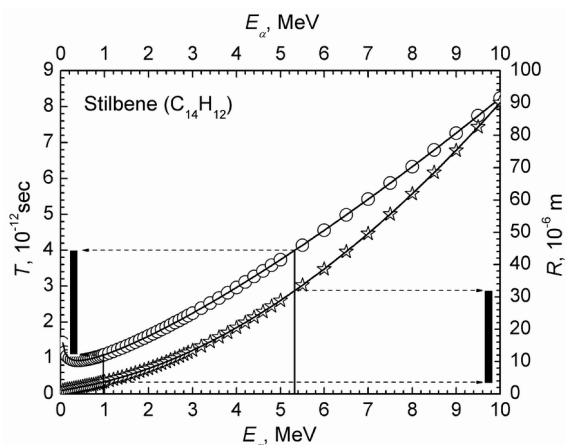
Fig. 3. Calculated values of the particle range R and the time of track formation T for alpha particles with energies E_α in stilbene.
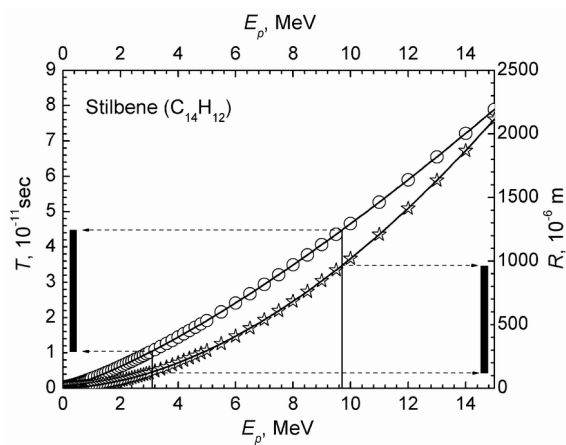

Fig. 4. Calculated values of the particle range R and the time of track formation T for protons with energies E_p in stilbene.
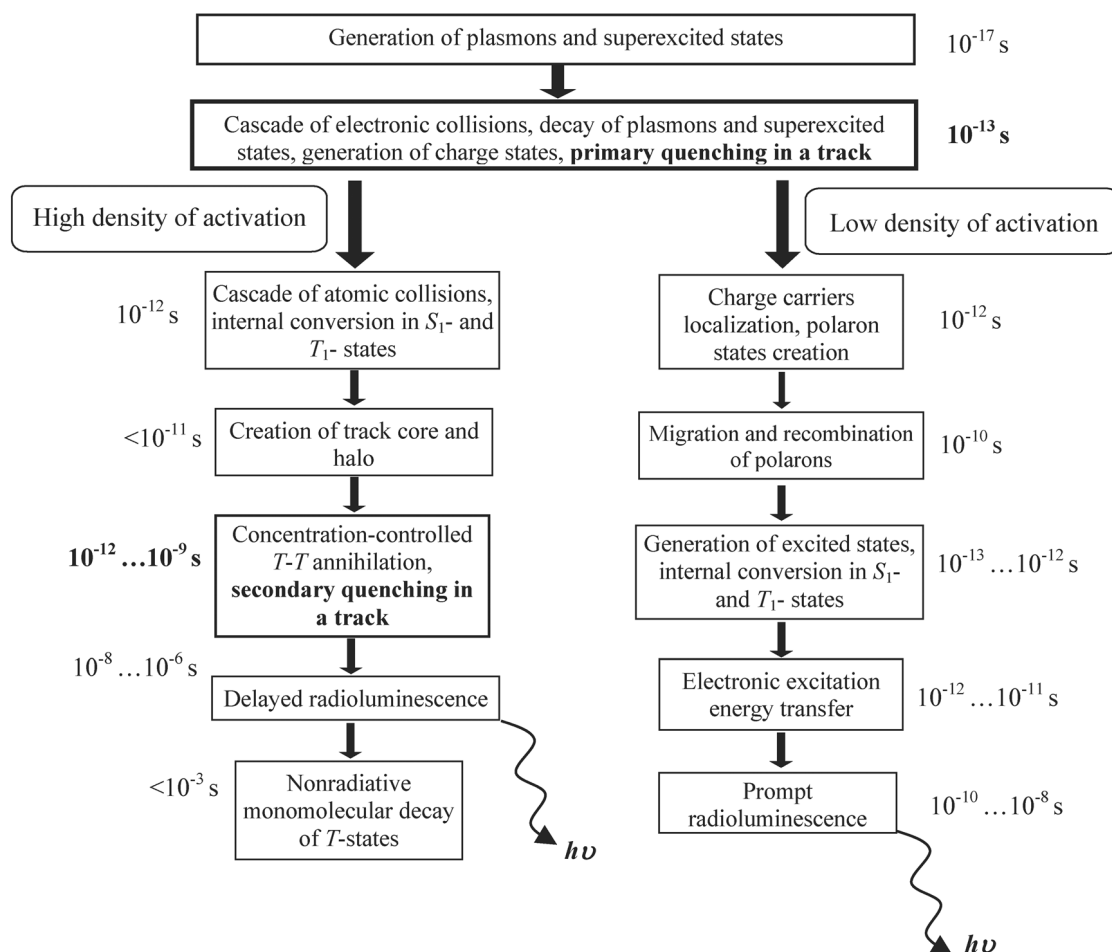

Fig. 5. The revised block diagram of the scintillation process in a molecular crystalline scintillator.

mechanism of organic scintillators. Figs. 3 and 4 shows the time T that is necessary for alpha particle and recoil proton to penetrate inside the scintillator on the distance that is equal to the length of track, respectively. To calculate these values we assumed that ionizing particle lost it energy in scintillator by slowing-down with constant value of acceleration. One can see that for the range of excitation energies that we

used in such experiments (see Fig. 1 and the ranges between dot lines on Figs. 3 and 4), the times of track formation T are about 10^{-12} s and are about 10^{-11} s for alpha particles and for protons, respectively. It means that the main quenching in track and thermalization of charge states in it is the faster process than formation the regions of low and high activation density. Therefore (see Fig. 5), the primary quenching process in track (as in the region of high activation density) accompanies the track formation. Simultaneously, it determines the formation of primary excitation of the region of low activation density (the region outside the track in which fast component of scintillation pulse is formed), because it controls the number of high energy secondary electrons those can left the track volume for concrete type of excitation. So, in contrast to up-to-date theory of scintillation process, according to which [3, 6] the main quenching has to take place in track and do not influence on the processes outside track volume, the cite results shows that the "specific quenching" has two "steps". The primary quenching (the first "step" of "specific quenching") is a very fast process in which the hot polaron pairs are involved. It defines the future processes of formation both fast and slow component of scintillation pulse. The secondary quenching (the second "step" of "specific quenching") takes place after track formation and thermalization, and results in decrease of the number

charge states and excited molecules, which is sufficiently weaker than for the primary quenching. It can influence only on formation of the slow component of scintillation pulse. The influence of the diffusion expansion of track on the secondary quenching process can be of primary importance [3, 6].

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До питання про первинне гасіння сцинтиляції в органічних конденсованих середовищах

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Уточнена модель сцинтиляційного процесу в органічних конденсованих середовищах враховує визначальний вплив поляризаційних ефектів, що відбуваються у треку іонізуючої частинки. Дуже швидкий процес первинного гасіння гарячих поляронних пар — це перший "етап" "специфічного гасіння". Він визначає наступні процеси формування як швидкої, так і повільної компонент сцинтиляційного імпульсу. Вторинне гасіння є другим "етапом" "специфічного гасіння". Цей процес протікає після формування та термалізації треку. Вплив первинного гасіння на "специфічне гасіння" набагато сильніше, ніж вплив вторинного гасіння.