The method of time-resolved magnetic field effect in recombination fluorescence with magnetic field switching

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ABSTRACT

A technique for studying the spin evolution of radical ion pairs is proposed, which is based on switching off the magnetic field with a certain time delay after the ionizing radiation pulse giving rise to the pairs. The spin evolution of radical pairs upon field switching is described by a quasiclassical model. The modeling of magnetic field effect curves, measured for n-decane solutions of deuterated and protonated paraterphenyl, provides fair agreement between theory and experiment.

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1. Introduction

The influence of stationary and radiofrequency magnetic fields on radical reactions in solutions has been the matter of current interest in the last few years [1]. The methods of spin chemistry are most effective in studying this effect. One of these methods is the method of time-resolved magnetic field effect [2–5] which can be used to study the properties of short-lived radical ions with lifetimes up to nanoseconds. The general principle of the method is described in [2] and shown in Fig. 1. Ionizing irradiation of nonpolar solutions is known to produce spin-correlated radical ion pairs (RIP) whose initial spin state is mainly singlet. In zero magnetic field the singlet state S is mixed up due to hyperfine interactions of unpaired electron and phase relaxation with all the three RIP triplet states. The resulting population of the singlet state is 0.25. In a fairly high magnetic field, however, the mixing occurs mainly with only one of the triplet levels, T_0. Therefore, in a magnetic field the recombination fluorescence intensity which is directly proportional to the population of the RIP singlet state is higher than that in zero field.

The form of recombination fluorescence kinetics is rather difficult to analyze. To avoid this analysis and to focus on the peculiarities of RIP spin dynamics it is convenient to analyze the $I_B(t)/I_0(t)$ ratio of recombination fluorescence kinetics measured in high and zero magnetic fields, respectively. This ratio is referred to as time-resolved magnetic field effect. At short fluorescence time it is independent of recombination kinetics but contains information about the values of hyperfine interaction constants, g-factors, and the rates of the paramagnetic relaxation of the radicals in the RIPs [5]. However, in this approach, experimental modeling should take a concurrent account of singlet-triplet transitions in both high and zero magnetic fields. This imposes some limitations upon identification of radical ions for which the HFI character is unknown. In addition, radical ions are also difficult to identify in the case where the chemical reaction leading to the conversion of radical ions, occurs within the time range recorded. Actually, these reactions can be studied by this method only at times shorter than that of RIP phase relaxation.

The present work reports the technique for observing RIP spin dynamics in the case where magnetic field is switched off. It is proposed to measure both the fluorescence kinetics, $I_0(t)$ in a zero magnetic field and the $I_{B\to0}(t)$ kinetics in a magnetic field with a jump from some value to zero at certain instants of time after ionizing radiation pulse. In this case, the field can be switched off at the time taken to complete the singlet-triplet mixing in zero field, i.e., when the value of the population of the RIP singlet state reaches 0.25. As a result, the $I_{B\to0}(t)/I_0(t)$ ratio will be determined solely by the evolution of the spin state of the RIPs subjected to the field jump. This evolution occurs in a zero magnetic field, and the non-equilibrium initial state depends on the evolution in the initial non-zero magnetic field. Varying the time at which the field is switched off, one can observe spin evolution in RIP ensembles with the different contribution of radical ion 'reagents' and 'products' which can provide a new possibility for studying the reactions of short-lived radical ions in liquid solutions. For this method to be more informative, the time of field switching-off should be substantially shorter than that of radical phase relaxation. In addition, to attain a larger amplitude of effects, the magnetic field (before being switched off) should noticeably exceed the width of the spectrum of electron paramagnetic resonance (EPR) of the radicals studied.

A similar approach has been used to study radicals by the CIDNP method [6–8]. The authors have demonstrated that the magnetic field switching in CIDNP-experiments provides additional information on the properties of the radical particles under study. Another

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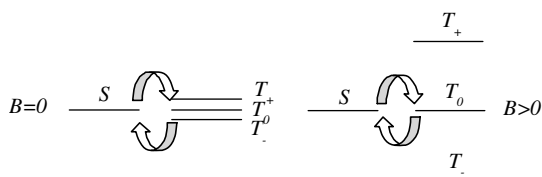
Fig. 1. Underlying principle of magnetic field effect generation.

example of this method is the real-time observation of the spin-state mixing process of a micellized radical pair in weak magnetic fields by nanosecond fast field switching proposed in [9].

2. Experimental

The setup intended for magnetic field switching-off is integrated in a nanosecond X-ray fluorimeter operating in the single-photon counting mode [11]. Fluorescence was excited at a frequency of 80 kHz by X-ray pulses with a duration of 2 ns with a quantum energy of about 20 keV. A quartz cuvette, containing

$$\widehat{U}(\boldsymbol{\Omega}, t) = \begin{pmatrix} \cos\boldsymbol{J} + (1 - \cos\boldsymbol{J})n_x^2 & (1 - \cos\boldsymbol{J})n_x n_y - \sin\boldsymbol{J}n_z & (1 - \cos\boldsymbol{J})n_z n_x + \sin\boldsymbol{J}n_y \\ (1 - \cos\boldsymbol{J})n_x n_y + \sin\boldsymbol{J}n_z & \cos\boldsymbol{J} + (1 - \cos\boldsymbol{J})n_y^2 & (1 - \cos\boldsymbol{J})n_y n_z - \sin\boldsymbol{J}n_x \\ (1 - \cos\boldsymbol{J})n_z n_x - \sin\boldsymbol{J}n_y & (1 - \cos\boldsymbol{J})n_y n_z + \sin\boldsymbol{J}n_x & \cos\boldsymbol{J} + (1 - \cos\boldsymbol{J})n_z^2 \end{pmatrix}. \tag{4}$$

luminophore solution with a volume of 0.5–1 ml, was located in a small solenoid in the immediate region of irradiation. The scheme of the setup for field switching on/off is presented in [12]. It provides a field of about 4 mT and the time 22 ± 2 ns during which the field is switched off to <0.2 mT.

The solvent – n-decane – was stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. Paraterphenyl-h_{14} (p-TP-h_{14}) and para-terphenyl-d_{14} (p-TP-d_{14}) served as electron and hole acceptors as well as luminophore, and were used without further purification as received from Aldrich.

3. Theory

The recombination fluorescence kinetics is proportional to the product of RIP recombination rate and singlet state population, $\rho_{ss}(t)$ [2–5]. Plotting the curves of the time-resolved magnetic field effect, defined as the ratio of recombination fluorescence kinetics with and without external magnetic field switching, we get the equation for singlet-state populations

$$\chi(t) = \frac{\rho_{ss}^{B \to 0}(t)}{\rho_{ss}^0(t)}. \tag{1}$$

This population depends on both the HFI and the interaction with the external field of radical ions composing RIPs. The quasi-classical approximation [10] which holds for HFI giving an unresolved ESR spectrum, was used to calculate spin dynamics upon external magnetic field switching. In this approximation, the HFI is replaced by the interaction between the electron spin and the effective internal magnetic field whose distribution in projection values provides the same value for the second momentum of ESR spectrum σ^2 which equals to that of the real HFI.

The calculations, performed in this approximation for zero magnetic field, give [10]

$$\rho_{ss}^0(t) = \frac{1}{4} + \Theta \frac{1}{12} e^{-t/T_0} (1 + 2C(\sigma_1 t))(1 + 2C(\sigma_2 t)), \tag{2}$$

where $C(x) = (1 - x^2)e^{-0.5x^2}$, Θ is the fraction of the spin-correlated singlet RIPs, i.e. fraction of RIPs which recombination goes with parent counterions, T_0 is the paramagnetic relaxation time in zero field, and indices 1 and 2 denote the two radicals of the RIP.

To calculate singlet state populations upon field switching, we use the fact [10] that during the interaction between the electron spins and a stationary homogeneous magnetic field this value obeys the equation

$$\rho_{ss}(t) = \frac{1}{4}\left\{1 + \Theta \sum_{i,k=1}^{3} U_{ik}^{(1)}(\boldsymbol{\Omega}, t) U_{ik}^{(2)}(\boldsymbol{\Omega}, t)\right\} \tag{3}$$

where $\widehat{U}(\boldsymbol{\Omega}, t)$ is the matrix of the spin moment rotation about magnetic field direction through the angle $\boldsymbol{J} = \boldsymbol{\Omega}t$, $\boldsymbol{\Omega}$ is the vector of the angular rate of the Larmor electron spin precession which can be called the magnetic field strength expressed in circular frequency units.

Thus, in the field whose direction is set by the unit vector $\boldsymbol{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, the rotation matrix is of the form

In the framework of the quasiclassical model, it is assumed that $\boldsymbol{\Omega} = \boldsymbol{\omega_0} + \boldsymbol{\omega}$, where $\boldsymbol{\omega_0}$ is the external field strength and $\boldsymbol{\omega}$ is the internal field strength. The magnitude and direction distribution function of vector $\boldsymbol{\omega}$ is

$$dW(\omega, \theta) = \frac{1}{(\sqrt{2\pi}\sigma)^3} e^{-\frac{\omega^2}{2\sigma^2}} \omega^2 \sin\theta d\omega d\theta. \tag{5}$$

To calculate the singlet state population upon instantaneous external field switching-off at time τ, the rotation matrices averaged over the values and directions of the internal field ω with the distribution function (5) should be substituted in Eq. (3). In this case, the matrix $\widehat{U}(\boldsymbol{\omega_0} + \boldsymbol{\omega}, t)$ should be used for times $t < \tau$ and the product $\widehat{U}(\boldsymbol{\omega}, t - \tau)\widehat{U}(\boldsymbol{\omega_0} + \boldsymbol{\omega}, \tau)$ should be used for times $t > \tau$.

The experiment was modeled in terms of these relations and the averaging over ω was performed by numerical integration. The paramagnetic relaxation in the external field was neglected because, according to the analysis, its times in the systems studied are long enough and have a weak effect on the modeling results.

4. Results and discussion

Fig. 2 shows the experimental and calculated curves of the $I_{B \to 0}(t)/I_0(t)$ ratio obtained in the 10^{-3} M p-TP-h_{14} solutions in n-decane with field switching delay of 100 ns (curve 1) and 225 ns (curve 2) relative to the ionizing radiation pulse. The modeling (smooth lines) was performed under the assumption that the main contribution to the magnetic field effect is made by the p-TP-h_{14}^+/p-TP-h_{14}^- pairs in which both the radical ions display one and the same value $\sigma = 0.2$ mT [13].

The fitting parameters of the modeling were the instant at which the field was switched off, τ, the fraction of spin-correlated pairs, Θ, and the paramagnetic relaxation time in zero field, T_0. The fact that the obtained values of τ slightly exceed the delay times is assigned to the finite time at which the field switching scheme has
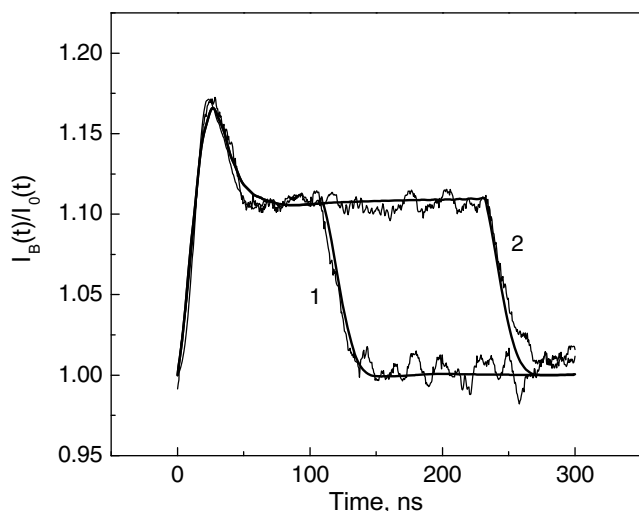
Fig. 2. Experimental and calculated (smooth line) curves for the $I_{B\to0}/I_0(t)$ ratio obtained in the 10^{-3} M p-TP-h_{14} solutions in n-decane at different delay times of field switching-off relative to ionizing radiation pulse. Modeling parameters: $\omega_0 = 4.0$ mT, $\sigma = 0.2$ mT, $T_0 = 40$ ns, $\Theta = 0.12$, the instant of external magnetic field switching-off: (1) $\tau = 110$ ns, (2) $\tau = 232$ ns.

operated. The best description corresponds to a fairly short relaxation time $T_0 = 40$ ns due to the fact that at times shorter than 50 ns a noticeable contribution to the magnetic field effect is made by the RH$^+$/p-TP-h_{14}^- radical ion pairs. The parameter σ of their solvent radical cation (n-decane) RH$^+$ substantially exceeds the one used in modeling, which causes a slightly faster initial increase in magnetic field effect which is corrected by the shortened T_0 value.

When the field is switched off, the singlet state population decreases to the value corresponding to the zero field and the observed $I_{B\to0}/I_0(t)$ ratio decreases to 1.

According to [2], a characteristic time of magnetic field effect decay in the zero field can be estimated as $1/\gamma\sigma$. For $\sigma = 0.2$ mT the decay time is estimated as 30 ns which is in agreement with experimental results.

Fig. 3 shows also the measurement results for the 10^{-3} M deuterated para-terphenyl (p-TP-d_{14}) solution in n-decane with a 110 ns delay in field switching-off relative to the ionizing radiation pulse. In this case, the observed decay time approaches 85 ns
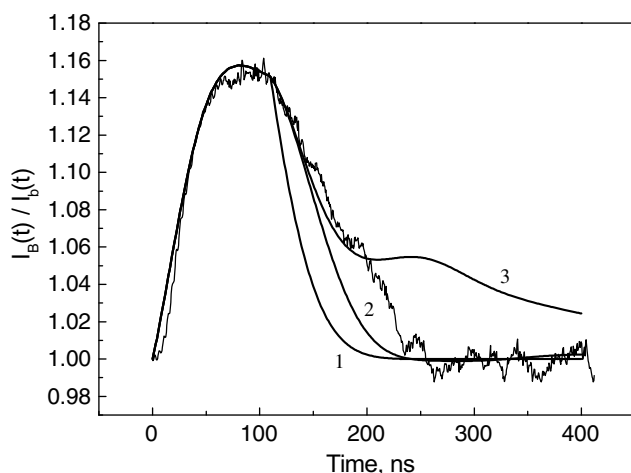
obtained from the value $\sigma = 6.7 \cdot 10^{-2}$ mT typical for p-TP-d_{14} radical ions [13]. Curve 1 on Fig. 3 is the calculation in the model described above with parameters presented in Fig. 3 caption. Quantitative agreement between the model calculation (Fig. 3, curve 1) and the experiment is in this case worse than in the previous one. The main difference is that model calculation predicts a faster decay of the MFE after switching in comparison with experiment. One of the reasons of this difference is using short relaxation time $T_0 = 40$ ns, which defines time of decay in calculations. As we mentioned above, such short relaxation time was used to describe the increase of MFE in the range of times less than 100 ns, where an appreciable contribution is given by RH$^+$/p-TP-d_{14}^- radical ion pairs. The characteristic time of the disappearance of such pairs is defined by positive charge capture rate constant on p-TP molecule and amounts to about 100 ns. This means that the contribution of these pairs after switching off magnetic field is too small and using such short relaxation time is unjustified. Curve 2 on Fig. 3 is the model calculation in our model with only one addition: relaxation time T_0 changes its value from $T_0 = 40$ ns to $T_0 = 200$ ns at the moment of switching off $\tau = 110$ ns. It can be seen that the decay in this case slows down notably, although still remains faster than in experiment. We assign this to the residual magnetic field whose magnitude in our setup can be comparable with the σ value which is sure to slow down the magnetic field decay. This assumption was verified by calculating the $I_{B\to0}(t)/I_b(t)$ ratio, where b is the magnetic field after switching, for two values of $b = 0.1$ mT and 0.2 mT. The calculated results are shown in Fig. 3 by curves 2 and 3. The residual field is observed to slow down the decay. Thus, the method proposed can be used to observe the RIP spin dynamics after magnetic field switching-off in real time. The distinction observed in the experiments on the solutions of p-TP-h_{14} and its deuterated analog p-TP-d_{14} indicates that the shape of the magnetic field effect curve decay after magnetic field switching is mainly determined by HFI in the RIP. This makes it possible to observe radical ions at times exceeding the phase relaxation ones.

5. Conclusions

We propose a version of the technique of time-resolved magnetic field effect in recombination luminescence, involving fast magnetic field switching-off with a controlled delay after the pulse giving rise to radical ions in solution. The simplest examples of radical ions with unresolved ESR spectra are used to demonstrate that the method is suitable for studying the dynamics of the spin state of radical ion pairs. In these cases, the spin dynamics is reduced to a simple decay of the magnetic field effect curve after field switching-off. The decay rate is proportional to the ESR spectrum width of the radicals. The method proposed can provide additional possibilities for studying short-lived radical ions in solutions such as the study of the kinetics of radical ion reaction transformations.

Fig. 3. Experimental and calculated (smooth line) curves for the $I_{B\to0}/I_b(t)$ ratio for the 10^{-3} M p-TP-d_{14} solutions in n-decane. Modeling parameters: $\Omega = 4.0$ mT, $\sigma = 0.067$ mT, $T_0 = 40$ ns, $\Theta = 0.175$, the calculated time of external magnetic field switching-off $\tau = 110$ ns. (1) $b = 0$ mT, (2) $b = 0.1$ mT, (3) $b = 0.2$ mT.

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