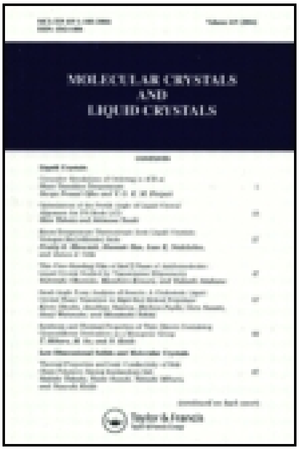

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THE RADIOLUMINESCENCE STUDY AS A METHOD FOR INVESTIGATION OF STRUCTURE FEATURES OF ORGANIC MOLECULAR SOLIDS

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Abstract The correlation between radioluminescence and structure characteristics of organic molecular systems is analyzed. It was shown, that using the results of investigation of scintillation characteristics one can study not only the properties of organic molecular solids but their structure features as well.

INTRODUCTION

For organic molecular systems the radioluminescence is caused by luminescence of molecules excited in the recombination process of charge carriers generated by ionizing radiation. In such systems the energy of intermolecular interaction and intramolecular one is about 10^{-3} eV and 10^{0} eV respectively. The generation of charge states causes the rise of an intermolecular interaction energy up to 10^{-1} eV [1], thereby upsets the balance of forces near such centers, and hence changes the nature of excitation energy transfer. Structure unperfections of an organic solid influence on localization of charge states and excited ones. Thus having investigated the radioluminescence of an organic molecular solid, one can study it structure features as well.

THEORY

The relaxation times needed for electronic (10^{-16}- 10^{-15} s) and vibronic (10^{-14} - 10^{-13} s) polarization of organic molecules does not exceed the time of charge carrier localization (10^{-12} - 10^{-11} s).[1,2] Therefore, it may be argued that the polarization surroundings of charge carrier should be formed during it moving in the substance. For nonviscous liquids, equating the thermal energy to polarization one at a distance R from charge carrier we obtain that the dimension of stable polarization zone is

$$R = \sqrt[4]{e^2\alpha / 2kT} \sim 10 \text{ Å}$$

where e is electronic charge, α is the mean molecular polarizability ($\alpha \sim 20$ Å[2,3]), k is Boltzmann constant, T is the temperature. Thus, the generation of excited molecules and therefore the radioluminescence of liquids are practically due to recombination which takes place between geminate molecules. In contrast with liquids the local polarization of a crystal lattice or polymer macromolecule occurs even though the charge carrier is captured by a trap with the depth of $E_t' \sim (1 - 2)kT$. The appearance of such polarization results in deeping the potential well by the value of $\delta E_t' \sim 0.1$ eV.[2] Thus, for the room temperature its depth is $E_t = E_t' + \delta E_t' \sim 0.12 - 0.17$ eV. Hence the charge carrier location time is

$$\tau_t = \nu^{-1} \exp(E_t / kT) \sim 10^{-10}\text{s} \qquad (1)$$

where $\nu \sim 10^{12}\text{s}^{-1}$ is the attempt-to-escape frequency.[2,4] The analysis of the situation discussed has shown[4,5] that in the case of high concentration of such shallow traps, and when the τ_t value exceeds characteristic time values of an excitation energy transfer, the shape of radioluminescence pulse fast component for such a system should be described by the function:

$$i(t) \sim f(t) * \exp(-t/\tau) \equiv \int_0^t f(t-\beta) \exp(-\beta/\tau)\, d\beta \qquad (2)$$

where

$$f(t) \sim \exp(-(t-n\sigma)^2/ 2\sigma^2) \qquad (3)$$

In Eqs.(2) and (3) t is the time after excitation, τ is decay time constant, σ is the time constant determined by additional delay of the times of a radioluminescence photon emission. This delay is caused by the statistic nature of molecular excitation which is due to recombination of charge states localized on the shallow trap system. If correlation between the process resulting in a charge carrier energy exchange in organic solids and their molecular luminescence is negligible then in Eq.(2) function f(t) is not the Gaussian one (3), and the addition delay of the moments of photon emission doesn't have to appear.

Losses of ionizing energy in organic molecular systems result in generation of secondary electrons both of high and low energies. Low energy electrons create the regions of a high activation density in which the probability of a triplet excited molecule generation is high due to the process of a charge carrier recombination which is specific to these regions.[1,3,6] In exchange interaction of two closed with each other triplet excitations the singlet one may be generated with probability 0.4. The luminescence delayed on a time needed for triplet excitations to meet each other appears, and hence radioluminescence pulse slow component is formed. It shape (for times t > 50 ns after excitation [6]) is described by function

$$I(t) \sim (1 + t/ t_D)^{-k} \qquad (4)$$

where $t_D = r_0^2 / 4D$, D is the diffusion coefficient of triplet excitation, r_0 is the mean value of a cross - section radius of high activation density regions. The symmetry of these regions defines the k - value in Eq.(4).[6] For radiations with a high ($\geq 10^1$ MeV/ cm) and a low ($\leq 10^{-1}$ MeV/cm) specific energy loss k = 1.0 (cylindrical symmetry) and k = 1.5 (spherical one) respectively. Formation of radioluminescence pulse slow component is a diffusion-controlled process with $t_D \sim 10^{-7}$s. Thus, only a presence of deep traps with a high location time (> 10^{-8}s) for charge carriers and excitations has an effect on it.

EXPERIMENT

The previous paper [5] has reviewed the experimental data for the radioluminescence pulse fast component study. For organic molecular crystals and vinylaromatic plastics the addition delay of the moments of photon emission was observed, and the pulse shape was described by Eq.(2) with f(t) in the form (3), n = 3, and $\sigma \sim$ 0.1 - 0.4 ns. The σ-value was defined by the type of the crystal or plastic, weakly increased with a decrease of root-mean-square random orientation of single crystal mosaic structure, and for plastics didn't depend on a type and concentration of added agents. For liquids function f(t) in Eq.(2) was not Gaussian one, and the addition delay of the moments of a photon emission was not detected.

The study [2,3,6] of radioluminescence pulse slow component has shown the following. The delay radioluminescence was observed for organic molecular single crystals and liquids as well as for plastics based on cross - linked copolymers. For all the cases the shape of the radioluminescence pulse slow component was well described by Eq.(4). For liquids the process of a delay radioluminescence pulse formation was defined by diffusion of triplet excited molecules, but for crystals and plastics it was defined by features of triplet exciton migration within the limits of the crystal lattice or cross - linked areas of plastic. The shape and intensity of delay radioluminescence was defined by the structure perfection of those parts of the organic solid along which the track of ionizing particle was orientated. With improvement of structure perfection t_D-values in Eq.(4) decreased, but their anisotropy increased. It was shown [4,6] that those structural unperfections of an organic crystals which affected the kinetics of a radioluminescence pulse slow component formed the traps ≥ 1.0 eV and ≥ 0.2 eV in depth for charge carriers and excitons respectively.

DISCUSSION

The additional delay (Eq.(3)) of a radioluminescence photon emission was detected only for organic molecular solids. Therefore, for such objects the correspondence between the shape of the radioluminescence pulse fast component and the structural features of molecular solid exist. The validity of this statement can be verified by the following analysis. If ΔE is the difference in the depth between the traps with location times τ_t (Eq.(1)) and $\tau_t + \Delta\tau$, then using Eq.(1) for $\Delta E/kT < 1$ it is not difficult to obtain that

$$\Delta E = \Delta\tau\ (kT/\tau_t) \qquad (5)$$

Hence both the energy and the location time distributions (Eq.(3)) for such traps should be described by the functions of the same type, i.e. Gaussian functions. That is just what has been obtained during the study of the energy distribution of trapping centers of polarization origin, which are formed in regions of the local compression and tension of individual edge dislocations of organic crystals.[2] It allows us to estimate mean trap depth E_t (Eq.(1)). Using values of $\sigma \sim 0.1 - 0.4$ ns, $\tau = n\sigma = 3\sigma$, we have obtained $E_t \leq 0.2$ eV, that is in a good agreement with values of $E_t \sim 0.12 - 0.17$ eV which have been estimated above.

The presence of deep traps ($E_t > 1.0$ eV) influences the shape of radioluminescence pulse. Nevertheless, the type and concentration of deep traps has the main effect on the t_D- value (Eq.(4)) and its anisotropy.

CONCLUSIONS

Up to now, the radioluminescence phenomenon was studied only as an aim of scientific or technical (certification of scintillation detector, for example) investigation. The material discussed allows not only to enunciate the radioluminescence theory of organic molecular systems, which takes account of charge carrier energy exchange process in them, but to consider the radioluminescence study as a method for investigation of structure features of organic molecular solids as well.

REFERENCES

1. Pope M., Swenberg C.E. Electronic processes in organic crystals.(Clarendon Press.: Oxford, N.-Y. 1982.)
2. Silinsh E.A., Kurik M.V., Capek V. Elektronie protsesi v organitcheskhih moleckuljarnikh kristallakh. Riga: Zinatne. 1988. 329 P.
3. Gutmann F., Lyons L.E. Organic semiconductors. (John Wiley and Sons, Inc. New York - London - Sydney. 1967. P.868).
4. Krainov I.P., Galunov N.Z., Budakovsky S.V. Cryst. Res.Technol., 24, 193 (1989).
5. Budakovsky S.V., Galunov N.Z., Krainov I.P. Mol. Cryst. Liq. Cryst., 186, 151 (1990).
6. Galunov N.Z., Koval L.P., Solomonov V.M., Shishov N.I. Izvestia Academii Nauk SSSR (Proceeding of the Academy of Science of the USSR) Ser. Fizicheskaya, 54, 485 (1990).