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## Time-resolved electric field effects in recombination fluorescence as a method of studying primary radiation–chemical processes

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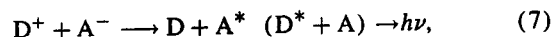
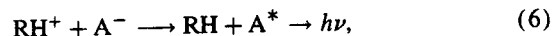
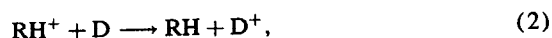
### Abstract

A new approach is proposed to identify the recombining particles in irradiated hydrocarbon solutions. It is based on the observation of time-resolved effects of an electric field in recombination fluorescence. The experiments demonstrate the possibility of observing molecular ions, electrons and holes that participate in radiation track recombination. The recombination processes involving the aforementioned particles can be reasonably distinguished in summary fluorescence kinetics by choosing the corresponding field strength. © 1997 Published by Elsevier Science B.V.

### 1. Introduction

For a number of years recombination fluorescence and the dependence of its intensity on time in irradiated organic luminophore solutions have been used to extract information about the processes of geminate recombination in a radiation track and about the particles involved.

The processes giving rise to recombination fluorescence exhibit a complex behavior and include several parallel and successive stages:



where RH is the solvent molecule; A is the electron acceptor; D is the hole acceptor.

A direct study of fluorescence kinetics [1,2] is complicated because of the great number of unknown parameters, such as particle mobility, the rate constants of capture by acceptors and the quantum yields of luminescence in reactions (5)–(7). Some advantages are provided by using the magnetic field effects and magnetoresonance methods [3,4] to analyse the ESR spectra information from recombination fluorescence.

The approach proposed can be used to identify the recombining particles with both low and high mobility. It is based on the observation of time-resolved effects of an electric field in recombination fluorescence. The evolution of these effects in time is determined by the mobility of recombining particles and the intensity of the applied electric field. Studying the time-dependence of electric field effects for different values of  $E$  one can distinguish the components responsible for the recombination of molecular ions, electrons and fast holes in the complex kinetics of recombination

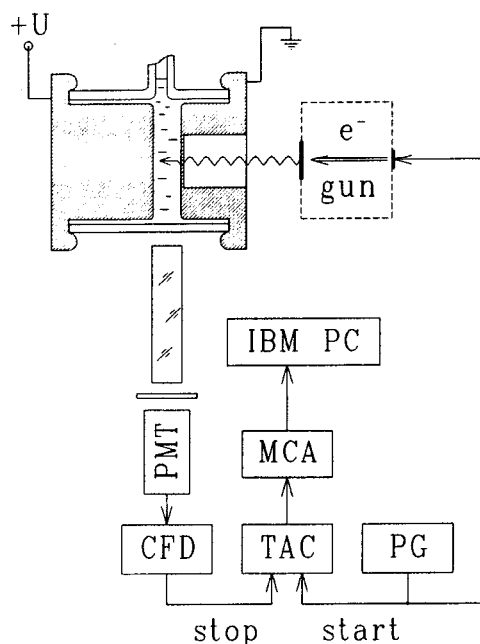


Fig. 1. Block-scheme of the pulsed X-ray fluorimeter with nanosecond time resolution for the measurement of electric field effects in recombination fluorescence.

fluorescence.

## 2. Experimental

Experiments on the effect of the electric field on recombination fluorescence were carried out using an X-ray fluorimeter schematically depicted in Fig. 1.

The setup operates in the single photon counting regime. A signal of a pulsed generator (PG) is supplied to the input of a pulsed electron gun and, in parallel, to the *start* input of a time-to-amplitude converter (TAC). The electron beam with time duration of about 2 ns is retarded in the target and creates X-rays. The X-rays penetrating the walls of an electrode ionize the sample. Processes (5)–(7) result in light which, passing through the quartz light-guide and light-filter falls onto a photomultiplier photocathode (PMT). The photomultiplier operates in the one-photon regime. The photomultiplier signal passing through the constant fraction discriminator (CFD) strikes the *stop* input of the TAC. The TAC signal, proportional to the

time interval between the *start* and *stop* enters a multi-channel analyzer (MCA) in which unity is added to the values of the corresponding channel. Since a great number of such events occurs ( $\sim 10^7$ ) the MCA memory accumulates the time dependence of the recombination luminescence intensity,  $I(t)$ .

The main parts of the cuvette are titanium electrodes and a quartz tube-insulator with an offset to pump and overfreeze the solution. To achieve a vacuum tightness indium was used as a gasket between the electrodes and the tube. One of the electrodes was made with a thin wall (thickness 0.2 mm) for X-rays to penetrate the sample. In a chosen geometry of the cuvette section only the central part of interelectrode space is irradiated. This provides a larger homogeneity of the electric field in the region under irradiation as well as practically excluding the detrimental luminescence of the quartz cuvette. This is favorable for studying slightly luminescing samples.

Cyclohexane, n-hexane, n-decane and n-dodecane were used as solvent. Hexafluorobenzene, 2,5-diphenyl-1,3,4-oxadiazole (PPD) and N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD) were used as acceptors. The solvents were treated with  $\text{KMnO}_4$ , shaken with concentrated  $\text{H}_2\text{SO}_4$ , washed with water and dried over  $\text{Al}_2\text{O}_3$ . The optical density of the solvents at 200 nm was less than 1. TMPD (Fluka) was purified by vacuum sublimation. Hexafluorobenzene (99.9%) and PPD (97%) were obtained from Aldrich and used without further purification. Experiments were done on deaerated (freeze-pump-thaw) solutions. All experiments were done at a temperature of 293 K.

Fig. 2 depicts the time dependence of fluorescence intensity arising under pulsed X-rays in the  $10^{-3}$  M PPD solution in n-decane on a logarithmic scale. The upper curve corresponds to zero electric field, the lower one belongs to the field of  $36 \text{ kV cm}^{-1}$ . The curves are normalized to the same absorbing dose. As follows from Fig. 2, in an electric field the fluorescence quenching increases in time after ionization (as is evident from Fig. 2, within 400 ns the fluorescence intensity in the field of  $36 \text{ kV cm}^{-1}$  is only a few percent in the corresponding intensity with no field). The quenching is related to the increase in distance between charges in the ion pair by an external field and the corresponding decrease in the fraction of recombining pairs [5].

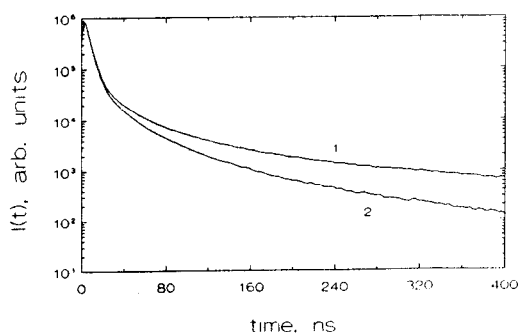


Fig. 2. Intensity of fluorescence vs time for  $10^{-3}$  M PPD solution in *n*-decane for electric field strengths of  $0 \text{ kV cm}^{-1}$  (1) and  $36 \text{ kV cm}^{-1}$  (2).

### 3. Results and discussion

At every instant the efficiency of  $Q(E, t)$  quenching is determined as:

$$Q(E, t) = 1 - I_E(t)/I_0(t), \quad (8)$$

where  $I_E(t)$  is the fluorescence intensity in the external electric field with strength  $E$ ;  $I_0(t)$  is the fluorescence intensity without the field.

As was shown in Ref. [6] at the chosen field strength  $E$  the  $Q(E, t)$  depends strongly on the viscosity of the solvent (and consequently, on a mutual diffusion coefficient of the recombining ions). In high-viscous solvents the effect of the electric field increases much more slowly than in low-viscous ones. Nevertheless the  $Q(E, t)$  curves for solvents with different viscosity are essentially coincident if universal time units [5]  $r_c^2/4D$  are used, where  $r_c$  is the Onsager radius and  $D$  is the sum of the diffusion coefficients of the ions. On the other hand, as was empirically found [6]:

$$Q(E, t) = f(pt), \quad (9)$$

where  $p$  is a function of  $E$ . To find the form of the dependence  $p(E)$  one can use the fact [7,8] that the integrated intensity of the recombination fluorescence is linearly dependent on the electric field strength:

$$\int_0^\infty [I(0, t) - I(E, t)] dt \propto E, \quad (10)$$

or, using (8):

$$\int_0^\infty I(0, t) Q(E, t) dt \propto E. \quad (11)$$

As the fluorescence kinetics is determined by diffusional drift processes, we may approximate it with the known asymptotic formula:

$$I(0, t) = Ct^{-3/2}, \quad (12)$$

where  $C$  is a constant. Transforming (11) further we obtain:

$$\begin{aligned} C \int_0^\infty f(pt) t^{-3/2} dt &= Cp^{1/2} \int_0^\infty f(x) x^{-3/2} dx \\ &= \beta p^{1/2} \propto E, \end{aligned} \quad (13)$$

where  $\beta$  is independent of  $E$ . Consequently

$$p \propto E^2, \quad (14)$$

as was observed in the experiment [6].

So, in the case of diffusion-controlled recombination kinetics the dependence  $Q(E, t)$  on  $E$  is quadratic. In the case of other types of recombination (e.g., tunneling), the dependence on the field strength should differ.

As mentioned above, the  $Q(E, t)$  curves for different solvents are coincident on the universal time scale in  $r_c^2/4D$  units. Therefore, for the parameter  $p$  we may write:

$$p = AE^2 D/r_c^2 = kE^2(\mu_+ + \mu_-), \quad (15)$$

as  $D \propto (\mu_+ + \mu_-)$ , where  $\mu_+$  and  $\mu_-$  are the mobilities of recombining ions.  $A$  and  $k$  are constants. Because of (9) we can write:

$$Q(E, t) = f(kE^2(\mu_+ + \mu_-)t). \quad (16)$$

Because the chosen field strength  $E$  was not changed during the experiment, in future we will denote  $Q(E, t)$  as  $Q(t)$ .

Experiments and Monte Carlo calculations [9] with different concentration of acceptors confirm the dependence of  $Q(t)$  on the mobility of recombining charges. On the other hand, the Monte Carlo calculations carried out in Ref. [9] demonstrate that  $Q(t)$  is actually independent of the track density, form and parameter  $r$  of the initial distance-distribution function in a recombining pair, with the values of  $r$  being

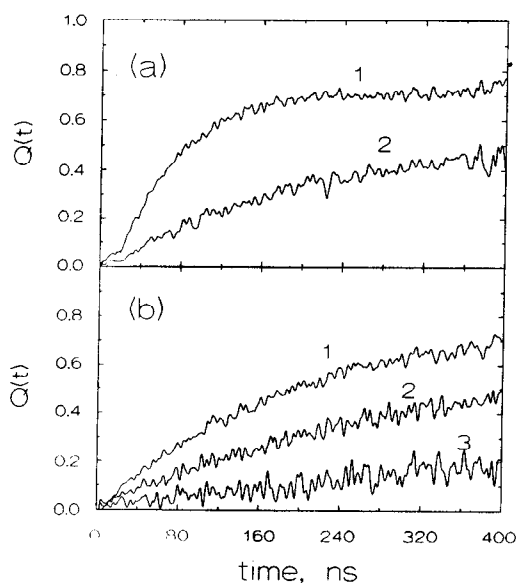


Fig. 3. (a) Electric field effect  $Q(t)$  for  $7 \times 10^{-3}$  M TMPD solution in *n*-decane for electric field strengths of  $8 \text{ kV cm}^{-1}$  (1) and  $4 \text{ kV cm}^{-1}$  (2). (b) The same for PPD solution for electric field strengths of  $36 \text{ kV cm}^{-1}$  (1),  $24 \text{ kV cm}^{-1}$  (2) and  $12 \text{ kV cm}^{-1}$  (3).

typical of hydrocarbons. Thus, when the recombination fluorescence kinetics is composed of recombination processes involving particles strongly differing in their mobility (molecular ions, electrons, fast holes) the electric field effects related to each of the processes can readily be distinguished by choosing the corresponding field strength. In this case, in the time range convenient for observation (e.g. the range of tens of nanoseconds) the profile of the electric effect curve will mainly be determined by the recombination of particles with the mobility of interest (e.g. electron-ion or ion-ion).

Fig. 3a depicts the  $Q(t)$  dependence for the  $7 \times 10^{-3}$  M TMPD solution in *n*-decane at different electric field strengths. TMPD is known to possess negative electron affinity and low ionization potential [10]. Therefore the TMPD molecules capture the holes effectively and fail to capture the electrons. Thus, the recombination fluorescence is caused only by process (5) where D is the TMPD molecule.

Due to the high electron mobility in hydrocarbons, the recombination of electrons with cations for

the most part completes in the picosecond and sub-nanosecond time range. At the same time, as follows from Fig. 3a, the  $Q(t)$  dependence for electron recombination in *n*-decane in fields of 4 and  $8 \text{ kV cm}^{-1}$  is measured with the appropriate signal-to-noise ratio within a submicrosecond time range. The existence of background distorts the  $Q(t)$  dependence only in the region of strong recombination fluorescence quenching by an electric field (with  $Q(t) > 0.6$ ). In this range the real kinetics is hardly detectable because it blends into the background determined by the recombination of impurity ions and instrumental effects. The existence of the background, insensitive to the electric field (for a strength of  $8 \text{ kV cm}^{-1}$ ), causes the  $Q(t)$  curve to pass to the plateau at  $Q \sim 0.7$  whereas theoretically,  $Q(t)$  tends to unity. As follows from Eq. (16), when the solvent viscosity corresponds to that of *n*-decane, the recombination fluorescence related to that of the molecular ions is practically insensitive to fields of 4 or  $8 \text{ kV cm}^{-1}$  in the time range from 0 to 400 ns. In the case of ion-ion recombination one should increase the electric field strength for the  $Q(t)$  dependence to manifest itself within this range. In Fig. 3b the  $Q(t)$  dependence for the  $7 \times 10^{-3}$  M PPD solution in *n*-decane is shown. Unlike TMPD, the PPD molecules display a positive affinity for electrons, and can capture both holes and electrons effectively. According to the calculated data [9] for this acceptor concentration, the main contribution to the recombination fluorescence results from the ion-ion recombination. Thus, the contour of the  $Q(t)$  curve depicted in Fig. 3a in the field of  $4 \text{ kV cm}^{-1}$ , can be obtained now in the field of  $24 \text{ kV cm}^{-1}$ .

So, the ratio of the field strengths for which the  $Q(t)$  profiles for electron-ion and ion-ion recombination in *n*-decane coincide, is 6. Because of (16) the ratio of the total mobilities  $(\mu_{\text{TMPD}^+} + \mu_{e^-})/(\mu_{\text{PPD}^+} + \mu_{\text{PPD}^-}) = 6^2 = 36$ . It is then concluded that the electron mobility in *n*-decane is 72 times as high as the ion one. According to [11], the electron mobility in *n*-decane is  $0.038 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Thus, for the ion mobility we obtain the value  $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is in tolerable agreement with the data on the diffusion coefficient of pyrene excited molecules in *n*-decane [12] ( $8.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ).

Since for low molecular weight solvents the mobility of the recombining molecular ions is inversely proportional to the solvent viscosity, the profile of the

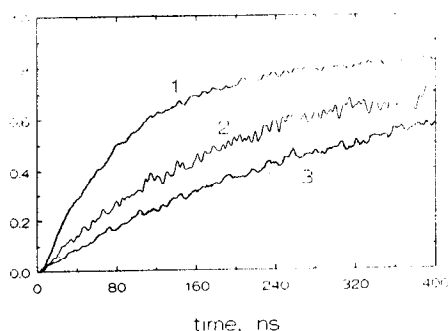


Fig. 4.  $Q(t)$  dependences for  $7 \times 10^{-3}$  M PPD solutions in *n*-hexane (1), *n*-decane (2) and *n*-dodecane (3) for an electric field strength of  $36 \text{ kV cm}^{-1}$ .

$Q(t)$  curve is the more sloping the higher the solvent viscosity. This is shown in Fig. 4 giving the  $Q(t)$  dependence for the  $7 \times 10^{-3}$  M PPD solutions in *n*-hexane, *n*-decane and *n*-dodecane for an electric field strength of  $36 \text{ kV cm}^{-1}$ . When the time range varies, in Fig. 4 in the ratio of solvent viscosities the  $Q(t)$  dependences merge into one curve which is in full agreement with relation (16).

The recombination described by reactions (1)–(7) is a multi-stage process. The recombination of molecular ions is preceded by the capture of electrons and primary holes. As a result, the mobility of charges with different signs in recombination is subjected to substantial changes. It is evident that the lower the acceptor concentration, the longer the residence time of the charges in the highly mobile state. It is then expected that the steepness of the  $Q(t)$  curve increase depends on acceptor concentration. This is confirmed by the Monte Carlo calculations given in Ref. [9]. According to these data, the  $Q(t)$  dependence on acceptor concentration in the range of low concentrations ( $< 10^{-3}$  M) is especially noticeable.

In Fig. 5a the experimental  $Q(t)$  dependence for the PPD solutions in *n*-decane for different acceptor concentrations are shown. The observed change in the  $Q(t)$  profile with concentration is close to the calculated one [9]. Surely, the change in the  $Q(t)$  curve profile with acceptor concentration results, first of all, from the capture of electrons by acceptors. However, if the mobility of the primary holes is higher than that of the molecular cations, the  $Q(t)$  curve will become more sloping upon the capture of holes. To verify this assumption, we have carried out experiments

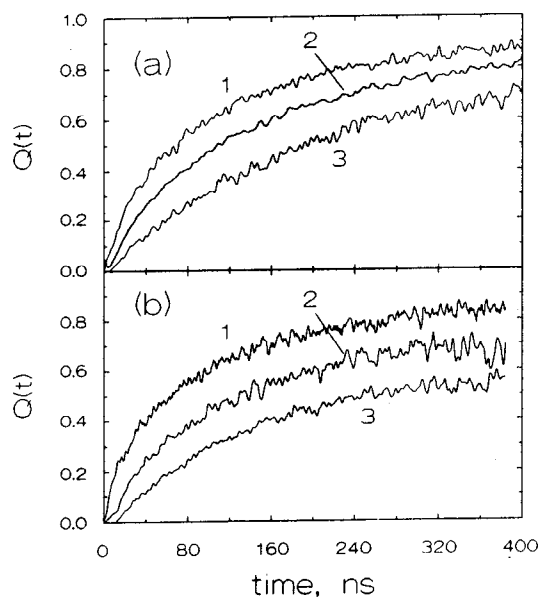


Fig. 5. (a) Electric field effect  $Q(t)$  for  $10^{-4}$  M (1),  $10^{-3}$  M (2) and  $7 \times 10^{-3}$  M PPD solutions in *n*-decane. (b) The same for  $10^{-4}$  M PPD (1),  $10^{-4}$  M PPD +  $10^{-1}$  M  $\text{C}_6\text{F}_6$  (2) and  $4 \times 10^{-3}$  M PPD +  $10^{-1}$  M  $\text{C}_6\text{F}_6$  (3) solutions in cyclohexane.  $E = 36 \text{ kV cm}^{-1}$ .

with cyclohexane solutions displaying, according to Ref. [13], a high hole mobility.

Fig. 5b shows the  $Q(t)$  dependence in a field of  $36 \text{ kV cm}^{-1}$  for cyclohexane solutions:  $10^{-4}$  M PPD (curve 1),  $10^{-4}$  M PPD +  $10^{-1}$  M  $\text{C}_6\text{F}_6$  (curve 2) and  $4 \times 10^{-3}$  M PPD +  $10^{-1}$  M  $\text{C}_6\text{F}_6$  (curve 3). Since the  $\text{C}_6\text{F}_6$  molecules are characterized by both high affinity for electrons and high ionization potential, they effectively capture electrons and fail to capture holes in cyclohexane solutions [10]. Thus, the change in the  $Q(t)$  profile due to addition of hexafluorobenzene to the  $10^{-4}$  M PPD solution is likely to be caused by the capture of electrons by  $\text{C}_6\text{F}_6$  molecules. For a given concentration of  $10^{-1}$  M, the major part of electrons is captured. Further, the introduction of electron acceptors into solution will have no effect on the mobility of negative charges which could change  $Q(t)$  (indeed, an increase in  $\text{C}_6\text{F}_6$  concentration to 0.2 M causes no changes in the  $Q(t)$  curve shape). At the same time, the addition to the solution of a comparatively small quantity of PPD, the molecules of which capture both electrons and holes, leads to further sub-

stantial changes in the  $Q(t)$  form (see curve 3). The change in the  $Q(t)$  dependence form due to the change in the mobility of a positive charge upon the capture of fast holes confirms the existence of the latter in cyclohexane. Simulating the experimental curves similar to those in Fig. 5b with the help of the Monte Carlo method one can actually estimate the magnitude of hole mobility in different solvents.

Thus, the experiments on time-resolved electric field effects demonstrate the possibility of identifying the charges with different mobility that participate in track recombination. The advantage of the method proposed is that it allows the high mobility to be fixed even when the residence time in the highly mobile state is short and lies within the picosecond range.

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