

# Observation of hyperfine structure in the optical detection of the EPR spectrum of short-lived ion-radical pairs in a fluid

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In this work we have resolved for the first time hyperfine structure in the optical detection of the EPR spectrum of short-lived ion-radical pairs, formed during interaction of ionizing radiation with a fluid.

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Recently, using an optical detection method, we recorded the unresolved EPR signal of short-lived ion-radical pairs formed in a fluid in the tracks of ionizing particles, for an average concentration of about 20 pairs in a sample.<sup>11)</sup> In this report using ion-radical pairs (biphenyl)<sup>+</sup>/(biphenyl)<sup>-</sup> it is shown that the optical detection method allows us to record the hyperfine structure (HFS) of the EPR spectrum by selecting proper conditions.

The principle of optical detection of the EPR spectrum for the actual case of ion-radical pairs of aromatic molecules in a nonpolar solvent reduces to the following. The electron and the hole occurring in the ionization of a solvent molecule are captured for a short time ( $< 10^{-10}$  sec) by molecules of the aromatic impurity. The ion-radicals thus formed are separated by a distance of  $\sim 100 \text{ \AA}$ , which does not exceed the Onsager radius and, therefore, they recombine inevitably, producing as a rule one molecule in an electron-excited state and another one in the ground state. Initially the spins of the pair radicals are oriented anti-parallel as in the original solvent molecule, i.e., the pair is in the singlet state. However, over the time for diffusion convergence ( $10^{-7} - 10^{-8}$  sec) the hyperfine coupling is capable of shifting the singlet and triplet states of the pair. Thus, in a strong external magnetic field only the  $T_0$  sublevel is populated, while the  $T_+$  and  $T_-$  sublevels are not mixed with the singlet state because of Zeeman splitting. As a result, depending on the multiplicity of the pair at the time of recombination, an electron-excited molecule will be formed either in a singlet luminescent state or in triplet ( $T_0$ ) state, which does not luminesce in the solution.

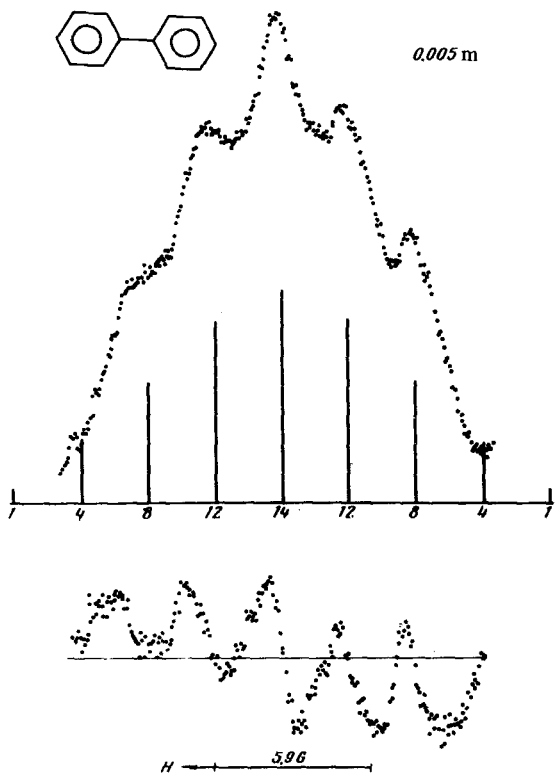


FIG. 1. Spectrum of an ion-radical pair (biphenyl)<sup>+</sup>/(biphenyl)<sup>-</sup> in squalane with 0.005 M biphenyl.

If we now superimpose a resonance shf-field causing transitions from the  $T_0$  level to the  $T_+$  and  $T_-$  sublevels, the population of the  $T_0$  level will be decreased which, in turn, leads to the depletion of the  $S$ -state mixed with  $T_0$  by the hyperfine coupling. As a result, the luminescence intensity will decrease, permitting the optical detection of the EPR spectrum.

To obtain the resolved HFS of the EPR spectrum it is necessary to reduce to a minimum the two basic contributions to the broadening, which are inherent in this method: broadening of  $H$ , by the shf-field which must be chosen rather large in order to obtain a good signal-to-noise ratio, and broadening due to the finite lifetime of the radical pair. In his connection, we applied a rather weak  $H$ , ( $< 0.5$  G), compensating for the drop in signal amplitude by increasing the build-up time (up to 1 hour). To increase the lifetime of a radical pair we used a viscous solvent, squalane, for which the recombination time for a pair of aromatic ion-radicals is about  $10^{-7}$  sec,<sup>[2]</sup> while the related broadening does not exceed 1 G.

The solution being studied with a volume of 0.5 ml was placed a Varian E-3 EPR spectrometer resonator in a quartz ampoule along with a  $\beta^-$  radioactive source  $^{90}\text{Sr}$  with a activity of  $15 \mu\text{Ci}$ , enclosed in a teflon container. The light from the sample was transmitted along a quartz light guide 560 mm long to a FEU-36 photomultiplier, placed in a permalloy shield. The fluorescence intensity was measured in the photon counting mode. The program assembly combined with the E-3 spectrometer field

analysis assembly and a Nokia LP 4840 multichannel analyzer allowed us to carry out multiple scanning for analyzing the field. The resulting information was stored in the analyzer memory and was output on a screen, a recorder, and on punched tape. Three hundred memory analyzer channels were used for which, following the output of the data to a computer, a smoothing procedure was carried out by summing over 9-11 adjacent channels, along with numerical differentiation.

Figure 1 shows the central region of the EPR spectrum and the first derivative of the spectrum for the radical pair (biphenyl)<sup>+</sup>/(biphenyl)<sup>-</sup>, formed by ionizing a solution of biphenyl ( $5 \times 10^{-3}$  M) in squalane at room temperature. Also shown schematically for comparison is the HFS spectrum for EPR of the biphenyl anion-radical plotted on the basis of data in the literature ( $A_0 = 2.73$  G,  $A_m = 0.43$  G,  $A_p = 5.46$  G<sup>(3)</sup>) without taking into account the small splitting by meta-protons which is not resolved experimentally. The splitting in the experimental spectrum is  $2.66 \pm 0.1$  G, which agrees with the result in the literature (2.73 G). As is known, the EPR spectra for anions and cations of aromatic compounds have similar HFS.<sup>(3)</sup> Thus, the spectrum which we observed most probably corresponds to the superposition of the spectra of a biphenyl anion and cation.

On increasing the biphenyl concentration in the solution we observed a smearing of the HFS and, subsequently, at concentrations of 0.25-0.5 M, a narrowing of the line. These changes are apparently due to charge transfer processes between ions and neutral molecules occurring before recombination, i.e., on a time scale of  $10^{-7}$  sec. Estimates using these data indicate that charge transfer occurs at each encounter between an ion and a neutral molecule.

According to simple estimates (see Ref. 1), the EPR spectra which have been considered are obtained at an average concentration of about 100 radical pairs in the sample. Comparison with the conventional EPR method shows that optical detection of the EPR spectrum leads to a gain in sensitivity by ten orders. Observation of HFS under these conditions may also open fundamentally new possibilities for identification and molecular dynamics of short-lived intermediate particles in the radiation track. This technique may also find application in the study of fast photochemical and thermal reactions accompanied by luminescence.

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