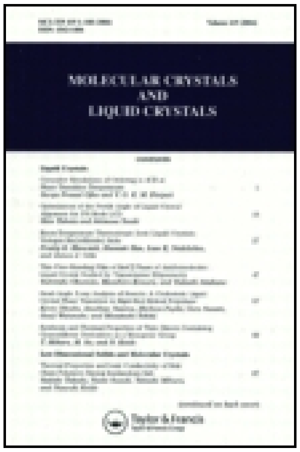

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Electronic Processes Causing the Radioluminescence of Organic Condensed Media

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The electronic processes causing the radioluminescence of organic single crystals, polycrystals, plastics and liquids are discussed. Material is based on the works of the authors in which they have formulated the main points of the modern theory of the radioluminescence mechanism of organic scintillators.

Keywords radioluminescence, polaron states, molecular solids and liquids.

INTRODUCTION

Scintillation is the act of radioluminescence (RL), i.e. the luminescence which appears as a result of ionizing radiation effect on a material. The first attempts to create the theory of the RL were made in 60-ies (see the review of materials in[1]). They based on the results obtained for the theory of the photoluminescence (PL). Such an approach practically didn't take into account the RL specific features, i.e. peculiarities of the process of charge carrier generation, transport and recombination in organic molecular materials. The first attempts to investigate the scintillation pulse shape in subnanosecond time range showed the incapability of the theory to explain the process of scintillation pulse formation[2]. The experiments made for high density of excitation[3,4] gave no possibility to explain them using the main postulates of the theory [1,2]. The theory of 60-ies and 70-ies was formed in absence of the experimentally proved theory of production of nuclear tracks in organic solids [5], as well as in that time when the first step in the polaron theory were just made[6]. Rewire of the situation with theory of prompt RL in 60-ies, 70-ies and 80-ies was given in[7] and for delay RL[8].

The investigation of the RL mechanism of organic solids and liquids[9-14] gives the possibility to understand the main features of scintillation process in organic condensed media and to develop the new theory of the RL of scintillation process in them[15,16].

THEORY

An ionizing radiation produces in organic medium low-energy secondary electrons with high dE/dx, and high-energy ones, (δ - electrons) with low dE/dx. The former ones are unable to leave the primary particle track region and form a region of high activation density (RHD) which symmetry close to cylindrical one for the primary particle with high dE/dx, and with spherical symmetry for the γ-rays, electrons, etc. The latter ones form their own tracks leaving the RHD. Their Coulomb interaction with molecules of substance results in formation of the regions of low density of activation (RLD). In RHD due to high concentration of charge states their recombination process results mainly in generation of the triplet (T) exited states, while in RLD the generation of singlet (S) ones are of the primary importance[1,14-16]. The prompt RL generated in RLD results in formation of the fast component of scintillation pulse, and due to the singlet channel of T-T - annihilation process in RHD delay RL takes place, i.e. the slow component of scintillation pulse is formed[1,2,10-16]. The pulse-shape of the prompt and delay RL are described by following functions

$$i_p(t) \sim f(t)*\exp(-t/\tau) \equiv \int_0^t f(t-\Theta)\exp(-\Theta/\tau)d\Theta \qquad (1)$$

$$i_d(t) \sim M(t)(1+t/t_D)^{-k} \qquad (2)$$

where "*" is the sing of convolution, t is the time after excitation, τ is the decay time constant of scintillation pulse fast component, $t_D=r_0^2/4D$, D is the diffusion coefficient of T-excitation, r_0 is the mean value of cross-section radius of RHD, k=1 and k=1.5 for the RHD of cylindrical symmetry and spherical one respectively. The Eq.(2) is valid for diffusion-controlled process of T-T annihilation, i.e. for times $t \geq 50$ns[11]. For the case of photoexcitation the function f(t) is exponential for nonviscous liquids and must be described according to Forster-Galanin kinetics for solids[1,16]

PROMPT RADIOLUMINESCENCE

Studies of the shape of scintillation pulse rise of plastic scintillators (PS)[2,7-9,11,13] , organic crystals (OC)[7-9,13] performed on the setups with subnanosecond time resolutions had given results inconsistent with predictions of the RL theory which was based on the solutions taken from the PL one[1]. There was no fast initial pulse rise with its following slow-down as it predicted by the theory for "rigin" solutions [1]. The slow initial pulse rise with it following speeding-up was observed. It was due to the additional delay of the movements of photon emission which was described by:

$$f_G(t) \sim \exp[-(t-q\sigma)^2/2\sigma^2] \qquad (3)$$

The pulse shape of pure and doped PS and OC was described by Eq.(1) with $f(t)=f_G(t)$ (see Eq.(3)). It was found that q ~ 3, σ ~ 0.2...0.26ns for PS, σ ~ 0.18...0.36ns for OC, and σ-value was the same for doped and undoped PS with the same type of base macromolecules. For high density of excitation σ-values decrease. For wide range of temperatures light yield of organic solid scintillators demonstrate the weak dependence upon temperature[16]. In contrast to solids for liquid scintillators (LS) the RL and PL kinetics were described by the same expression, i.e. by (1) with $f(t)\sim\exp(-t/\tau_l)$, where τ_l is the time constant[9].

It is quite reasonable to assume that the additional delay of moments of the RL photons emission described by expression (3) is due to the process of charge carrier generation, transport and recombination in solids, i.e. the process which is specific for RL and which is absent for PL. The charge carriers trapping by shallow traps for the mean time τ_t must result in the appearance of RL photons delayed for the same mean time τ_t. If the mean depth of traps is E_t then ([6])

$$E_t = kT\ln(\tau_t \nu) \tag{4}$$

where ν is attempt-to-escape frequency, k is the Boltzman constant, and T is the absolute temperature. For the values $\tau_t \sim 3\sigma$ one can obtain $E_t < 0.18$eV for OC and PS. It is shallow traps. It is reasonable that traps with large E_t couldn't influence of prompt RL formation because theirs $\tau_t > \tau$ (see Eq.(1)). Nevertheless, why for the systems with essentially different structure the very close σ-values (and therefore the E_t-values) were obtained?

In molecular organic solids the localization of a charge carrier on a structural trap results in polarization of it surrounding (molecules of OS or fragments of macromolecule of PS). It causes deepening the initial trap on the characteristic value δE_t which is almost the same for a wide variety of organic systems and is about 0.1eV[5,16]. In such a case the estimated depth of the initial structural trap is $E_t - \delta E_t \leq 0.07$ eV, i.e. is about 2kT at room temperature. Thus, the presence of very shallow traps which can be formed on the first stage only due to temperature - activated vibrations of the OC lattice or PS macromolecules fragments explains quite satisfactorily appearance of additional delay of RL photon emission described by Eq.(3). It can be shown[16] that function (3) has the Gaussian form due to plural nature of the process of such charge carrier localizations those form the time dependence of probabilities of excitation of the molecules in S-states. The localization time about 10^{-10}s is enough to form not only the molecular, but the lattice polaron as well[6]. It is known that the temperature dependence of mobilities for this two types of polarons are not only different but can "compensate" each other making the mobility of lattice - molecular polaron constant for wide temperature range[6]. Only such a mechanism can explain well-known fact of the very weak temperature dependence of light yield of the RL of organic solids in the range of -40...+60C^0 [16]. Only such a mechanism which takes account of the generation of the dynamic traps of polarization origin (those can move through the organic system as molecular-lattice polaron states and those recombination results in excitation of the molecules of organic solids) gives the possibility to explain the decrease of σ-value for the high density of excitation. When the tracks are overlap and the mean distance between such a states decreases the mean time of theirs recombinations becomes more short. Such a mechanism doesn't contradict the results obtained for LS. Really, let us equating the energy of thermal molecular motion kT and that of polarization created by unit charge in molecular medium. For the systems under discussion one can obtained the value of the radius of the stable polarization surroundings of the excess electron to be about 1nm, i.e. comparable to a molecular size[8,9]. It means that the duration of the recombination process is defined by the characteristic frequency of molecular collisions (i.e. 10^{12} s^{-1}) and is smaller than the duration of the electron excitation energy transfer from solvent molecules to doped ones. Therefore the rise time of prompt RL pulse for LS is determined by the latter process.

DELAYED RADIOLUMINESCENSE

The investigations of the shape of the slow components of RL pulse OC, cross-linking and routine PS, LS have shown that for the times t ≥ 50ns, the process of T-T-annihilation become diffusion-controlled and function M(t) in Eq.(2) accurate within 4% can be represented as a constant[16]. For the ionizing radiations with dE/dx ≥ 10^1 MeV/cm k=1.0, and for ones with dE/dx ≤ 10^{-1} MeV/cm k=1.5 accurate within 6%[11]. With dE/dx increase r_0-value decreases and doesn't show the dependence from type of scintillators. E.g. r_0-values are equal respectively to 100,70...60,50 nm for the excitations with dE/dx ~ 10^{-2}, 10^1...10^2,10^3 MeV/cm, and for the latter case 94...98% of ionizing (alpha) particle energy is loosed within a RHD (i.e. within track) [12,15]. All these results in contrast to the prediction of the theory of 60-ies [1] agree with the theory and experimental data obtained for organic tracking detectors[5]. Anisotropy of RL light yield and values of t_D (i.e. D) is observed for SC. It is caused by anisotropy of the crystal lattice characteristics[12]. In contrast to prompt RL presence of deep traps of charge carriers and excitons essentially effects on light yield of the RL slow component. E.g. the variation of the root-mean-square random orientation of mosaic structure of a single crystal from 26′ to 160′ results in decrease of the slow component intensity more than by three times[15]. It should be mentioned that the necessary condition for appearance of diffusion-controlled T-T-annihilation process, which takes place for the t ≥ 50ns, is the low concentration of T-states in "diffusion-expanding" RHD. The study of the scintillation pulse shape and light yield has shown that the concentration of T-states decreases rapidly after excitation mainly due to concentration-controlled process of T-T-annihilation [16]

CONCLUSIONS

Specific features of RL process are caused by the stage of generation, transport and recombination of charge carriers which due to the specific of polarization process in organic media exist as hot secondary particles and then as lattice-molecular polaron states. The recombination of the latter ones results in prompt RL formation. The process of RHD formation and one of "specific quenching" are caused by dE/dx of ionizing particle. Formation of the slow component of scintillation pulse is defined by RHD shape, concentration of T-states in such a regions and T-states diffusion coefficients D in them.

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