Experimental and theoretical study of spin evolution 'freezing' of the radical ion pair in MARY spectroscopy

V.N. Verkhovlyuk [a,*], V.A. Morozov [b], D.V. Stass [a,c], A.B. Doktorov [a], Yu.N. Molin [a]

[a] *Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia*
[b] *International Tomography Centre, 630090 Novosibirsk, Russia*
[c] *Novosibirsk State University, 630090 Novosibirsk, Russia*

Received 30 June 2003; in final form 30 June 2003

Abstract

The Letter presents a method of describing the process of single charge transfer in the partner of a radical ion pair, accompanied by changes in its hyperfine structure. In the particular case of 'freezing' of spin evolution in the pair due to collapse of hyperfine interactions upon single charge transfer and in the approximation of exponential recombination kinetics the suggested model describes MARY spectra for three important classes of processes in nonpolar solutions: chemical decay of the pair partner, 'dark capture' of the partner, and slowing down of spin evolution in the partner upon abrupt narrowing of its ESR spectrum.
© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Magnetically affected reaction yield (MARY) spectroscopy of radical ion pairs in nonpolar solutions is based on studying sharp extrema, which appear on the curve of the intensity of recombination fluorescence, produced by ionizing irradiation of solution of a suitable luminophore, as a function of the external static magnetic field applied to the sample, referred to as the magnetic field effect (MFE) curve [1–6]. The physical origin of the extrema is crossing of the eigenstates of the spin-Hamiltonian of the spin-correlated radical ion pair in the region of weak magnetic fields, where their dependence on the field is nonlinear [7–10]. The positions and shapes of the extrema, referred to as MARY lines, are determined by the magnetic (ESR spectra) and kinetic (lifetimes, recombination and relaxation rates, etc.) parameters of the recombining radical ions and thus bear important information on these short-lived paramagnetic species. Experimentally the most convenient is the strongest MARY line occurring at zero magnetic field, and further on the discussion will be restricted to the symmetric vicinity of the zero of the applied field.

* Corresponding author. Fax: +7-3832-342350.
E-mail address: v_ver@ngs.ru (V.N. Verkhovlyuk).

An important process exploited by MARY spectroscopy is charge transfer from partners of the primary radical ion pair 'electron⁻/solvent radical cation⁺', induced by irradiation of the solution, to suitable acceptors to form the observable secondary pairs with required magnetic, kinetic, and fluorescing properties. It is a common situation that such a charge transfer is accompanied by instantaneous transformation of the hyperfine structure of one of the pair partners in the recombining radical ion pair A/B. This process can be described as a monomolecular reaction

$$A \xrightarrow{\tau_c^{-1}} C \qquad (1)$$

with rate constant equal to the inverse of the average residence time prior to transfer τ_c. Because of the universality of this process understanding its manifestations in MARY spectra is very important for correct interpretation of experimental results. In this work, we shall consider one of the particular cases of process (1), when the transfer is accompanied by abrupt narrowing of the ESR spectrum of partner A, the other partner B having narrow ESR spectrum.

2. Experimental

Magnetic field effect under X-ray irradiation was recorded under stationary conditions as first described in [11]. The experimental MARY setup and sample preparation have been described in [12]. The sample, containing about 1 ml of degassed solution in a quartz cuvette, is put into the magnetic field of a Bruker ER-200D ESR spectrometer equipped with an X-ray tube for sample irradiation (Mo, 40 kV × 20 mA), a pair of coils with a separate current source to provide constant 'negative' shift 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 get 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 ± 3 °C).

The solvents – *n*-hexane, *n*-nonane, *n*-hexadecane, isooctane – were stirred with concentrated sulfuric acid, washed with water, distilled over sodium, and passed through a column of activated alumina. N,N,N',N'-Tetramethyl-1,4-phenylenediamine (TMPD), hexafluorobenzene (C_6F_6), deuterobenzene (C_6D_6), deuteroparaterphenyl (PTP-d_{14}) served as electron and hole acceptors and were used without further purification.

3. Theoretical description

Radical ion pairs generated by ionization of nonpolar solutions and contributing to steady-state MARY spectra have the following convenient properties [13]: they are formed in the singlet spin-correlated state, can produce quantum of fluorescence upon recombination in the singlet state, and spin evolution of the pair partners is independent from each other and is decoupled from molecular motion until the moment of recombination, which proceeds at first 'contact' at a distance of about 1–2 nm and is spin-independent. In this situation the stationary MFE G_s is theoretically described as the convolution of the time-dependent population of the singlet state $\rho_{ss}(t)$ with recombination kinetics $f(t)$

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

where $\rho_{ss}(t)$ is given by [14,15]

$$\rho_{ss}(t) = \frac{1}{4} \left\{ 1 + \mathrm{Tr} \left[U_A(t) U_B^+(t) \right] \right\}, \qquad (3)$$

where $U_A(t)$ and $U_B(t)$ are the spin evolution operators of the partners, the sign '+' denotes Hermitian adjoint of the operator, and Tr is the usual operation of matrix trace. Both $\rho_{ss}(t)$ and G_s depend parametrically on magnetic field H, and for simplicity we shall for now neglect relaxation. In the spin evolution operator formalism reaction (1) leads to transformation of $U_A(t)$ into operator $U_{AC}(t)$ for effective partner AC

$$U_{AC}(t) = U_A(t) \cdot e^{-t/\tau_c} + \int_0^t U_C(t-\tau) U_A(\tau) \cdot e^{-\tau/\tau_c} \frac{d\tau}{\tau_c}. \qquad (4)$$

Substituting (4) in (3) for $U_A(t)$ gives the following expression for the singlet state population of the pair:

$$\rho_{ss}(t) = \frac{1}{4}\left\{ 1 + \mathrm{Tr}\left[U_A(t)U_B^+(t)\right] \cdot \mathrm{e}^{-t/\tau_c} \right.$$
$$\left. + \int_0^t \mathrm{Tr}\left[U_C(t-\tau)U_A(\tau)U_B^+(t)\right] \cdot \mathrm{e}^{-\tau/\tau_c} \frac{\mathrm{d}\tau}{\tau_c} \right\}$$
$$(5)$$

which can be rewritten as

$$\rho_{ss}(t) = \rho_{ss}^{(i)}(t) \cdot \mathrm{e}^{-t/\tau_c} + \int_0^t \rho_{ss}^{(f)}(\tau) \cdot \mathrm{e}^{-\tau/\tau_c} \frac{\mathrm{d}\tau}{\tau_c}, \qquad (6)$$

where the following notation was introduced:

$$\rho_{ss}^{(i)}(t) = \frac{1}{4}\left\{ 1 + \mathrm{Tr}\left[U_A(t)U_B^+(t)\right] \right\},$$
$$\rho_{ss}^{(f)}(t,\tau) = \frac{1}{4}\left\{ 1 + \mathrm{Tr}\left[U_C(t-\tau)U_A(\tau)U_B^+(t)\right] \right\}.$$
$$(7)$$

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

Although expression (6) can in principle be evaluated for certain classes of hyperfine structures of the three partners (equivalent nuclei, semiclassical approximation, and several other special cases, see, e.g. [16,17]), the results are expected to be rather cumbersome. More instructive are compact analytical solutions that can be obtained in certain limiting cases, in particular when hyperfine couplings (HFC) in partners B and C are negligibly small. Since in the weak fields that we are considering HFC are the only driving force for spin evolution in the pair, this leads to $U_C = U_B$, and taking into account that $U_{B,C}(t)$ here (in the absence of relaxation) are unitary operators, we obtain

$$\rho_{ss}^{(f)}(t,\tau) = \frac{1}{4}\left\{ 1 + \mathrm{Tr}\left[U_A(\tau)U_B^+(\tau)\right] \right\} = \rho_{ss}^{(i)}(\tau). \quad (8)$$

As can be seen from (8), in this case dependence on time t disappears, and the pair B/C just inherits and keeps the spin state of the initial pair A/B at the moment of charge transfer $\rho_{ss}^{(i)}(\tau)$, since S-T evolution in the pair without HFC is frozen. Expression (4) for $\rho_{ss}(t)$ then takes the form

$$\rho_{ss}(t) = \rho_{ss}^{(i)}(t) \cdot \mathrm{e}^{-t/\tau_c} + \int_0^t \rho_{ss}^{(i)}(\tau) \cdot \mathrm{e}^{-\tau/\tau_c} \frac{\mathrm{d}\tau}{\tau_c}. \qquad (9)$$

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

$$f(t) = \frac{1}{\tau_0} \cdot \mathrm{e}^{-t/\tau_0} \qquad (10)$$

with the single cumulative parameter τ_0, the effective recombination time. The distribution (10) is a reasonable approximation for recombination kinetics of radical ion pairs in nonpolar solutions of moderate viscosity [18] 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 into simple exponentials [19].

4. Results and discussions

4.1. Expected transformations of MARY spectra

Before analyzing experimental results, let us first consider the consequences of the collapse of HFC as a result of charge transfer to acceptor on the following model system: partner A has 10 equivalent protons with $A_{HF} = 1$ mT, partners B and C contain no magnetic nuclei, effective recombination time $\tau_0 = 10$ ns, and characteristic charge transfer time τ_c is varied. The general expression for G_s for a system with even numbers of spin-1/2 nuclei in the partners in the case of exponential recombination kinetics can be found in [4]

$$G_s = \sum_{I_1=0}^{M_1} \sum_{I_2=0}^{M_2} W_1(I_1)W_2(I_2)\tilde{\rho}_{ss}(p,I_1,I_2), \qquad (11)$$

where summation is carried out over nuclear subensembles 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, $\tilde{\rho}_{ss}(p,I_1,I_2)$ is p times Laplace transform of $\rho_{ss}^{(i)}(t)$ for subensemble with nuclear spins I_1 and

I_2 (we shall not quote it here), 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 [20]

$$W(I) = \frac{(2I+1)^2}{2^n(n+1)} C_{n+1}^{n/2-I}, \qquad (12)$$

where C_m^k is the conventional binomial coefficient. We shall consider here only the special case of $I_2 = 0$, i.e., all magnetic nuclei in one partner.

The expression for G_s for the complete function $\rho_{ss}(t)$ (9) with charge transfer (1) taken into account then differs from (11) just by shifted parameter $p: p \rightarrow p + 1/\tau_c$. To compare with experiment, the spectra are computed as first derivatives $\delta G_s/\delta H$.

Thus calculated MARY spectra are shown in Fig. 1. The curves differ only by τ_c, which shortens from bottom to top. The figure shows that decreasing τ_c leads to broadening of the zero field MARY line, which reflects shortening of the time
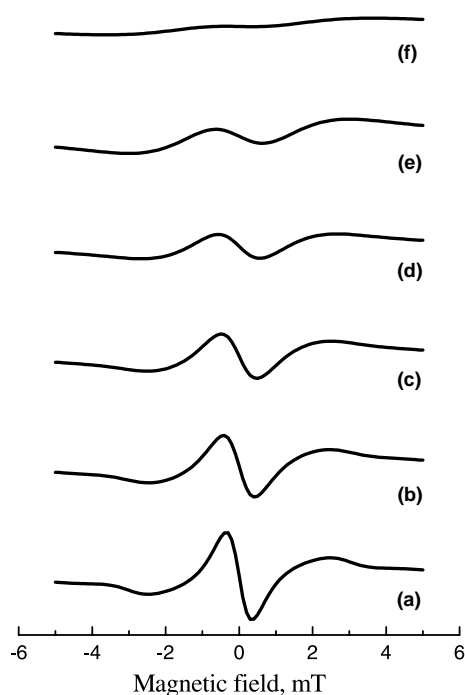

Fig. 1. The calculated MARY spectra: manifestation of the spin evolution 'freezing' due to single electron charge transfer. (a) $\tau_c = \infty$; (b) 32 ns; (c) 16 ns; (d) 8 ns; (e) 4 ns; (f) 2 ns. See text for other details.

available for spin evolution in the pair. Furthermore, the intensities of the MARY line and the 'normal' MFE – the wings in the opposite phase to the line – both decrease with decreasing τ_c, and the signal nearly vanishes for $\tau_0 = 2$ ns. The reason for this is that rapid freezing of spin evolution leads to rapid blocking of the spin state of the pair irrespective of the applied magnetic field, and thus to disappearance of the signal as derivative with respect to the field.

Besides the freezing of spin evolution, the width of the zero field MARY line is affected by other processes that shorten time available for coherent spin evolution, such as recombination, relaxation, and decay of the pair partners (if present). The peak-to-peak width of the line is proportional to the sum of the rates of all exponential processes in the system, i.e., the inverses of their characteristic times, which is true even for nonexponential recombination kinetics [19]. Since theoretically the contribution of the charge transfer τ_c is described by the exponential in expression (9), in the case of exponential kinetics of recombination (10) the two rates just add up yielding shorter effective lifetime of the pair.

The first term in (9) describes the probability for the initial pair A/B to survive by the moment of recombination t provided that charge capture $A \rightarrow C$ proceeds with characteristic time τ_c. This term when used alone describes decay of the pair A/B with time τ_c. Straightforward calculations show that the expression for the yield of singlets G_s can then be obtained from (11) by the substitution

$$\tilde{\rho}_{ss}(p, I_1, I_2) \rightarrow \frac{\tau_c}{\tau_0 + \tau_c} \tilde{\rho}_{ss}(p + 1/\tau_c, I_1, I_2). \qquad (13)$$

When both terms in (9) are considered, the expression describes true freezing of spin evolution, and the expression for G_s is obtained from (11) by the formal substitution

$$\tilde{\rho}_{ss}(p, I_1, I_2) \rightarrow \tilde{\rho}_{ss}(p + 1/\tau_c, I_1, I_2). \qquad (14)$$

That is how the spectra of Fig. 1 were calculated. It then follows that in the model of exponential recombination kinetics the transformations of the shape of MARY line are identical for the cases of freezing of spin evolution in the pair and chemical

decay of the pair except for the dimensionless amplitude scaling factor $\tau_c/\tau_0 + \tau_c \leqslant 1$ for the decaying pairs. The physical origin of this amplitude scaling is that in the case of freezing spin evolution is eventually blocked, but fluorescence is not dampened as is the case for chemical decay of the pair, when the magnetosensitive fluorescence from the pair is lost.

In the next three subsections we shall provide examples of real experimental situations when the suggested model is applicable, and comment on the validity of the approximation of exponential recombination kinetics.

4.2. 'Freezing' case I: chemical decay

Fig. 2 shows experimental MARY spectra for solutions of hexafluorobenzene in nonane with added isopropyl alcohol, obtained in [21]. Introduction of alcohol into alkane solution leads to diffusion-controlled reaction of the alcohol monomer with solvent radical cation, which removes the radical cation from spin evolution of the pair, most probably due to irreversible separation of spin and charge via proton transfer to the alcohol molecule [22]. Put another way, alcohol molecule destroys the radical ion pair via separation of spin and charge in one of the partners. The concentration of alcohol in these experiments was kept below the association threshold.

The smooth curves in Fig. 2 show the results of theoretical description in the model of spin evolution freezing. ESR spectrum width of the nonane radical cation (partner B, $2\sigma = 1.23$ mT [23]) is substantially lower than the width of $C_6F_6^-$ (partner A, six equivalent fluorines with couplings of 13.5 mT, $2\sigma = 33$ mT) and was taken to be equal to zero in the simulations, as was the width of the virtual partner C. Effective recombination time for this set of spectra was determined from fitting the spectrum without alcohol, which yielded $\tau_0 = 4$ ns. The only varied parameter is the charge transfer time τ_c, which shortens from bottom to top as the concentration of alcohol in solution is increased.

The time τ_c in this approach characterizes the rate of the reaction between alcohol molecules and solvent radical cations, and fitting of the concentration dependencies yields rate constant $k = 3 \times 10^{10}$ M^{-1} s^{-1}, which is about three times greater than
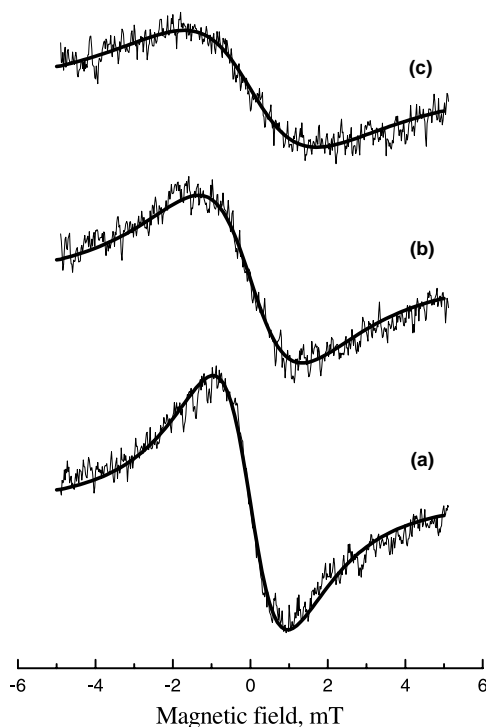

Fig. 2. The field dependencies of the fluorescence intensity of nonane solution of 6×10^{-3} M C$_6$F$_6$ containing isopropanol (i-C$_3$H$_7$OH) in different concentration taken as the first derivatives. The smooth curves are simulations for singlet-born radical pair with six equivalent nuclei with hfi constant equal to 13.5 mT in one of the partners (C$_6$F$_6^-$) and no magnetic nuclei in the second partner (nonane$^+$), and varying τ_c, $\tau_0 = 4$ ns. (a) [i-C$_3$H$_7$OH] = 0, $\tau_c = \infty$; (b) 3.3×10^{-3} M, 10 ns; (c) 6.6×10^{-3} M, 5 ns.

diffusion-controlled value for nonane in these conditions, in line with interpretation of results in terms of exponential recombination kinetics (see Section 4.5). In this case there is no real partner C to which the radical cation would relay its spin and charge, i.e., process (1) does not take place, but because of the discussed similarities between the processes of chemical decay and spin evolution freezing the suggested model is still adequate. The rather close shape reproduction demonstrated in Fig. 2 also supports the sensibility of the exponential recombination approximation in this system. And finally, we note that although the model implies that the hyperfine structure of the 'wide' partner collapses, in the case of chemical decay which partner experiences transformation is immaterial.

4.3. 'Freezing' case II: 'dark capture'

Another process that can be formally described as decay of the radical ion pair is the so-called 'dark capture' – the process, in which charge transfer from one of the partners of the pair leads to irreversible formation of a pair with normally evolving spin dynamics but with zero quantum yield of recombination fluorescence. One of the candidates for such a 'dark' system is the pair $C_6F_6^-/TMPD^+$ [24], in which both partners are known to be stable radical ions on the time scale of MARY experiment. The physical origin for this is the rather high electron affinity of C_6F_6 and rather low ionization potential of TMPD, so that upon recombination of such a pair the produced energy is not sufficient to generate a quantum of fluorescence.

Fig. 3 shows experimental MARY spectra for solutions of C_6F_6 in hexadecane with added TMPD. Introduction of TMPD into the solution indeed leads to broadening of the zero field MARY line coming from the pair $C_6F_6^-/$hexadecane$^+$, which reflects shortening of the time available for spin evolution of the pair due to its transformation into the 'dark' pair $C_6F_6^-/TMPD^+$. As opposed to the previous case, there does exist a partner that captures the charge (TMPD), but since it is not visible with the used registration technique, such a capture is equivalent to decay of the observed pair. The actual hyperfine structure of the 'dark' acceptor radical ion and whether the hyperfine structure in the pair collapses is again not important.

As with nonane, ESR spectrum width of the hexadecane radical cation ($2\sigma = 0.46$ mT [23]) is substantially lower than the width of $C_6F_6^-$ and was taken to be equal to zero in the simulations shown in Fig. 3 with smooth lines, effective recombination time $\tau_0 = 7$ ns. Again the only varied parameter is the characteristic time of charge transfer to TMPD τ_c, and the fit of the concentration transformation produced apparent rate constant 2×10^{10} M^{-1} s^{-1}.

4.4. 'Freezing' case III: freezing of spin evolution

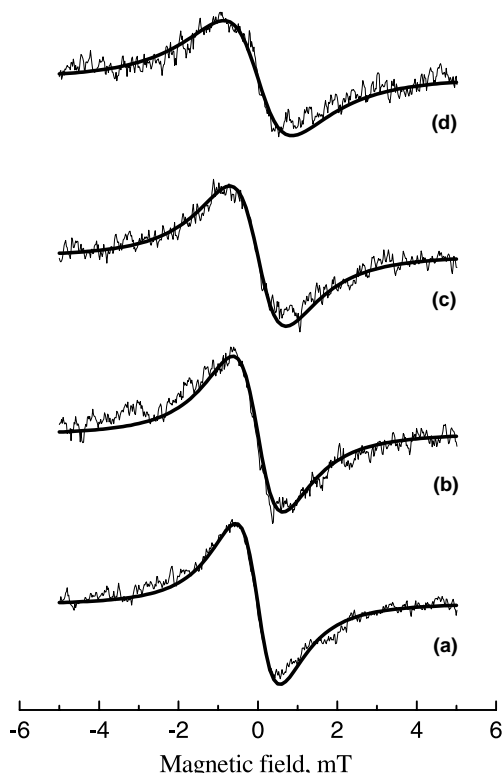Until now we considered systems, in which lifetime of the observable radical ion pair was

Fig. 3. The field dependencies of the fluorescence intensity of hexadecane solution of 1.3×10^{-2} M C_6F_6 containing TMPD in different concentration taken as the first derivatives. The smooth curves are simulations for singlet-born radical pair with six equivalent nuclei with hfi constant equal to 13.5 mT in one of the partners (C_6F_6) and no magnetic nuclei in the second partner (hexadecane), and varying τ_c, $\tau_0 = 7$ ns. (a) [TMPD] = 0, $\tau_c = \infty$; (b) 1.1×10^{-3} M, 50 ns; (c) 2.2×10^{-3} M, 25 ns; (d) 4.4×10^{-3} M, 12.5 ns.

shortened by some process, so that the result can be described in the model of spin evolution freezing assuming exponential recombination kinetics. Now we turn to the case of real slowing down of spin evolution in the observable pair. In practice this can be realized by constructing initial pair A/B with hyperfine couplings predominantly concentrated only in one, 'broad' partner A, and then arrange transfer of the radical ion from the 'broad' partner to an acceptor forming radical ion with narrow ESR spectrum, so that the produced pair B/C has appreciable quantum yield of recombination fluorescence.

Fig. 4 shows experimental MARY spectra for solutions of PTP-d_{14} and isooctane in hexane. The types and the concentrations of the two acceptors (low for PTP-d_{14} and rather high for isooctane) were chosen so as to rapidly form the pair PTP-d_{14}^-/isooctane$^+$, in which the role of the 'narrow' partner *B* is played by radical anion of PTP-d_{14} ($2\sigma \sim 0.094$ mT), and the 'broad' partner *A* is the radical cation of isooctane ($2\sigma \sim 4.5$ mT), which practically does not participate in the reaction of degenerate electron exchange and thus retains its substantial hyperfine couplings [25]. MARY
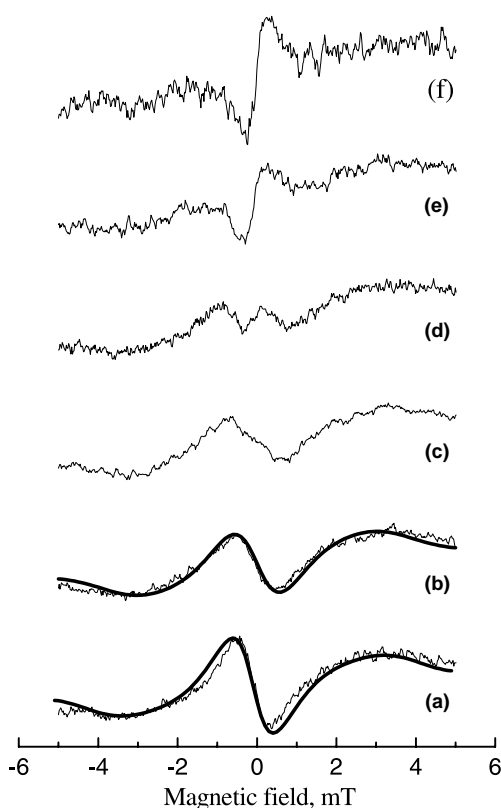

Fig. 4. The field dependencies of the fluorescence intensity of hexane solution of 10^{-4} M paraterphenyl-d_{14} and 0.6 M isooctane containing C_6D_6 in different concentration taken as the first derivatives. The smooth curves are simulations for singlet-born radical pair with 10 equivalent nuclei with hfi constant equal to 1.4 mT in one of the partners (isooctane) and no magnetic nuclei in the second partner (paraterphenyl-d_{14}), $\tau_0 = 9$ ns. (a) $[C_6D_6] = 0$, $\tau_c = \infty$; (b) 10^{-3} M, 30 ns; (c) 2×10^{-3} M; (d) 4×10^{-3} M; (e) 8×10^{-3} M; (f) 1.6×10^{-2} M.

spectrum for this system has the form of an intense narrow ($\Delta H_{pp} \sim 0.8$ mT) zero field line against the background of a broad (~ 7 mT) MFE (Fig. 4a). Introduction of deuterobenzene into the solution leads to diffusion-limited transfer of radical cation from isooctane$^+$ to C_6D_6, because of the high concentration of isooctane in solution the channel of direct charge transfer from solvent radical cation to C_6D_6 is not important. The formed $C_6D_6^+$ radical cation has rather narrow ESR spectrum ($2\sigma \sim 0.25$ mT) and plays the role of partner *C* in the pair *B/C* with frozen spin evolution – the dominating HFC has dropped more than an order of magnitude. Experimentally this is reflected as broadening of the zero field line and decreasing of its amplitude relative to MFE (Figs. 4b and c), the transformation that we saw in the calculations for the model system (Fig. 1). However, further transformations of the experimental MARY spectra (Figs. 4d–f) with increasing concentration of C_6D_6 departs from the model calculations – a narrow MFE overlapping the MARY line emerges at zero of the field. The explanation is that in real experimental system spin evolution, although significantly slowed down upon the charge transfer, is not completely frozen due to small but finite HFC in the partners of the PTP-d_{14}^-/$C_6D_6^+$ pair. The contribution of the narrow MFE increases with increasing C_6D_6 concentration, and the model of complete freezing of spin evolution is capable of reproducing only the first two spectra of this set.

4.5. 'Freezing': concluding comments

Faithful quantitative reproduction of the entire concentration transformation of experimental MARY spectra for the case of 'true' freezing of spin evolution can be achieved by explicit consideration of the finite hyperfine structures of the 'narrow' partners, e.g., as was done in [26] to account for the effect of single charge transfer in the analysis of the time-resolved microwave field effects. Although possible for certain types of hyperfine structure, this would significantly complicate the model without providing new qualitative insights, and thus was at this stage refrained from. In this work, we rather focussed on developing a simple analytic model of complete freezing

of spin evolution in radical ion pairs upon charge transfer to acceptor, which was then applied to three classes of relevant experimental systems.

Theoretical simulations can also be potentially improved by accounting for such factors as non-exponential kinetics of recombination, and finite relaxation and monomolecular decay times of the radical ions. If needed recombination kinetics can be treated following [19] by expanding into exponentials. However, as the presented results and the conclusions of [19] show, exponential distribution of recombination times is a reasonable approximation for interpretation of experimental MARY spectra for these particular systems, when there are other rather fast exponential processes such as chemical decay, dark capture or freezing of spin evolution. One should just keep in mind that the extracted effective rate constants for these processes can be apparently higher (by a factor of about 2) than their actual values due to the multiplicative contribution of kinetics with power law asymptotics to the peak-to-peak width of MARY lines.

Spin relaxation in the vicinity of zero magnetic field can be effectively represented by a single relaxation time $T_{1,2}$ [27]. Departures from this rule can appear for certain very simple systems (e.g., one magnetic nucleus), but rapidly vanish as the system grows more complex [27]. Relaxation can then be easily accounted for by multiplying spin evolution operators $U(t)$ by the factor $e^{-t/T_{1,2}}$. This modification, which renders the operators nonunitary, for the purpose of this Letter is transparent for the partner A which undergoes transformation, but relaxation in partner B makes the transition from (7) to (8) illegal. Because of its exponential form, straightforward analytic results can again be obtained in the approximation of exponential recombination kinetics. However, in the covered experimental systems this contribution is not critical and thus was omitted from consideration to keep the model as simple and transparent as possible. Similar arguments apply also to the exponential processes of monomolecular decay of the radical ions. Of all the involved partners solvent radical cations have the shortest coherent lifetime (tens of nanoseconds [28]), which can reflect either chemical decay or relaxation of the radical ion.

However, these times are still long enough to let us omit this channel from explicit consideration. As the results show, the simplest possible model of freezing spin evolution in spin-correlated radical ion pairs presented in this work allows adequate description of experimental MARY spectra in several important classes of systems, and the suggested approach can be easily transferred to other processes of interest.

Acknowledgements

References

[1] H. Fischer, Chem. Phys. Lett. 100 (1983) 255.

[2] O.A. Anisimov, V.M. Grigoryants, S.V. Kiyanov, K.M. Salikhov, S.A. Sukhenko, Yu.N. Molin, Theor. Exp. Chem. 18 (1983) 256.

[3] C.A. Hamilton, J.P. Hewitt, K.A. McLauchlan, U.E. Steiner, Mol. Phys. 65 (1988) 423.

[4] D.V. Stass, B.M. Tadjikov, Yu.N. Molin, Chem. Phys. Lett. 235 (1995) 511.

[5] M. Sacher, G. Grampp, Ber. Bunsenges. Phys. Chem. 101 (1997) 971.

[6] V.M. Grigoryants, S.D. McGrane, S. Lipsky, J. Chem. Phys. 109 (1998) 7354.

[7] B. Brocklehurst, J. Chem. Soc. Faraday Trans. 2 (72) (1976) 1869.

[8] F.S. Sarvarov, K.M. Salikhov, React. Kinetics Catal. Lett. 4 (1976) 33.

[9] S.A. Sukhenko, P.A. Purtov, K.M. Salikhov, Sov. J. Chem. Phys. 2 (1985) 29.

[10] C.R. Timmel, U. Till, B. Brocklehurst, K.A. McLauchlan, P.J. Hore, Mol. Phys. 95 (1998) 71.

[11] O.A. Anisimov, V.M. Grigoryantz, V.I. Melekhov, V.I. Korsunsky, Yu.N. Molin, DAN SSSR 5 (1981) 1151 (in Russian).

[12] D.V. Stass, N.N. Lukzen, B.M. Tadjikov, Yu.N. Molin, Chem. Phys. Lett. 233 (1995) 444.
[13] B. Brocklehurst, Int. Rev. Phys. Chem. 4 (1985) 279.
[14] V.A. Morozov, A.B. Doktorov, Chem. Phys. 153 (1991) 313.
[15] K. Schulten, P.G. Wolynes, J. Chem. Phys. 68 (1978) 3292.
[16] K.M. Salikhov, Yu.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, Spin Polarization and Magnetic Effects in Radical Reactions, Elsevier, Amsterdam, 1984.
[17] U.E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
[18] A.A. Zharikov, N.V. Shokhiver, Z. Phys. Chem. 177 (1992) 37.
[19] Yu.V. Toropov, F.B. Sviridenko, D.V. Stass, A.B. Doktorov, Yu.N. Molin, Chem. Phys. 253 (2000) 231.
[20] V.A. Bagryansky, O.M. Usov, V.I. Borovkov, T.V. Kobzeva, Yu.N. Molin, Chem. Phys. 255 (2000) 237.
[21] F.B. Sviridenko, unpublished results.
[22] F.B. Sviridenko, D.V. Stass, Yu.N. Molin, Mol. Phys. 101 (2003) 1839.
[23] V.I. Borovkov, V.A. Bagryansky, I.V. Yeletskikh, Yu.N. Molin, Mol. Phys. 100 (2002) 1379.
[24] D.W. Werst, Chem. Phys. Lett. 251 (1996) 315.
[25] S.V. Anishchik, V.I. Borovkov, V.I. Ivannikov, et al., Chem. Phys. 242 (1999) 319.
[26] V.A. Morozov, E.V. Gorelik, N.N. Lukzen, R.Z. Sagdeev, S.V. Anishchik, Chem. Phys. Lett. 325 (2000) 106.
[27] M.V. Fedin, P.A. Purtov, E.G. Bagryanskaya, J. Chem. Phys. 118 (2003) 197.
[28] F.B. Sviridenko, D.V. Stass, Yu.N. Molin, Chem. Phys. Lett. 297 (1998) 343.