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Luminescence energy yields of organic solid materials exited by photons of light or gamma-radiation

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In this paper we compare the energy yields both for the case of excitation by light photons of the visible range and for the excitation by gamma radiation for some organic scintillation crystals and polystyrene plastic scintillator. In the first case the energy of excitation is lower than the ionization potential of molecules, and in the second one the energy of excitation is higher than the ionization potential of molecules. It has been obtained that the energy yield in the case of excitation by photons of gamma radiation Y_γ is in the range from 0.018 to 0.056. These values are an order of magnitude smaller than the energy yield Y_f obtained for photoexcitation.

Проведено сравнение значений энергетического выхода при возбуждении фотонами света в видимом диапазоне длин волн и при возбуждении фотонами гамма-излучения для ряда сцинтилляционных органических монокристаллов и полистирольного пластмассового сцинтиллятора. Показано, что в первом случае энергия возбуждения ниже потенциала ионизации молекул вещества, тогда как во втором - энергия возбуждения превышает потенциал ионизации молекул. Получено, что энергетический выход при возбуждении фотонами гамма-излучения (Y_γ) лежит в диапазоне 0,018–0,056, что на порядок меньше величины энергетического выхода Y_f при фотовозбуждении.

1. Introduction

Energy yield in organic scintillation materials decreases with increase of specific energy loss dE/dx of an ionizing particle that moves along the direction x and has the energy E [1]. It means that the effect of such a decrease of the scintillation light energy yield has to grow in going from the excitation by photons of gamma radiation, from gamma radiation to protons, from protons to alpha particles and from alpha particles to heavy ions. It accompanied with growth of non-linear relation between the energy of light photons and energy of ionizing radiation. For excitation by photons of gamma radiation or electrons of middle energies, such relation is linear. With dE/dx-value growth the effect of non-linearity increases. The physical mechanism of this effect was not yet revealed, and an effect of the similar loss was called "the specific quenching" [1].

According to the basic concept developed in 60s–70s years of the twentieth century ionizing radiations transfer their energy in a series of acts of collective excitations of molecules groups, but not in excitation of single molecules, i.e. in a form of plasmons or super-excited states. In a single act of such interaction, it becomes possible for ionizing particle to transfer to substance a portion of energy, which is much higher than the ionization potential of molecules of the substance [2–6]. It was verified by experiment and it was obtained that the average energy E_p of plasmons in organic crystals and plastic scintillators could be estimated as 20–22 eV [2–4], whereas the ionization potential of molecules of organic scintillators does not exceed 7–8 eV [5]. So-called "spur" is created in the point where a single act of transferring of a portion of the energy to the substance takes place. A spur is the local area, which contains one or more pairs of charge states and one or more excited states arising from the decay of short-lived plasmons or super-excited states. Recent studies have only confirmed and expanded the description of the mechanism of substance excitation by ionizing particle (see the review of these studies in [4, 7, 8]).

In contrast to photoluminescence, the aspects of generation, transport and recombination of the charge states [9, 10] determine the process of radioluminescence of organic condensed matter. Growth of the energy loss with increasing of dE/dx explains the fact that individual spurs created by ionizing radiations with high values of dE/dx (protons, alpha particles, heavy ions) overlap in a unit region — the particle track. It causes the additional energy loss of ionizing particle determinated by the quenching effects in the track regions [8–10]. Therefore, the conversion efficiency of organic scintillators is sharply reduces, and the value of the radioluminescence energy yield becomes the non-linear function of ionizing particle energy E.

This paper is devoted to the least explored problem, which, it seems, is very important to study the mechanism of the specific quenching. Let us consider the primary excitation by gamma radiation photons of the medium energies (10^5–10^6 eV), which create secondary recoil electrons. In this case, as it is known, the non-linearity of the scintillation yield as the function of ionizing radiation energy E is not observed. Formally, the effect of the specific quenching should disappear, because tracks don't form [1, 8, 9]. However, if we consider that the above-described conventional explanations of the specific quenching are correct, then this effect should show tendency for this "boundary" case, because the energy transferred in a single act of excitation is much higher than the ionization potential of substance molecules [4–8]. To study this effect we have compared the quantum and energy yields of photofluorescence and radioluminescence for widely used scintillation crystals, namely, anthracene, stilbene and *p*-terphenyl (both pure and activated by 1,4-diphenyl-1,3-butadiene), as well as for a polystyrene plastic scintillator.

2. Theory

The absolute photofluorescence quantum yield Φ_f is a very important parameter of a fluorophor. It is a ratio of the number of emitted photofluorescence photons to the number of absorbed photons:

$$\Phi_f = \frac{photons_{em}}{photons_{abs}}. \qquad (1)$$

The measurement of the absolute quantum yield Φ_f is quite a difficult task, and therefore the value of the relative photofluorescence quantum yield is often measured by comparing with the reference material with a known value of the absolute quantum yield Φ_f.

According to [11] the absolute energy yield of photofluorescence is defined as the ratio of the total energy of emitted photons to the total energy absorbed by a fluorophor. It is assumed that there is no reabsorption of the fluorescence photons within a fluorophor, i.e. the ratio of the energies should be calculated for an infinitesimal volume. In this formulation, taking into account Eq.(1), the absolute photofluorescence energy yield Y_f can be written as:

$$Y_f = \Phi_f \cdot \frac{\lambda_{ex}}{\lambda_{em}^{av}}, \qquad (2)$$

where λ_{ex} is an excitation wavelength and $\lambda^{av}{}_{em}$ is an average value of a wavelength of the emission spectrum. In the case of bulk samples one can use the technical photofluorescence quantum yield q_f, which takes into account the process of reabsorption of light [1].

Wright [12] measured the absolute photofluorescence quantum yields Φ_f of *p*-terphenyl and *trans*-stilbene crystals and compared these values with anthracene which quantum yield was 0.80±0.05. At temperature of 290°K Φ_f-values for *p*-terphenyl and *trans*-stilbene crystals were equal to 0.52 and 0.65, respectively [12]. Katoh et al. [13] measured Φ_f of several aromatic hydrocarbon crystals: *p*-terphenyl, *trans*-stilbene, anthracene, pyrene and α-perylene. The authors of [13] estimated the lower limit values of Φ_f to be 0.80 for *p*-terphenyl, > 0.65 for *trans*-stilbene, > 0.64 for anthracene, 0.68 for pyrene, and 0.31 for α-perylene.

The energy yield of radioluminescence Y_r for an ionizing particle of the energy E, according to [11], one can define as:

$$Y_r = \frac{dL}{dE}, \tag{3}$$

where dE is the energy that a particle lost passing the distance dx, and dL is the energy of radioluminescence photons emitted due to absorption of the energy dE. According to (3), for the case of a particle with the initial energy E_0 crossing the maximum range in scintillator the average value of the radioluminescence energy yield is equal to:

$$Y_r = \frac{1}{E_0}\int_0^{E_0} Y_r(E)dE = \frac{L}{E_0}, \tag{4}$$

where L is the total energy of radioluminescence photons. The radioluminescence energy yield Y_r is often called the scintillation efficiency [1].

According to [11, 14, 15] in the case of excitation by gamma radiation photons of a radionuclide source ^{60}Co, the value of the energy yield $Y_\gamma = Y_r$ varies in the range from 0.056 to 0.097.

3. Experimental

Photofluorescence spectra were measured by a spectrofluorimeter Varian Cary Eclipse. Fluorescence was excited at wavelengths corresponding to the maximum of absorption for each of the investigated scintillation material. The slits for the excitation and emission channels were 2.5 and 5 nm, correspondingly. To measure the photofluorescence an attachment for solid samples was used. The obtained spectra were corrected using the calibration file. It allowed us to make a correction for sensitivity of the light detector.

The amplitude scintillation spectra were measured by a multichannel amplitude analyzer AMA-03F. The light yield values for the scintillators were calculated using the value of the absolute light yield C (10,200 photons per 1 MeV of gamma radiation) of a ∅ 30 mm×5 mm reference stilbene single crystal. The measurements of the light yield as well as the correction procedure for light collection were carried out according to [16]. To calibrate the scale of the analyzer in the energy scale the following sources of gamma radiation photons were used: ^{22}Na, ^{60}Co, ^{137}Cs and ^{152}Eu. The measurements of the relative photofluorescence quantum yield and the light yield of organic solid materials were obtained for room temperature.

4. Measurements and estimations

We have studied organic single crystals of stilbene, anthracene, *p*-terphenyl (both pure, and grown from the melt containing 0.1 % of 1,4-diphenyl-1,3-butadiene), as well as a plastic scintillator on the base of polystyrene doped with 1.5 % of *p*-terphenyl and 0.02 % of POPOP. All samples were 5 mm thick.

Analysis of the results obtained by different authors (see, for example, [12, 13]) has shown that the most stable value of the absolute photofluorescence quantum yield $\Phi_f = 0.65$ was obtained for stilbene single crystals. Therefore, we used this crystal as the reference one. Fig. 1 demonstrates the fluorescence spectra for the organic materials under investigation, measured by a spectrofluorimeter Varian Cary Eclipse. The ratio of areas under the curves of the fluorescence spectra allows estimating the photofluorescence quantum yield using the absolute value Φ_f for the reference material. In that manner, we estimated Φ_f-value for other organic materials. The value Φ_f = 0.55 that we obtained for anthracene crystal is closer to the results obtained in [13], whereas $\Phi_f = 0.48$ for pure *p*-terphenyl single is closer to the results of measurements reported in [12]. The difference in Φ_f-values reported by different authors is due to both the technology used to obtain a specific sample, and the experimental error of measurements.

The measurements of emission spectra (see Fig. 1) allow us to obtain the values of average wavelengths $\lambda^{av}{}_{em}$ for each sample under investigation. After that, we have calculated the values of the photofluorescence energy yield Y_f according to (2) and the mean energy δ_f, which is necessary to generate a light photon with energy E_{ph} (i.e. the energy that corresponds to wavelength $\lambda^{av}{}_{em}$). Table 1 presents the values of λ_{ex} and $\lambda^{av}{}_{em}$, the corresponding values of light photon energies $E_{ph}(\lambda_{ex})$ and $E_{ph}(\lambda^{av}{}_{em})$, as well as the calculated values Y_f and δ_f.

Measurement of the amplitude scintillation spectra of investigated organic materials allowed checking the linearity of the scintillator response and calibrating the scale of the analyzer. The measurements run with refer-

Table 1. The values of λ_{ex}, λ^{av}_{em}, $E_{ph}(\lambda_{ex})$, $E_{ph}(\lambda^{av}_{em})$, Y_f and δ_f for the case of photoexcitation

Organic material	λ_{ex}, nm	$E_{ph}(\lambda_{ex})$, eV	λ^{av}_{em}, nm	$E_{ph}(\lambda^{av}_{em})$, eV	Y_f	δ_f, eV
Stilbene single crystal	340	3.65	402	3.08	0.55±0.03	5.60
p-Terphenyl single crystal (pure)	340	3.65	396	3.13	0.41±0.02	7.63
p-Terphenyl single crystal (0.1 % of 1,4-diphenyl-1,3-butadiene in a melt)	340	3.65	430	2.88	0.77±0.04	3.74
Anthracene single crystal	420	2.95	458	2.71	0.50±0.03	5.42
Polystyrene (1.5 % of *p*-terphenyl + 0.02 % of POPOP)	280	4.43	437	2.84	0.49±0.03	5.80

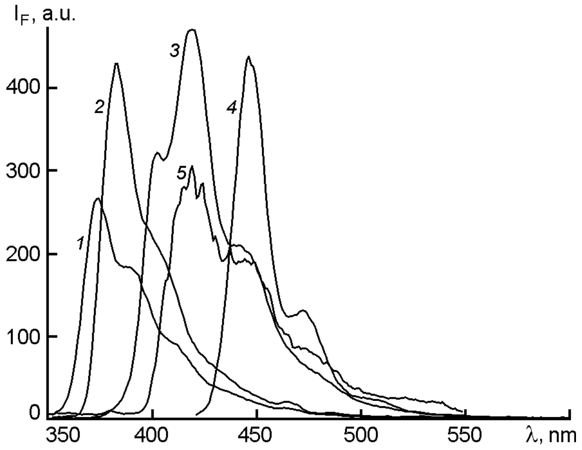

Fig. 1. Photofluorescence spectra of organic single crystals: *1* - stilbene (λ_{ex} = 340 nm), *2* - pure *p*-terphenyl (λ_{ex} = 340 nm), *3* - *p*-terphenyl doped with 0.1% of 1,4-diphenyl-1,3-butadiene (λ_{ex} = 340 nm), *4* - anthracene (λ_{ex} = 420 nm), *5* - plastic scintillator on the base of polystyrene (λ_{ex} = 280 nm).

ence stilbene single crystal (with known absolute light yield) gave a possibility to recalculate the results of the calibration in the number of photons in scintillation pulse for the organic solid scintillators. Fig. 2 shows the results of these measurements (points) as well as the approximations obtained by the least squares method (lines).

In the investigated range of energies of gamma radiation photons, the light response of organic scintillators is a linear function of the excitation energy. The linear dependence of the number of photons P_γ against gamma radiation energy E_γ (see Fig. 2) confirms this well-known statement. According to (4), the energy yield of radioluminescence for the case of gamma excitation (Y_γ) is the product of the slope of approximation line (Fig. 2) and the average energy E_{ph} of a light photon (that is, light with a wavelength λ^{av}_{em}). Table 2 shows both the calculated values of Y_γ and the mean energy δ_γ that is necessary to produce radioluminescence photon with energy $E_{ph}(\lambda^{av}_{em})$ in the case of gamma radiation excitation.

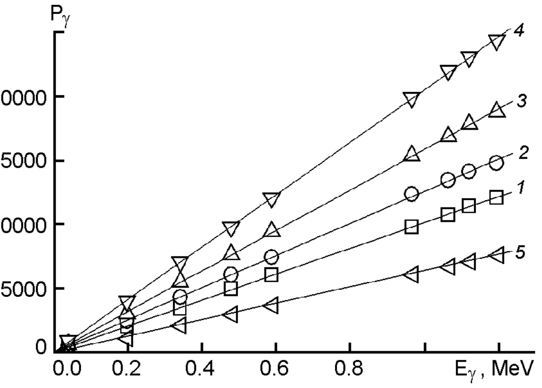

Fig. 2. The values of the number of scintillation photons P_γ for organic solid scintillators excited by gamma radiation. Opened symbols are the calculated experimental values of P_γ versus the energy of gamma radiation E_γ. Solid lines present the approximation linear dependences of P_γ versus E_γ. The symbols *1, 2, 3, 4* and *5* are the same as in Fig. 1.

It is interesting to answer the following question: What is the range of temperatures, in which the results shown in Tables 1 and 2 are true? It is known that the yields of the both photoluminescence and radioluminescence are temperature dependent [1, 17, 18]. The calculation results of the relative light yield (gamma excitation by ^{137}Cs [18]) and the relative technical quantum yield (photoexcitation [1, 17]) as a function of temperature for the bulk single crystal of anthracene, presented in Fig. 3, indicate the following.

According to [1] a similar dependence of the quantum yield of photofluorescence is observed for organic single crystals of stilbene and *p*-terphenyl as well, whereas the value of the light yield of radioluminescence photons weakly depends on tempera-

Table 2. The values of Y_γ and δ_γ for the case of gamma radiation excitation

Organic material	Y_γ	δ_γ, eV
Stilbene single crystal	0.031±0.001	99.35
p-Terphenyl single crystal (pure)	0.039±0.001	80.26
p-Terphenyl single crystal (0.1 % of 1,4-diphenyl-1,3-butadiene in a melt)	0.046±0.001	62.61
Anthracene single crystal	0.056±0.002	48.39
Polystyrene (1.5 % of *p*-terphenyl + 0.02 % of POPOP)	0.018±0.001	157.78

Table 3. Temperature dependences of the relative light yield C_{rel} for single crystals of stilbene, *p*-terphenyl and anthracene, and for a plastic scintillator on the base of polystyrene

Organic material	T_1, K	T_2, K	a, rel.un.	Δa, rel.un.	b, K^{-1}	Δb, K^{-1}
Stilbene	180	350	1.20	$\pm 2.0\cdot 10^{-2}$	$-7.5\cdot 10^{-4}$	$\pm 7.8\cdot 10^{-5}$
p–Terphenyl	160	370	1.02	$\pm 1.9\cdot 10^{-2}$	$-1.1\cdot 10^{-4}$	$\pm 6.8\cdot 10^{-5}$
Anthracene	160	300	1.30	$\pm 1.8\cdot 10^{-2}$	$-1.0\cdot 10^{-3}$	$\pm 7.9\cdot 10^{-5}$
Polystyrene	145	375	0.93	$\pm 4.0\cdot 10^{-2}$	$+2.6\cdot 10^{-4}$	$\pm 1.6\cdot 10^{-4}$

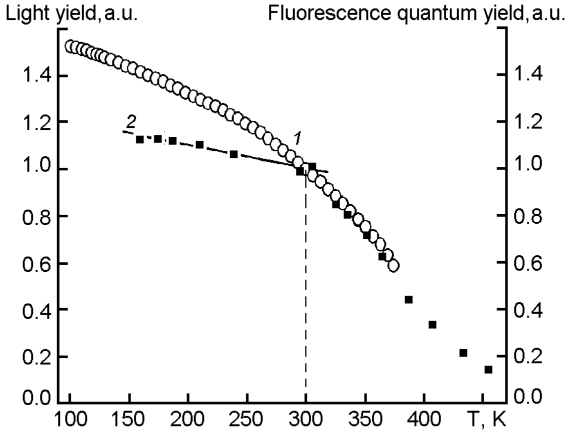

Fig. 3 [1, 17, 18]. The calculated values of the relative quantum yield of the photofluorescence (*1*) and the relative light yield of the radioluminescence (*2*) versus a temperature T for a bulk anthracene single crystal. Solid line is a linear approximation of the values of the relative light yield in the range from 160 to 300 K (see Table 3). For T = 300 K the values of the light yield and the quantum yield are taken as a unit.

ture over a wide temperature range. The physical mechanisms that cause this behavior of the scintillation response have been discussed in [18]. In the context of this work it is important that, in accordance with the results of [18] for organic scintillation crystals and plastics excited by ionizing radiations (photons of gamma radiation, fast neutrons, alpha particles) a very weak temperature dependence of the light yield is observed in some temperature range from T_1 to T_2. This range is individual for each scintillation material. If we approximate the dependence of relative light yield C_{rel} on temperature in the temperature range from T_1 to T_2 by the least squares method as:

$$C_{rel} = a + bT, \qquad (5)$$

then the approximation parameters a and b will be determined with an accuracy of Δa and Δb, correspondingly. One can find the values of these parameters in Table 6.5 of Ref. [8]. Table 3 cites this information as well.

So, one can use the values of Y_γ from Table 2 in the temperature range from T_1 to T_2. Table 3 presents this range for every individual scintillation material. It should be note that the values Δa and Δb determinate the measurement error of the relative light yield C_{rel} versus temperature.

5. Conclusions

In this paper we compared the energy yield of photoluminescence and radioluminescence for scintillation crystals of stilbene, anthracene, and *p*-terphenyl (pure and activated by 1,4-diphenyl-1,3-butadiene), as well as for polystyrene plastic scintillator. The radioluminescence was excited by photons of gamma radiation of medium energies ($E_\gamma \sim 10^5$–10^6 eV). The radioluminescence light yield varied linearly with the energy E_γ of gamma radiation photons. The radioluminescence energy yield for organic condensed media excited by photons of gamma radiation (Y_γ) is in the range from 0.018 to 0.056. These values are in a good agreement with the results of the earlier studies [11, 14, 15]. These values are an order of magnitude smaller than the energy yield (Y_f) obtained under photoexcitation.

We investigated excitations that did not cause the track formation, and therefore the additional energy loss as the result of the quenching process in the track was not observed. However, in this case the the radioluminescence energy yield is much lower than for the photoexcitation. This result confirms the fact that, in comparison with the photoluminescence, the scintillation process in organic molecular condensed media proceeds through a number of additional stages characterized by the additional energy loss. The values of the energy yields obtained in this work allow us to estimate the magnitude of this loss.

In the case of track formation, the loss of two groups arises. A spur formation causes the first group of loss and the other group of loss is the result of spurs overlap [4, 7–10]. One can use the values obtained in this work to estimate the contribution of the first group. Therefore, the results obtained give the possibility to estimate the influence of the processes of the first and second groups of the loss that occurs during a track formation for the particles with high specific energy loss dE/dx.

References

1. J.B.Birks, The Theory and Practice of Scintillation Counting, Pergamon Press, London (1967).
2. N.Swanson, C.J.Powell, *J.Chem.Phys.*, **39**, 630 (1963).
3. M.Schott, *Mol.Cryst.*, **5**, 229 (1969).
4. M.Pope, C.E.Swenberg, Electronic Processes in Organic Crystals, Clarendon Press, Oxford (1982).
5. F.Gutmann, L.E.Lyons, Organic Semiconductors, John Wiley and Sons, New York-London-Sydney (1967).
6. R.L.Platzman, *Radiat.Res.*, **17**, 419 (1962).
7. A.Mozumder, Fundamentals of Radiation Chemistry, Academic Press, San Diego, London, Boston, New York, Sydney, Tokyo, Toronto (1999).
8. N.Z.Galunov, O.A.Tarasenko, Formirovanie Trekov Ioniziruyushchih Izlucheniy v Organicheskih Kondensirovannyh Sredah, ISMA, Kharkov (2011) [in Russian].
9. O.A.Tarasenko, *Functional Materials*, **19**, 5 (2012).
10. N.Galunov, O.Tarasenko, *Radiat.Meas.*, **45**, 380 (2010).
11. I.M.Rozman, S.F.Kilin, *Uspehi Fiz.Nauk*, **LXIX**, 459 (1959).
12. G.T.Wright, *Proc.Phys.Soc.*, **B68**, 701 (1955).
13. R.Katoh, K.Suzuki, A. Furube et al., *J.Phys. Soc.*, **C113**, 2961 (2009).
14. G.T.Wright, *Proc.Phys.Soc.*, **B68**, 929 (1955).
15. M.Furst, H.Kallmann, B.Kramer, *Phys.Rev.*, **89**, 416 (1953).
16. E.Sysoeva, V.Tarasov, O.Zelenskaya, *Nucl. Instr.and Meth. Phys. Res.*, **A486**, 67 (2002).
17. I.I.Kucherov, A.N.Faidysh, *Izv.Akad.Nauk SSSR (Ser.Fiz.)*, **22**, 29 (1958).
18. J.H.Baker, N.Z.Galunov, O.A.Tarasenko, *IEEE Trans.Nucl.Sci.*, **55**, 2736 (2008).

Енергетичний вихід люмінесценції органічних твердотільних матеріалів при збудженні фотонами світла або гамма-випромінювання

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Проведено порівняння значень енергетичного виходу при збудженні фотонами світла у видимому діапазоні довжин хвиль і при збудженні фотонами гамма-випромінювання для низки сцинтиляційних органічних монокристалів та полістирольного пластмасового сцинтилятора. Показано, що у першому випадку енергія збудження нижче потенціалу іонізації молекул речовини, тоді як у другому - енергія збудження перевищує потенціал іонізації молекул. Отримано, що енергетичний вихід при збудженні фотонами гамма-випромінювання (Y_γ) лежить у діапазоні 0,018–0,056, що на порядок менше величини енергетичного виходу Y_f при фотозбудженні.