Radiation Physics and Chemistry 152 (2018) 114–124

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Exploring the mesoscopic structure of radiation track: The magnetic field effect in the radiation-induced fluorescence in the presence of an external electric field

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ARTICLE INFO

Keywords:
Recombination fluorescence
Spin-correlated radical pair
Spin-lattice relaxation
Local ionization density
Stochastic computer simulation

ABSTRACT

A novel approach to probe the spatial structure of not-too-dense radiation track in condensed matter on the scale that, on the one hand, substantially exceeds the mean size of a single spur (< 10 nm), and, on the other hand, is less than a characteristic size of the whole track, produced by a single electron of an energy of ~10 keV in an organic media (several microns), is suggested. Such an approach is based on the analysis of the joint effects of both external magnetic field, which allows obtaining information about intraspur recombination, and the external electric field, which increases the probability of the encounter of ions from neighbouring spurs, on the radiation-induced fluorescence from an irradiated medium.

The computer simulation of ion recombination in model tracks, which are to represent the real track formed by a single quantum of energy of about 20 keV in liquid dodecane and squalane, has been performed. It has been demonstrated that within the first microsecond after irradiation the ion recombination process in the studied alkane solutions can be represented using a set of 25–30 spherical spurs, which contain 3–4 primary ion pairs and have radii of 3–4 nm. Within the frameworks of the model used, the closest fit has been obtained assuming that in the model track the neighbouring spurs are located successively in random directions with a characteristic distance between them as large as 45 nm.

1. Introduction

The primary structure of the track of an ionizing particle in an organic medium, i.e., spatial distribution both of ionized and excited molecules and of excess electrons immediately after the passage of a high-energy particle, has been the object of close attention for more than 100 years, see, *e.g.*, refs (Pikaev, 1985; Freeman, 1987a; Schmidt, 1997; Mozumder, 1999). This structure is rather complex and characterized by different spatial scales. The penetration distance of high-energy radiation into the media that varies with both energy and the type of radiation within a very wide range determines the maximal characteristic size of the track. This parameter is essential for protection against ionizing radiation and is now well known for various materials.

To develop detailed models of radiation-induced processes in a medium of interest is the particle distribution on smaller scales since it determines the kinetics and the yield of the reactions involving short-lived intermediates. The acceptable simplifications for such models depend on the problems solved. For example, in analyzing the conductivity of dielectrics exposed to a low linear energy transfer radiation the initial structure of the track may be considered as a set of spatially separated primary ion pairs, which are composed of excess electron and corresponding ionized parent molecule. In this model, the conductivity is determined by the probability of the ion escape into the bulk that is by a characteristic distance between the thermalized primary charge carriers, see, *e.g.*, refs. (Schmidt and Allen, 1970; Freeman, 1987b).

To estimate a characteristic shape of the distribution function of the primary ion pairs, an external electric field (Casanovas et al., 1975; Dodelet and Freeman, 1974), as well as kinetic simulations of geminate recombination (Yoshida et al., 1991) are typically used. As an example, in normal alkanes in the liquid state, the spatial distribution is typically described by an exponential or similar decaying function with a characteristic decay length of 4–6 nm (Abell and Funabashi, 1973; Gee and Freeman, 1987; Freeman, 1987b).

However, data on the interaction between a high-energy particle

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https://doi.org/10.1016/j.radphyschem.2018.08.014
Received 8 May 2018; Received in revised form 7 August 2018; Accepted 15 August 2018
Available online 18 August 2018
0969-806X/

and condensed matter show that a one-time energy portion transferred into the environment from the particle often amounts to ~100 eV or more (Mozumder and Magee, 1967) that substantially exceeds the typical ionization potential of any molecule. This entails a need to introduce structure elements of the track such as spurs (Paretzke, 1987; Kaplan and Miterev, 2007), i.e., the relatively small domains, in which the distance between ionized molecules is either less than the thermalization length of excess electrons or comparable with it. In the not-too-dense tracks, the spurs, as well as the single pairs may be taken as the main structure elements, which are spatially isolated on scales of < 10 nm. Generally, one should discriminate also the larger structural elements of the track such as blobs and short tracks. However, in studies of the processes at rather short times, it looks acceptable to consider the track as a set of spatially separated spurs with some averaged characteristics.

The mean spur size and the number of primary ion pairs in the spur determine the kinetics of the intratrack reactions of short-lived intermediates (Schwarz, 1969; Hummel and Bartczak, 1988; El Omar et al., 2013; Kouchi and Tagawa, 1991; Magee and Chatterjee, 1987; Hummel, 1987), the yield of excited molecules with regard to their multiplicity (Brocklehurst, 1977; Holroyd et al., 1997; Appleton et al., 1986), as well as the magnitude of magnetic field effects in the recombination luminescence of irradiated solutions (Sargent et al., 1977; Pimblott et al., 1991; Brocklehurst, 1997). Thus, the structure of the "characteristic" spur may be actually determined in experiments shedding light on the processes mentioned, if a sufficient part of other parameters of the problem is available from independent measurements. Note that the cases of multi-particle spur and of a set of the same number of isolated pairs also differ in the yield of free ions, see, *e. g.*, refs (Bartczak and Hummel, 1997; Siebbeles et al., 1997). Therefore, it is reasonable to use more complex models, which take into account the formation of spurs, to analyze the conductivity of irradiated media, too.

As one of the approaches that estimated the characteristics of an isolated "characteristic" spur, separate measurements of the time-resolved magnetic and electric field effects in radiation-induced fluorescence has been suggested (Borovkov and Velizhanin, 2007a). These measurements were realized using dodecane solutions of the positive charge acceptor *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD). Computer simulation was used to choose the set of parameters of the "characteristic" spherical spur such as radius, the number of the primary pairs in it, and the characteristics of the distance distribution function of primary pairs that could allow one to explain quantitatively both the data on the free ions and the results of the field effects in recombination fluorescence.

Note that studies of possible multi-spur effects (Saeki et al., 2005; Pimblott et al., 1992; Kim et al., 1996; Green and Harris, 1992), which actually are a manifestation of the track structure on the scales that exceed the size of an individual spur, showed that within the frameworks of computer modeling, these effects may be considered as noticeable, but it is very hard to isolate them in experimental data obtained by pulse radiolysis technique.

The computer simulation can surely be applied to describe completely the formation of the primary radiation track and the kinetics of subsequent reactions starting from the electron thermalization process. This approach was realized (Uehara and Nikjoo, 2002, 2006; Horne et al., 2016; Pimblott and LaVerne, 1997) for water and aqueous solutions only since there are detailed data on the interaction cross-sections between water molecules and electrons of relatively low energy. However, independently on the availability of such data, to verify the results of any computer simulations, it is necessary to compare these results with those obtained in the relevant nature experiments. In particular, to verify experimentally the estimates of the characteristic distance between the neighbouring spurs, one should measure a quantity, which substantially depends on this distance.

Thus, measuring the kinetics of the product yield of any chemical reaction by the method of pulsed radiolysis seems rather ineffective for solving the task set. This can be supported by a series of reasons:

i) the products of possible intratrack reactions are typically independent of either in the same or in different spurs the initial reagents were formed;
ii) for the particles formed in the same spur, the kinetics of bimolecular reactions shows the weakly decaying hyperbolic tails that mask the possible contribution of the particles that were later involved in the reactions due to the remote spatial position;
iii) the number of the feasible intermediates, including the electron- and vibrationally excited ones, that contribute to optical absorption upon radiolysis of even pure organic liquids, is so great that some of these almost inevitable should be neglected that calls into question the reliability of the results obtained.

In this work, an attempt was made to examine the experimental possibility to measure the effect of the interaction of particles, formed in neighbouring spurs, using another approach. To do this by an example of irradiated alkanes, it is suggested to observe the joint effect of external both magnetic and electric fields on the kinetics of the radiation-induced fluorescence from irradiated solutions.

The advantage of this approach is that the magnetic field allows one to distinguish the radical ion pairs (RIPs), formed in the same spur. This is because only for geminate RIPs noticeable spin correlation and magnetic field effects on the yield of the singlet-excited recombination products can be observed. The relative contribution to the fluorescence intensity of the pairs formed in different parts of the track can be changed using an external electric field. It is well known that the field increases, on average, the probability of ion escape. However, it can be anticipated that in the radiation track, in a not-too-early time domain electric field increases the probability for some oppositely charged ions from the remote parts of the track to encounter. The recombination of these pairs should also result in the formation of the electron-excited luminophore states, but the spin correlation effects for such RIPs should be negligibly small.

The following sections describe the algorithm of computer simulation and used track models, the principles of the experimental techniques used, and the comparison of the experimental and the simulation results obtained.

2. Materials and methods

2.1. Experimental

The delayed fluorescence of diphenylacetylene (DPA) solutions in *n*-dodecane and squalane was excited by X-ray pulses of an energy of about 20 keV and of the duration of < 1.5 ns and was recorded by the method of photon counting using the X-ray fluorimeter described elsewhere (Anishchik et al., 1989). The dose per pulse was no more than 100 nGy, so the mean concentration of ion pairs just after irradiation is sure to be less than 10^{-13} mol/l. Note that the yield of the secondary radical ions is even several times less and decay rapidly with time.

The fluorescence of irradiated DPA solutions was recorded using a light filter with a transmission band of 360–430 nm. The cuvette for measuring the effects of external magnetic and electric field was constructed from diamagnetic materials and described elsewhere (Borovkov et al., 1997). To decrease the influence of possible instrumental drifts, the fluorescence decays were recorded for periods of 250 s, alternatively, with and without electric or magnetic field under computer control. The zero magnetic fields were adjusted to within ± 0.05 mT, the non-zero magnetic field as large as 0.1 T was applied. The electric field strength of up to 36 kV/cm was used. All measurements were performed at 293 ± 1 K. Solutions were carefully deoxygenated by several "freeze-pump-thaw" cycles to avoid influence of triplet dioxygen molecules regarding both electron transfer reactions with DPA