

Experimental and theoretical study of spin evolution ‘switching on’ of the radical ion pair in MARY spectroscopy

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The paper treats the consequences of abruptly switching on the spin evolution in a spin-correlated radical ion pair as a result of the transformation of its hyperfine structure upon charge transfer to an acceptor to form a radical ion with substantial hyperfine couplings. A simple model is developed, evaluated, and checked in a specifically chosen experimental system using MARY spectroscopy. The predictions are compared with the opposite limiting case of ‘freezing’ spin evolution in the pair after charge transfer, and the relation between them is discussed.

Keywords: MARY spectroscopy; Spin evolution; Radical ion pair

1. Introduction

The technique of the magnetic field dependence of reaction yield (MARY) spectroscopy of spin-correlated radical ion pairs is based on the examination of sharp extrema, which appear on the curves of the magnetic field effect in the region of weak magnetic field due to the crossing of radical pair energy levels [1–12]. The shape and positions of these extrema are determined by ESR spectra and the lifetimes of the radical pair partners and can be used to extract spectroscopic information concerning short-lived radical ions [13–15].

In a radiation chemical experiment the desired pair is usually prepared by capturing the partners of the primary pair, the solvent hole and electron that are produced by ionization of the solvent molecule, by suitable acceptors [16]. It is a common situation that charge transfer to an acceptor is accompanied by the instantaneous transformation of the hyperfine structure of one of the partners in the recombining radical ion pair A/B. This process can be described as a monomolecular reaction:



Understanding its manifestations in experimental spectra is very important for the correct interpretation of experimental data. In this work we will discuss the specific situation of MARY spectroscopy under X-irradiation [15].

In our previous work [17] we analysed one of the limiting cases of reaction (1), when the reaction leads to effective ‘freezing’ of the spin evolution in radical ion pairs. In this case, hyperfine couplings in the partners of the final pair C/B were negligible, and partner A had a ‘wide’ ESR spectrum, providing all the hyperfine interactions in the pair. In this work we turn to the opposite limiting case of reaction (1), with hyperfine couplings in the initial pair A/B being negligible and partner C having a wide ESR spectrum. This transformation of the ESR spectra of the pair partners is shown schematically in figure 1. This situation corresponds to

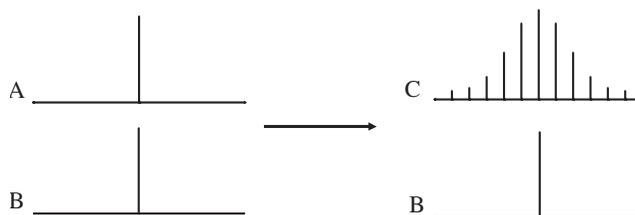


Figure 1. Scheme for the transformation of ESR spectra of the partners in a radical pair upon ‘switching on’ of spin evolution in the pair.

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‘switching on’ of the spin evolution in pair partner A/C and thus in the pair as a whole.

2. Experimental

Magnetic field effects under X-irradiation were recorded under stationary conditions as first described in [18]. The experimental MARY setup, sample preparation, and the experimental approaches of MARY spectroscopy as used here were recently described in detail [15, 19]. The sample, containing about 1 ml of degassed solution in a quartz cuvette, is placed in the magnetic field of a Bruker ER-200D CW ESR spectrometer equipped with an X-ray tube for sample irradiation (Mo, 40 kV \times 20 mA), a pair of coils with a separate current source to provide the constant ‘negative’ shift of the field required to sweep through the zero of the field, and a PMT for fluorescence detection. The scanned magnetic field was modulated at a frequency of 12.5 kHz with an amplitude up to 1 mT. A Stanford SR-810 Lock-In Amplifier and computer averaging over 20–40 scans were used to obtain the spectra, obtained as the first derivatives of the actual field dependencies. No microwave pumping was applied to the sample. All experiments were carried out at room temperature ($20 \pm 3^\circ\text{C}$).

The solvents, *c*-hexane, *n*-nonane and *n*-decane, were stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. *p*-Terphenyl-*d*₁₄ (PTP-*d*₁₄, Aldrich, 98 at.% D) and durene (Fluka, >99%) served as electron and hole acceptors, respectively, and were used as received.

3. Theoretical description

A detailed description of the spin evolution operator formalism based on the theoretical approach that we use to take into account reaction (1) in the simulation of MARY spectra was given in our work on spin evolution freezing [17]. Here we will only briefly reproduce the key formulae and the final expression of this general description, from which the desired limiting cases can be obtained. The stationary magnetic field effect curve (MFE) G_s is theoretically described as a convolution of the time-dependent population of the singlet state of the pair $\rho_{ss}(t)$ with recombination kinetics $f(t)$

$$G_s = \int_0^{\infty} \rho_{ss}(t) f(t) dt, \quad (2)$$

where $\rho_{ss}(t)$ is given by [20, 21]

$$\rho_{ss}(t) = \frac{1}{4} \{1 + \text{Tr}[U_A(t)U_B^+(t)]\}, \quad (3)$$

where $U_A(t)$ and $U_B(t)$ are the spin evolution operators of the two partners of the pair. Both $\rho_{ss}(t)$ and G_s depend parametrically on magnetic field H , and for simplicity we neglect relaxation. To take into account reaction (1) we rewrite expression (3) [17]

$$\rho_{ss}(t) = \rho_{ss}^{(i)}(t) e^{-t/\tau_c} + \int_0^t \rho_{ss}^{(f)}(t, \tau) e^{-\tau/\tau_c} \frac{d\tau}{\tau_c}. \quad (4)$$

Here $\rho_{ss}^{(i)}(t)$ is the singlet state population of the initial pair A/B, and $\rho_{ss}^{(f)}(t, \tau)$ is the population of the pair A/B that has undergone transition into the pair C/B at moment τ ($t > \tau$).

In the case of switching on of the spin evolution in the pair, i.e. when hyperfine couplings in partners A and B are negligibly small and partner C has a wide ESR spectrum (figure 1), the following expressions for the population of the singlet state in the initial and the final pairs are obtained:

$$\begin{aligned} \rho_{ss}^{(i)}(t) &\approx 1, \\ \rho_{ss}^{(f)}(t, \tau) &= \frac{1}{4} \{1 + \text{Tr}[U_C(t-\tau)U_B^+(t-\tau)]\} = \rho_{ss}^{(f)}(t-\tau). \end{aligned} \quad (5)$$

Here $\rho_{ss}^{(f)}(t-\tau)$ is the singlet state population in pair C/B which was born at moment τ and evolved during the time $(t-\tau)$ until the moment of observation. In other words, in this case we will observe a magnetic field effect only from the final pair C/B with the time delay equal to τ , and expression (4) takes the form

$$\rho_{ss}(t) = \rho_{ss}^{(i)}(t) e^{-t/\tau_c} + \int_0^t \rho_{ss}^{(f)}(t-\tau) e^{-\tau/\tau_c} \frac{d\tau}{\tau_c}. \quad (6)$$

Using this function $\rho_{ss}(t)$, it is now possible to calculate the stationary MFE for any suitable model of the spin motion in radical C. In this work we again chose the model with equivalent nuclei, which allows straightforward analytical solution. As the kinetics of recombination we used the exponential distribution

$$f(t) = \frac{1}{\tau_0} e^{-t/\tau_0}, \quad (7)$$

with the single cumulative parameter τ_0 , the effective recombination time. The distribution (7) is a reasonable approximation for the recombination kinetics of radical

ion pairs in non-polar solutions of moderate viscosity [22, 23] and allows analytical evaluation of the integral for the sought function G_s (2). If necessary, more complex recombination kinetics can then be treated by expanding them into simple exponentials [24].

4. Results and discussion

4.1. Expected transformations of MARY spectra

First we will consider the consequences of bringing HFC into the pair as a result of charge transfer to an acceptor in the following model system: partner C has 12 equivalent protons with $A_{\text{HF}} = 1.25$ mT, partners A and B contain no magnetic nuclei, the effective recombination time is $\tau_0 = 5$ ns, and the characteristic charge transfer time τ_c is varied.

The general expression for G_s for a system with an even number of spin-1/2 nuclei in the partners in the case of exponential recombination kinetics can be found in [7]

$$G_s = \sum_{I_1=0}^{M_1} \sum_{I_2=0}^{M_2} W_1(I_1) W_2(I_2) \tilde{\rho}_{\text{ss}}(p, I_1, I_2), \quad (8)$$

where summation is carried out over nuclear sub-ensembles with total spins I_1 and I_2 for the first and second radical, respectively, M_1 and M_2 are the maximum values of the total nuclear spins in the partners, $\tilde{\rho}_{\text{ss}}(p, I_1, I_2)$ is p times the Laplace transform of $\rho_{\text{ss}}(t)$ (6) for the sub-ensemble with nuclear spins I_1 and I_2 , the Laplace parameter p is taken to be $p = 1/\tau_0$, and the expression for the statistical weights $W_1(I_1)$ and $W_2(I_2)$ can be found in [25]

$$W(I) = \frac{(2I+1)^2}{2^n(n+1)} C_{n+1}^{(n/2)-I}, \quad (9)$$

where C_m^k is the conventional binomial coefficient.

If we take into consideration reaction (1), $\tilde{\rho}_{\text{ss}}(p, I_1, I_2)$ must be changed to

$$\tilde{\rho}_{\text{ss}}(p, I_1, I_2) \longrightarrow \frac{\tau_c/\tau_0}{1 + \tau_c/\tau_0} \tilde{\rho}_{\text{ss}}^{(i)}(p + 1/\tau_c, I_1, I_2) + \frac{1}{1 + \tau_c/\tau_0} \tilde{\rho}_{\text{ss}}^{(f)}(p, I_1, I_2). \quad (10)$$

We will consider here only the special case of $I_2 = 0$, i.e. all magnetic nuclei are contained in one partner. For comparison with experiment, the spectra are computed as first derivatives $\delta G_s/\delta H$.

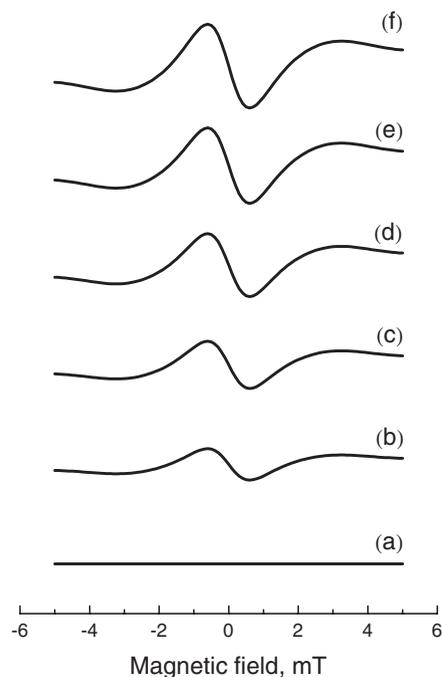


Figure 2. Calculated MARY spectra: manifestation of spin evolution 'switching on' as a result of single electron charge transfer. (a) $\tau_c = \infty$; (b) 10 ns; (c) 5 ns; (d) 2.5 ns; (e) 1.25 ns; (f) 0.6252 ns. See text for further details.

As can readily be seen, expression (10) consists of two parts. The first term corresponds to the signal from the initial pair A/B. Its shape depends on the time the spin evolution is switched on via the shifting parameter p as $1/\tau_c$, similar to the situation of spin evolution freezing [17], and its intensity increases with increasing ratio τ_c/τ_0 . However, in the case of negligibly small hyperfine couplings in partners A and B (see equation (5)), this term only produces an intensity shift that does not depend on the applied magnetic field and thus vanishes upon differentiation $\delta G_s/\delta H$. It then follows that the observed signal will, in this case, be determined only by the second term of expression (10), i.e. by the population of the singlet state in the final pair C/B. It can also be seen that the shape of the MARY spectrum now does not depend on the characteristic time of reaction (1) τ_c , and its intensity increases with decreasing ratio τ_c/τ_0 .

Figure 2 shows the calculated MARY spectra for this model system when switching the spin evolution on. The only difference between the curves is the 'switching time', τ_c , which decreases from bottom to top.

As can be seen, with decreasing switching time the intensity of the calculated MARY spectrum increases, but its shape remains unchanged. This should be compared with the situation of spin evolution freezing [17], where shortening of the switching time leads to damping and broadening of the MARY spectrum.

The qualitative difference between these two situations is that, in the case of freezing, the infinite tail of the distribution of the times available for spin evolution is cut off, whereas in the case of switching on, only a finite initial portion of the infinite distribution is removed.

4.2. Experimental transformations of MARY spectra: *c*-hexane solutions

Experimentally, the effect of switching on the spin evolution in MARY spectra was checked on solutions of durene and PTP- d_{14} in *c*-hexane. The pair *c*-hexane⁺/PTP- d_{14}^- plays the role of the initial pair A/B, since both these radical partners have rather narrow ESR spectra: the second moment of the PTP- d_{14} radical anion $\sigma \approx 0.09$ mT, whereas the solvent hole of *c*-hexane is narrowed by the fast reaction of degenerate ion–molecular charge transfer in its own matrix. The final pair C/B is the pair durene⁺/PTP- d_{14}^- , where the radical cation of durene is the wide partner with $\sigma \approx 2$ mT. Figure 3 shows the results of this experiment. The concentration of durene increases from bottom to top, which corresponds to shortening of the switching time.

As can be seen from figure 3, increasing the concentration of durene in solution results in a

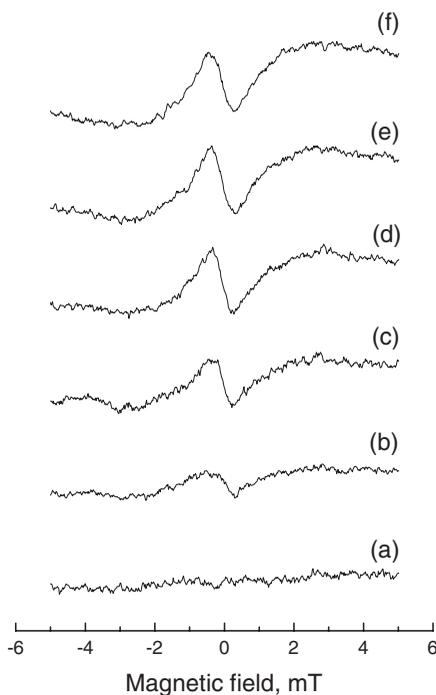


Figure 3. Field dependence of the fluorescence intensity from a *c*-hexane solution of 10^{-4} M PTP- d_{14} containing durene ($(\text{CH}_3)_4\text{C}_6\text{H}_2$) at different concentrations taken as the first derivatives. (a) $[(\text{CH}_3)_4\text{C}_6\text{H}_2] = 0$; (b) 10^{-3} M; (c) 2×10^{-3} M; (d) 4×10^{-3} M; (e) 8×10^{-3} M; (f) 1.6×10^{-2} M.

transformation of the experimental MARY spectra, as predicted by modeling the switching process (figure 2): the intensity of the signal increases while its shape does not change, and the observed signal is the signal from the pair durene⁺/PTP- d_{14}^- . These experiments were performed under identical conditions that determine the absolute intensity of the signal: the PMT voltage, modulation amplitude, settings of the lock-in amplifier and the number of scans remained constant throughout the series of spectra. The vertical scales in figures 2 and 3 are also identical for all spectra in the figure.

4.3. Experimental transformations of MARY spectra: *n*-alkane solutions

Figure 4 shows experimental MARY spectra for solutions of 10^{-4} M PTP- d_{14} in *n*-decane (figure 4(a)) and *n*-nonane (figure 4(b)). The original idea to compare the concentrational transformations in solutions of cyclic and normal alkanes originated from a comparison of the mobilities of solvent holes in these solutions. If radical cations of *n*-alkanes have, in their own matrices, normal mobilities of molecular radical ions, solvent holes in *c*-hexane have an order of magnitude greater mobility than guest molecular ions [26]. If a cyclic and a normal alkane with similar viscosity are taken, and concentrations of all acceptors are

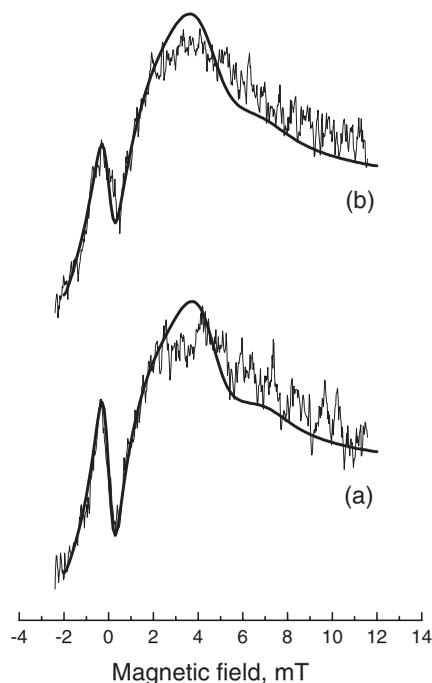


Figure 4. Field dependence of the fluorescence intensity for a *n*-nonane (a) and *n*-decane (b) solution of 10^{-4} M PTP- d_{14} taken as the first derivatives. Smooth curves are the simulation. See text for further details.

kept equal, then the rates of all viscosity-dependent ion–molecular processes, such as recombination and degenerate ion–molecular charge transfer, should be equal. The only exception will be the process of solvent hole capture by a hole acceptor, in our case durene, which will be much faster in cyclic alkane and which leads to switching on of spin evolution in the pair. In other words, in a pair of linear and cyclic solvents of similar viscosity, in our case *c*-hexane and *n*-decane with a viscosity of about 1 cP at room temperature, the only difference will be the difference in switching time, which was expected to be observable in the MARY experiment.

However, in contrast to solutions of *c*-hexane (figure 3(a)), here MARY spectra show that even without deliberately introducing a hole acceptor (durene), the spin evolution in the pair is not frozen, and a rather well-defined MARY spectrum is observed. This can most likely be explained by minute admixtures of impurities such as solvent isomers or solvent-derived olefins with ESR spectra of appreciable width that can act as positive charge acceptors. The alternative that the observed MARY spectra originate from solvent holes themselves can rather safely be ruled out after considering the results of simulation (*vide infra*), and other impurities such as aromatics and olefins not related to the solvent, if any, were removed by the solvent preparation procedure. If we consider this possibility, we obtain a system with reaction (1) without adding the other acceptor, durene, in which the role of the initial pair A/B is played by the pair *n*-nonane⁺(*n*-decane⁺)/PTP-*d*₁₄⁻, and the role of the final pair C/B is played by impurity⁺/PTP-*d*₁₄⁻. The results of the modeling of this situation are shown in figure 4 by bold lines and yielded numerical values for the second moments of the ESR spectra of the ‘narrow’ partner σ_{nar} (PTP-*d*₁₄⁻), the ‘wide’ partner σ_{wide} (impurity), as well as the characteristic time of recombination τ_0 and τ_c of reaction (1), which are collected in table 1.

The most important column of table 1 is the value of τ_c , which is, in our opinion, the time of positive charge transfer from the solvent hole to a molecule of an unknown admixture. This can be converted into the concentration of the admixture as follows. The rate constant of solvent hole transfer to the acceptor in *n*-decane is estimated to be about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Table 1. Results of MARY spectra simulation. See text for definitions of parameters.

Solvent	σ_{nar} (mT)	σ_{wide} (mT)	τ_0 (ns)	τ_c (ns)
<i>n</i> -Decane	0.09	2.45	7	50
<i>n</i> -Nonane	0.09	2.45	6	56

This value is obtained from the recently measured rate constant for charge transfer in *n*-hexane under almost identical conditions [27], about $4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and observing that this reaction is diffusion controlled and the viscosities of the two solvents differ by a factor of 3 (0.31 cP for C₆H₁₄ and 0.92 cP for C₁₀H₂₂ at room temperature). This yields an estimate for the concentration of the admixture, which, in this case, amounts to about $2 \times 10^{-3} \text{ M}$. The relative intensity of the line in zero field turned out to be rather sensitive to the value of τ_c , therefore the latter can be extracted with a rather high (for such experiments) relative accuracy of $\sim 10\%$. We also note that the magnitude of the second moment of the ESR spectrum for the narrow partner σ_{nar} from table 1 corresponds to the known value for the radical anion of PTP-*d*₁₄, whereas the estimated second moment for the wide partner σ_{wide} does not correspond to the known second moments for radical cations of *n*-decane ($\sigma \approx 0.54 \text{ mT}$) and *n*-nonane ($\sigma \approx 0.62 \text{ mT}$) [28], which indirectly confirms the presence of an unknown wide cationic partner in this system. Finally, we note that the values of the characteristic recombination times τ_0 are also very reasonable.

5. Conclusions

In this work we have extended the theoretical approach for taking into account monomolecular transformations of ESR spectra of radical ions due to the reaction of single ion–molecular charge transfer in the modeling of MARY spectra, put forward by Verkhovlyuk *et al.* [17], to cover another limiting case of reaction (1)—switching on of spin evolution in a radical ion pair. Theoretical analysis of the consequences of switching the spin evolution on using a model system showed that, compared with the opposite limiting case of spin evolution freezing, the shape of the MARY spectrum does not change. The only manifestation of spin evolution switching on is a change in the MARY signal intensity, which increases with shortening switching time. The observed spectrum is the spectrum for the final pair, in which spin evolution is driven by substantial hyperfine couplings in the newly acquired wide partner. Experimentally, this prediction was verified for solutions of PTP-*d*₁₄ and durene in *c*-hexane.

As an interesting by-product of the theoretical simulation of MARY spectra taking into account the effect of the switching on of spin evolution we obtained a procedure for estimating the amount of impurities that are always present in normal alkanes, such as their structural isomers, and which are very difficult to

eliminate using conventional solvent purification techniques. The estimated concentration of impurities in *n*-nonane and *n*-decane used in this work is about 2×10^{-3} M.

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