Optical-detection ESR tomography of short-lived ion–radical pairs in a radiation track

B. M. Odintsov and R. G. Yakhin
E. K. Zavoĭskiĭ Physicomechanical Institute, Kazan Science Center, Russian Academy of Sciences, 420029, Kazan, Russia

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The method of optical detection of ESR has been used for an ESR-tomography study of irregularities in the spatial distribution of short-lived paramagnetic centers in a radiation track. Samples of polystyrene with a 10^{-3} M admixture of paraterphenyl-d_{14} were used as models. It was shown with their help that optical detection raises the sensitivity of conventional ESR tomography by three or more orders of magnitude, and it expands the capabilities of the method in a fundamental way in research on new classes of compounds. The results show that the method of optical-detection ESR tomography proposed here makes it possible to carry out studies in the space of irregularities of short-lived ion–radical states. These states are crucial to fast solid-state chemical reactions which are of fundamental importance.

The problem of studying the structure and other properties of ion-radical states in a radiation track includes investigating not only the time-varying characteristics of reactions, the structure of the short-lived paramagnetic centers which are formed during the radiolysis, and other properties of these centers but also the spatial distribution of reacting particles. Obtaining information of this type may also be important for estimating the penetrating power and geometry of ionizing radiation. The methods of ESR and ESR tomography cannot be used for these purposes, because the paramagnetic centers that form are at an exceedingly low concentration, and they recombine rapidly.[1]

Methods of ESR tomography have been developing very rapidly in recent years.[2,3] In these methods, a nonuniform magnetic field with a constant gradient is superimposed on the steady-state uniform magnetic field H_0 of the ESR spectrometer. As the field H_0 is scanned, the conditions for a resonance become gradually satisfied in the layers of the sample perpendicular to the direction of the magnetic field gradient. The ESR spectrum which is measured thus contains information on the spatial distribution of paramagnetic centers and constitutes a convolution

$$C=(R\eta)S, \tag{1}$$

where S is the ESR spectrum in a uniform magnetic field, η is a characteristic function describing the attenuation of the ionizing beam in the material, and R is a one-dimensional projection of the distribution of paramagnetic centers onto the direction of the gradient.

The effectiveness of ESR tomography is governed primarily by the technical possibilities for creating magnetic field gradients and by the sensitivity of the receiver. The resolution of the method depends, in general, on the ESR linewidth in a uniform magnetic field, ΔS, and on the quantity $K_x = dH/dx$, i.e., the field gradient:

$$\Delta x = \Delta S / K_x . \tag{2}$$

Raising the sensitivity of the method is particularly desirable since ESR tomography is based on the detection of lines which are broadened in a nonuniform magnetic field. The effective sensitivity of the method is lowered in this case, since the signal intensity is inversely proportional to the linewidth. There is accordingly a great deal of interest in the possibility of raising the sensitivity of ESR tomography by methods of optical detection of magnetic resonances. Among these methods, the most sophisticated from the technical standpoint and in terms of the development of various applications is the method of optical detection of ESR (ODESR).[4,5] This method is based on the detection of changes in the intensity of the luminescence of the products of radical reactions caused by the absorption of a resonant microwave field. It has the exceedingly high sensitivity characteristic of optical methods. According to the results of Ref. 6, an ODESR signal can be observed at a steady-state concentration of radical pairs of only a few tens of ion-radical pairs with a lifetime $\sim 10^{-7}$ s. If an ordinary ESR spectrometer were used to detect a signal of this sort, the concentration of radical pairs would have to be higher by nine or ten orders of magnitude. (As we know, a standard ESR spectrometer operating with 100-kHz modulation has a sensitivity on the order of 10^{11} spins in a sample with $\Delta S \sim 1$ Oe and a lifetime $\sim 10^{-3}$ s.)

We can get a basic idea of the ODESR method by examining a simplified scheme for the formation of ion-radical pairs $A^- \cdots B^+$:

$$A^- \cdots B^+ \rightarrow A^* + B \rightarrow A + B + \hbar\nu .$$

An excited molecule A^* can arise in either a single or triplet state, depending on the multiplicity of the $A^- \cdots B^+$ radical pair at the time of recombination. We know from Ref. 1 that excited molecules of aromatic acceptors effectively fluoresce from only the singlet excited state. The multiplicity of the radical pairs can be altered before the recombination by means of the hyperfine-interaction or Δg mechanisms, which mix the singlet state S and the triplet state T_0 in an external magnetic field. In strong magnetic fields, the T_+ and T_- levels are away from resonance with an S level because of Zeeman splitting. The imposition of a resonant microwave field gives rise to transitions from T_0 to $T_\pm$ and to a depopulation of the S state. In turn, there is a decrease in the probability for singlet recombination and luminescence of the sample. It thus becomes possible to detect the ESR optically.

The primary disadvantage of ODESR is the limitation to the class of reactions in which the product arises in an electronically excited state and is capable of emitting light. In addition, an ESR spectrum can be measured only if the orientation of the electron spins changes substantially over the lifetime of the radical pair.

In this letter we are reporting a first attempt to study the spatial distribution of short-lived radical pairs by ODESR in a nonuniform magnetic field.

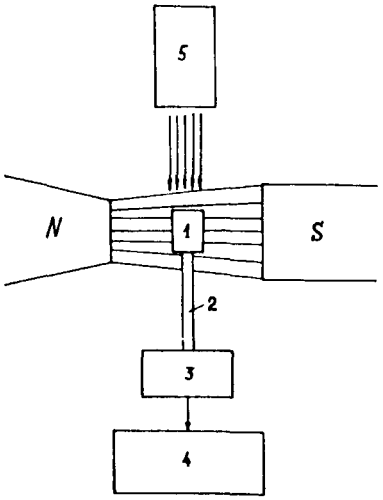

FIG. 1. Schematic diagram of the apparatus for optical detection of the ESR of ion–radical pairs produced by x radiation in a nonuniform magnetic field. *1*—Cavity; *2*—quartz optical fiber; *3*—photomultiplier; *4*—lock-in detector of the ESR spectrometer; *5*—x-ray tube.

As a model we selected the spatial distribution of ion-radical pairs which form during the radiolysis of paraterphenyl-d_{14} with a concentration of 10^{-3} M in a polystyrene matrix, using samples with various configurations.

Figure 1 is a schematic diagram of the ODESR apparatus. The magnetic field gradient is set up with the help of a special ZZG-1 tomographic attachment developed at the Instrument Construction Center, Academy of Sciences of the German Democratic Republic. This attachment consists of a set of oppositely connected, water-cooled Helmholtz coils mounted between the pole tips of the magnet of the ESR spectrometer and a system for regulating the current in the coils. The sample is held in a goniometer holder and a T_{102} microwave cavity. The use of a goniometer makes it possible to record a set of ESR spectra for various orientations of the sample with respect to the direction of the gradient. This set of spectra is required for reconstructing a 2D spatial distribution of paramagnetic centers.

The sample, with a volume of about 1 cm^3, is placed at the center of the ESR cavity, at the end of a quartz optical fiber. The ionizing radiation reaches the sample through a special aperture in the cavity. The emission intensity is monitored with the help of an FÉU-39 photomultiplier with a sensitivity spectrum of 160–600 nm. The sample is bombarded with the help of a BSV-24 x-ray tube with a tungsten anode at a dose rate on the order of 50 krad/h. According to Ref. 6, this dose rate would create a steady-state ionization of more than 10^6–10^8 radical pairs in the radiation track. The tube axis is parallel to the axis of the magnet. The exit window of the tube is 160 mm away from the surface of the sample. The photomultiplier and the x-ray tube are surrounded by special multilayer magnetic shields as protection against the field of the magnet of the ESR spectrometer. The ESR spectra are recorded as the external magnetic field is swept out with amplitude modulation. The output signal from the photomultiplier goes to the input of a U2-8 tuned amplifier, tuned to the 100-kHz modulation frequency, and then to the lock-in detector of the ESR spectrometer. The spectra are recorded directly on a Bruker ER-200 ESR spectrometer with an Aspekt-

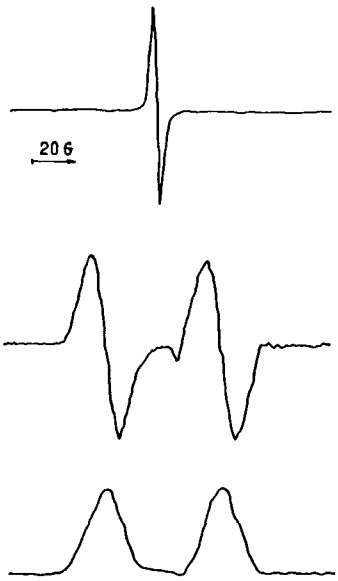

FIG. 2. Spectra of the $PTPD^+/PTPD^-$ ion–radical pair in polystyrene during x irradiation of a hollow-cylinder sample ($d_{out}=6$ m; $d_{in}=3$ mm). *a*—Spectrum of the optical detection of ESR in a uniform magnetic field; *b*—the same, in a nonuniform field with a gradient of 12 G/cm; *c*—1D projection along the direction of the gradient.

2000 computer at a frequency of 9500 mHz. The spectra (a set of projections onto the direction of the gradient) are sent to an IBM PC-compatible computer for further processing. The spatial distribution of paramagnetic centers is reconstructed by a special program[7] which uses the algorithms described in Ref. 8. All measurements were carried out at room temperature.

Figure 2 shows an ODESR spectrum of PTPD in polystyrene for a hollow-cylinder sample in uniform and nonuniform magnetic fields. The ODESR spectrum of $PTPD^-/PTPD^+$ pairs in a uniform field consists of a singlet of Lorentzian shape with a width of about 7 Oe and a *g*-factor close to that of a free electron. The time required to record the spectra was about 10 min at an instrumental time constant of 5 s. The modulation amplitude was 2 G for the spectra in the uniform field and 5 G with a field gradient. Increasing the microwave power to 0.5 W results in a monotonic increase in the intensity of the spectrum without a change in its shape and without "spin-locking" effects.[1] For a solid-cylinder sample, the imposition of a magnetic field gradient simply broadens the ODESR spectrum. The ESR spectrum of a hollow-cylinder sample changes significantly in a nonuniform magnetic field (Fig. 2). In this case, the integral intensities of the ESR spectra in nonuniform fields are essentially 1D spatial distributions of the paramagnetic centers along the gradient direction. Figure 3 shows corresponding tomographic images and tomograms of the test samples, constructed from nine projections (the sample was rotated through 20°). The tomogram of the solid cylinder indicates a uniform distribution of paramagnetic centers in the sample and an unobstructed passage (without attenuation) of the x radiation through the layer of polystyrene. We can thus set $\eta=\text{const}$ in expression (1). The tomogram of the hollow cylinder reflects the geometry of the sample accurately. For the selected value of the magnetic field gradient, $K_x=142$ G/cm, the linear spatial resolution of these ESR images does not exceed 5×10^{-2} cm according to (2). A deconvolution algorithm

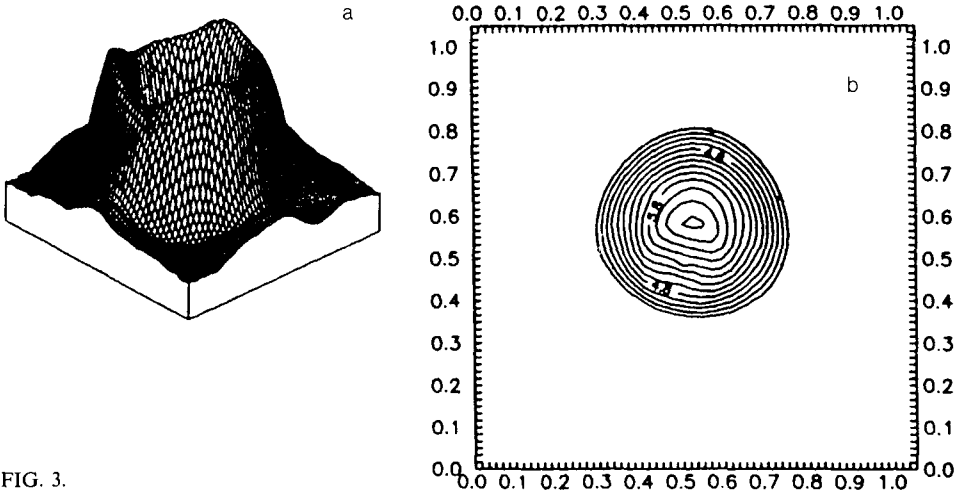

FIG. 3.

introduces negligible changes in the spatial distribution of paramagnetic centers, as would be typical of samples having an isolated ESR line.

This study has shown that optical detection increases the sensitivity of conventional ESR tomography by three or more orders of magnitude, and it expands the capabilities of the method for studying new classes of compounds in a fundamental way. The results obtained here show that ODESR tomography can be used to study spatial irregularities of short-lived ion-radical states, which are crucial to some fast solid-state chemical reactions of fundamental importance.

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