High-Field Supercage Model for Radical Pair Reactions in Micelles

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An analytic expression for the escape yield of a radical pair (RP) in a micelle under high magnetic fields is derived by the supercage model. This model is a two time scale model which divides the time evolution into two consecutive stages. The short time stage describes the initial separation of the partners of the RP, and the magnetic field dependence of the recombination yield can be described by the usual radical pair theory of freely diffusing radicals. The decay of a quasi-equilibrium during the second stage is described by rate equations for the spin density matrix, which for well-defined conditions can be reduced to a set of equations for the diagonal elements of the density matrix in the basis of true eigenstates of the Hamiltonian of the free radicals. In the present work we examine the applicability of the high-field limit of this approximation, which is closely related to the kinetic approach of H. Hayashi and S. Nagakura (*Bull. Chem. Soc. Jpn.* **1984**, *57*, 322). General analytic expressions for the magnetic field and relaxation dependence of the recombination yield during the second stage and for the decay constants are derived. The decay constants derived by H. Hayashi and S. Nagakura agree with our results. We show that the contribution from the first stage is significant and how it can be included.

Introduction

Magnetic field effects (MFEs) on photophysical and photochemical reactions involving an intermediate radical pair (RP) have been well documented in liquid and solid phases; see for example ref 1. Usually only singlet RPs recombine, and thus for a triplet precursor the recombination yield is due solely to the fraction of RPs that evolved into singlet pairs before reencountering. Consequently, a large recombination yield requires an effective mixing of singlet and triplet states and/or a large reencounter probability. Reactions taking place in micellar solutions are of special interest since the wall of the micelle acts as a semireflective barrier for the diffusive motion of the radicals. This confinement effect effectively enhances the lifetime of the RP and the probability for the individual partners of the RP to meet again. Therefore, a much more effective mixing of states takes place. As a result reactions in micelles show both very large and quite unusual dependences on the strength of an external magnetic field.[2−11]

Under normal conditions in homogeneous solutions, only the so-called radical pair mechanism (RPM) is operative. For separate radicals at high fields, the singlet state (S) and the T_0 triplet state are degenerate and effectively mixed by the difference in the Zeeman and hyperfine interactions of the two radicals. For high magnetic fields the energy difference between the T_+ and T_- states are too large for any significant mixing to occur. At low magnetic fields more states are nearly degenerate, and the ST mixing is maximal when the Zeeman and hyperfine interactions are of similar magnitudes. The ST_- mechanism[12] is a level-crossing mechanism that is operative only when the separation of the radicals are such that the S and T_- states are nearly degenerate. Since the exchange interaction varies rapidly with the separation of the radicals, the time spend in the ST_- mixing region is usually too short to give rise to any significant effect.

Hayashi and Nagakura[13] pointed out that the RP lifetime in a micelle could easily be of the same order or even larger than the spin−lattice relaxation time of the unpaired electron. Since spin relaxation mixes all electron spin states, it could be the most important ST-mixing mechanism for micellar or other confined systems. This mechanism is called the relaxation mechanism, and Hayashi and Nagakura[13] introduced a kinetic model in order to explain the observed magnetic field dependence of the escape yield and of the time dependence of the decay of the radical concentration. The model consists of a set of linear rate equation for the populations of the singlet and the three high-field triplet electronic spin states of the RP, and in accordance with the experimental observation the time dependence of the decay of the radical concentration is described as a sum of exponentials. The model of Hayashi and Nagakura[13] has been very successful for the interpretation and classification of MFEs observed in micelles for a variety of RPs. It has been applied by many authors, e.g., by Steiner and Wu[14] to investigate the experimentally observed effect of the size of the micelle on the MFE using an analytic expression for the relaxational rate caused by the dipolar interaction between the unpaired electron spins.

Lüders and Salikhov[15] treated the relaxation by a Bloch type equation for the electron spin density matrix. The diffusive motion of the radicals were described by three simple models that, however, are not applicable to micellar systems.

For micellar systems a quantitative calculation of MFEs is considerably complicated by a significant contribution from spin relaxation. In principle the stochastic Liouville equation (SLE) can be solved numerically.[16,17] But, unfortunately the relaxation couples almost all of the spin states, and thus so far the problem has been intractable even on the largest and fastest computers. A simplified approach is therefore necessary. Recently, it was shown that the supercage model of micellar systems reduces the full problem of solving the SLE into two simpler problems.[18−20] The model is essentially a two time scale model; i.e., the time evolution of a RP in a micelle is divided into two consecutive steps.

The first step of the supercage model describes the initial separation of the RP. It terminates approximately when one of the partners reaches the boundary of the micelle and is reflected back into the interior of the micelle. The characteristic time of

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the first (or geminate) stage is too short for spin relaxation to be important. Consequently the contribution from this stage can be calculated by well-established numerical methods[17] without having to consider the complications introduced by spin relaxation.

The second step describes the decay of a quasi-equilibrium state. When the radicals have collided a few times with the boundary of the micelle, a quasi-equilibrium distribution of RP separations is established which decays due to recombination of the singlet RPs or by escape from the micelle. The second step is also called the exponential stage because it is described by rate equations for the spatially averaged spin density matrix.[19] Since the spatial variable has disappeared, the computational problem is reduced to the same size as the usual relaxational problems. Furthermore a tremendous simplification is possible if the coherent transition rates between *all* states are much larger than any noncoherent rate (relaxation, recombination, escape, etc.). In that case only the diagonal elements (the populations of the states) need to be retained in the description. This simplification is called the Johnson−Merrifield approximation,[21,19] whose high-field limit is closely related to the kinetic approach of Hayashi and Nagakura.[13]

The supercage description of MFEs in micellar systems is presently the most accurate solvable model. It clarifies the validity of the rate equation approach of Hayashi and Nagakura[13] and provides explicit expressions for the rate constants. Usually, the dominant contribution to the MFEs arises from the exponential stage, which is the stage described by the rate equations. But the contribution from the primary stage can also be significant and should be included, in particular for high magnetic fields. The Δg mechanism (and in fact the radical pair mechanism) is operative only in the primary (geminate) stage, and it becomes increasingly important for high magnetic fields.

Theoretical Description

The diffusion of a pair of radicals (a and b) in a micelle can be modeled as diffusion in a spherically symmetric potential well. The exact form is probably not important. We use

$$U(r) = kTu(r) = kTu_0\{\tanh[\eta(r - R)] - 1\}/2 \qquad (1)$$

where R is the radius of micelle. For simplicity one of the radicals is assumed to be fixed in the center of the micelle, while the other radical diffuses with a spatially dependent diffusion coefficient that models the decrease of the diffusion coefficient from D_s in the surrounding solution to $D_m \ll D_s$ in the interior of the micelle. The width η^{-1} of the boundary layer of the micelle is typically much smaller than the radius of the micelle, i.e., $\eta R \gg 1$. The diffusion operator for the relative motion of the radicals is $\Gamma = \nabla D(\nabla + \nabla u)$.

The spin Hamiltonian of the RP is

$$H(r) = H_0 - J(r)(^1/_2 + 2\mathbf{S}_a\mathbf{S}_b) \qquad (2)$$

where

$$H_0 = \beta_e B(g_a S_{az} + g_b S_{bz}) + \sum_j^a A_j \mathbf{S}_a \mathbf{I}_j + \sum_k^b A_k \mathbf{S}_b \mathbf{I}_k \qquad (3)$$

is the isotropic part of the spin Hamiltonian of the free radicals consisting of the Zeeman interaction and the hyperfine interaction. The electron spin exchange interaction is assumed to depend exponentially on the separation r of the RP

$$J(r) = J_0 e^{-\alpha(r-d)} \qquad (4)$$

where d is the distance of closest approach.

We assume that only singlet RPs at contact ($r = d$) can react and use the conventional anticommutator form of the recombination superoperator, i.e.

$$\hat{K}\rho = (k_s/2)[\Pi_s,\rho]_+\delta(r - d) \qquad (5)$$

where $\Pi_s = |S\rangle\langle S| \otimes E_I$ is the projection operator onto the singlet state of the RP and E_I is the unit operator in the nuclear spin space.

The Stochastic Liouville Equation. The most general description of the kinetics of RP recombination is provided by the stochastic Liouville equation (SLE)[22]

$$\dot{\rho} = (\Gamma - iH^\times - \hat{K} - \hat{R})\rho(r,t) \qquad (6)$$

that describes the complete space/spin evolution of the spin density matrix $\rho(r,t)$ of the RP. The solution to this equation generally contains more information than is needed for a particular problem, and for example the recombination yield F is calculated as

$$F = 4\pi d k_s \operatorname{Tr}[\Pi_s \tilde{\rho}(d,0)] \qquad (7)$$

where the Laplace transform of the spin density matrix

$$\tilde{\rho}(r,s) \equiv \int_0^\infty \rho(r,t)\, e^{-st}\, dt \qquad (8)$$

satisfies the steady state SLE

$$s\tilde{\rho} - \rho(r,0) = (\Gamma - iH^\times - \hat{K}_s - \hat{R})\tilde{\rho} \qquad (9)$$

The superoperators appearing in eqs 6 and 9 have the usual meaning, $H^\times = [H, ...]$ is the commutator of the spin Hamiltonian, Γ is the diffusion operator, $\hat{K}_s$ is the spin dependent recombination operator, and $\hat{R}$ is a relaxation superoperator.

The Supercage Model. The results of the previous articles[23,19,20] can be summarized as follows. The spin/space evolution of RPs within micelles can be divided into two stages: The first stage consists of an initial spatial separation of the RP within the micelle, and it ends with an equilibration of the spatial distribution due to multiple reflections from the boundary of the micelle. The second stage is an exponential evolution and decay of the quasi-equilibrium of the RP in the micelle. The total recombination yield F is equal to the sum of the contributions from the two stages

$$F = F^{(1)} + F^{(2)} \qquad (10)$$

The characteristic times of the two stages are usually very different. That of the first stage is R^2/D_m, which is typically of the order 50 ns and is too short for spin−lattice relaxation to have any effect. The characteristic time for the second stage is equal to the residence time of the RP in the micelle, which typically is of the order of 1 μs. Thus spin relaxation may be important for the second stage.

The First or Geminate Stage. The characteristic time of the first or geminate stage is R^2/D_m, which is the average time it takes a radical to diffuse to the micellar boundary, where it is most likely reflected. If this time is larger than the reciprocal of the energy difference $\omega_{ij} \equiv (E_i - E_j)/\hbar$ between all states i and j, i.e.

$$\omega_{ij} > D_m/R^2 \quad \text{for all} \quad i, j \qquad (11)$$

then there is sufficient time for the $S - T_0$ mixing to occur before the radical collides with the boundary. Consequently the recombination probability during the first stage is identical to that obtained for a geminate RP in an unconstrained volume, and it can thus be calculated using the free diffusion model. For high magnetic fields, $\omega_{jj'}$ is simply two times the singlet−triplet mixing parameter

$$Q \equiv {}^{1}/_{2}[(g_a - g_b)B\beta_e/\hbar + \sum_j{}^{a} A_j m_j - \sum_k{}^{b} A_k m_k] \quad (12)$$

and the above condition can therefore be reformulated as

$$q \equiv \frac{Qd^2}{D_m} > \frac{d^2}{2R^2} \quad (13)$$

The value on the right-hand side is typically of the order of 0.02 corresponding to a magnetic interaction of 0.04 mT (0.4 G). If the recombination is diffusion controlled and condition 13 is satisfied, then the recombination probability can be calculated by the previously derived expression[24]

$$F^{(1)} = P_s^{(0)} + P_{T_0}^{(0)} \frac{\sqrt{q}}{2 + (2r_e/d - 1)\sqrt{q}} \quad (14)$$

where the spin exchange relaxation radius is given by[25,26]

$$r_e = \begin{cases} d + \alpha^{-1}\,[\ln(2|\bar{J}_0|) + 1.16] & \text{if } |\bar{J}_0| > 1 \\ d & \text{if } |\bar{J}_0| < 1 \text{ and } (k_s d)/D_m > 1 \end{cases} \quad (15)$$

$\bar{J}_0 = J_0/(D_m\alpha^2)$, and, e.g., $P_s^{(0)}$ indicates the initial population of the singlet state.

Exponential Model. During the second (or exponential) stage a quasi-equilibrium distribution of RP separations is maintained in the micelle. Averaging the SLE (eq 9) over this distribution yields a simple exponential SLE[26]

$$s\tilde{\rho}_c - \rho_0 = -(iH^\times + \hat{W}_r + \hat{W}_e + \hat{W}_s + \hat{W}_d)\,\tilde{\rho}_c \quad (16)$$

where all superoperators are independent of the spatial variable.

The superoperators $\hat{W}_e$ and $\hat{W}_s$ describe the effects of the distance dependent spin exchange interaction, eq 4, and reactivity, eq 5, respectively. They can be written as[19]

$$\hat{W}_e = w_e \sum_{\nu=0,\pm} (|ST_\nu\rangle\langle ST_\nu| + |T_\nu S\rangle\langle T_\nu S|) \quad (17)$$

and

$$\hat{W}_s = w_s|SS\rangle\langle SS| = w_s(\Pi_s \ldots \Pi_s) \quad (18)$$

where the rates are given by

$$w_e = 4\pi(D_m r_e/V) \quad (19)$$

$$w_s = 4\pi(D_m r_s/V) \quad (20)$$

and $V = (4\pi/3)R^3$ is the volume of the micelle. The quantity $r_s \leq d$ denotes the effective reaction distance, with $r_s = d$ corresponding to the diffusion-controlled case. The spin exchange relaxation radius r_e is given by eq 15 and is typically 1−2 times d.

The irreversible escape from the micelle is described by a spin independent superoperator $\hat{W}_d$ that is equal to a unit operator multiplied by the rate

$$w_d = 4\pi(D_s R/V)\exp(-u_0) \quad (21)$$

Intraradical spin−lattice relaxation is described by the operator $\hat{W}_r$. It can be written in the general form

$$\hat{W}_r = \hat{W}_{r_a} \otimes \hat{E}_b + \hat{E}_a \otimes \hat{W}_{r_b} \quad (22)$$

where $\hat{E}_a$ and $\hat{E}_b$ are unit operators in the spin spaces of radicals a and b, respectively. The specific form of the relaxation operator depends on the relaxation mechanism.

The effect of ST_--transitions can be incorporated, but in the present work it is omitted since it is negligible for high magnetic fields.

The recombination yield F is obtained from the $s = 0$ solution of eq 16 as

$$F^{(2)} = \mathrm{Tr}[\hat{W}_s(iH^\times + \hat{W}_r + \hat{W}_e + \hat{W}_s + \hat{W}_d)^{-1}\rho_i] \quad (23)$$

Johnson−Merrifield Approximation. The JMA approximates the exponential SLE, eq 16, by retaining only the diagonal elements of the spin density matrix in the basis of eigenstates of the free Hamiltonian H_0; cf. ref 19. The diagonal elements of the density matrix are of course equal to the population of the states, but it is important that these states are true eigenstates of the Hamiltonian of the separated radicals. Previous kinetic treatments applied a basis consisting of singlet and triplet states which are not eigenstates of the free Hamiltonian.

In the JMA the expression for $F^{(2)}$ is obtained by retaining only the diagonal elements of the EM expression, eq 23, i.e.

$$F^{(2)} = \mathrm{Tr}[\hat{W}_s^d(\hat{W}_r^d + \hat{W}_e^d + \hat{W}_s^d + \hat{W}_d^d)^{-1}\sigma_i] \quad (24)$$

where σ_i contains the diagonal elements of the spin density matrix ρ_i and the superscript d indicates that only the diagonal elements (i.e. elements of the type $W_{nn,mm}$) of the superoperators are included. Notice that there is no contribution from the $H^\times$ superoperator.

The JMA is applicable if the splittings $\omega_{jj'}$ of *all* pairs of states of the spin Hamiltonian H_0 are larger than *all* the characteristic values of the above mentioned rates w_ν (ν = r, e, s, d).[19] This rather restrictive condition can be written as

$$\omega_{jj'} > w_\nu \quad (25)$$

For many systems this condition will be satisfied for high magnetic fields, but it can be violated, e.g., due to accidental degeneracies of the states or if the magnetic interactions are small due to small hyperfine constants and/or almost identical *g*-values of the radicals.

High-Field Results

In high fields the eigenstates of the free Hamiltonian H_0, eq 2, are simply the direct product of the eigenstates of the *z* components of the spins of all unpaired electrons and nuclei. Since the *z* components of the nuclear spins are conserved, the nuclear spin state appears as an index only. It is therefore sufficient to consider the electron spin part of the eigenstates which we will denote by 1, 2, 3, and 4, where

$$\{|1\rangle, |2\rangle, |3\rangle, |4\rangle\} \equiv \{\alpha_1\alpha_2, \alpha_1\beta_2, \beta_1\alpha_2, \beta_1\beta_2\} \quad (26)$$

In this basis the matrix representations of the diagonal part of the superoperators, needed in eq 24, are easily found. The diffusive escape out of the micelle is proportional to an identity matrix, i.e.

$$\mathbf{W}_d = w_d\,\mathbf{1} \quad (27)$$

The recombination superoperator has the form

$$\mathbf{W}_s = w_s\begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 1 & 1 & 0\\ 0 & 1 & 1 & 0\\ 0 & 0 & 0 & 0\end{pmatrix} \tag{28}$$

and the superoperator for dephasing due to spin exchange and recombination is given by

$$\mathbf{W}_e = \frac{w_e}{2}\begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 1 & -1 & 0\\ 0 & -1 & 1 & 0\\ 0 & 0 & 0 & 0\end{pmatrix} \tag{29}$$

Spin−lattice relaxation is described by the usual Bloch equations. In the present work we consider only intraradical relaxation, and thus the radicals relax independently, e.g.

$$\frac{d\rho^{a}_{\alpha,\alpha}}{dt} = -w_{r1}(\rho^{a}_{\alpha,\alpha} - \rho^{a}_{\beta,\beta}) \tag{30}$$

where the relaxational rate of radical a is related to its spin−lattice relaxation time T_{1a} by $w_{r1} = 1/(2T_{1a})$. The relaxation matrix for the RP is easily obtained from the Bloch equations for the individual radicals. The resulting matrix is

$$\mathbf{W}_r = \begin{pmatrix}w_r & -w_{r2} & -w_{r1} & 0\\ -w_{r2} & w_r & 0 & -w_{r1}\\ -w_{r1} & 0 & w_r & -w_{r2}\\ 0 & -w_{r1} & -w_{r2} & w_r\end{pmatrix} \tag{31}$$

By introducing the notation

$$\mathbf{W} = \mathbf{W}_d + \mathbf{W}_e + \mathbf{W}_s + \mathbf{W}_r \tag{32}$$

the recombination probability can be written compactly as (cf. eq 24)

$$F^{(2)} = \vec{1}\cdot\mathbf{W}_s\cdot\mathbf{W}^{-1}\cdot\vec{\sigma}_i \tag{33}$$

where $\vec{1}$ is a vector with all elements equal to unity and $\vec{\sigma}_i$ contains the initial populations of the states 1−4. For an unpolarized triplet state $\vec{\sigma}_i = (^1/_3, ^1/_6, ^1/_6, ^1/_3)$, and for an initial singlet state $\vec{\sigma}_i = (0, ^1/_2, ^1/_2, 0)$.

Equation 33 can be evaluated explicitly. For a completely general initial spin configuration of the RP the following analytic expression is obtained

$$F^{(2)} = \frac{w_s[(P_s + P_{T_0})w_d + Pw_r]}{2w_d^2 + 4w_dw_r + w_dw_s + w_rw_s} \tag{34}$$

where P_s and P_{T_i} are the initial populations of the singlet and triplet states, and

$$P = (P_s + P_{T_0}) + (P_{T_+} + P_{T_-}) \tag{35}$$

is the total population of the RP, i.e., the fraction of RPs that survived the first step. Note that P_s and P_{T_0} do not appear separately but only as the sum $P_s + P_{T_0}$ which is equal to $P_2 + P_3$, i.e., the total population of eigenstates 2 and 3. For an unpolarized triplet initial state the expression simplifies to

$$F^{(2)}(T) = \frac{w_s(w_d + 3w_r)}{3(2w_d^2 + 4w_dw_r + w_dw_s + w_rw_s)} \tag{36}$$

Equation 34 is very convenient for analysis of experimental data and does not appear to have been given before. Several important conclusions can be drawn from it. Only the total relaxation rate w_r appears in the expression; precisely how the individual relaxation rates of the radicals contribute to the total rate is immaterial. The result is independent of the dephasing rate w_e. And perhaps most importantly, there is no difference between S and T_0 precursors. In the present description this is not surprising since S and T_0 states contribute equally to the true eigenstates $|2\rangle$ and $|3\rangle$. But in the previous kinetic approach, where the singlet and triplet states were used as the basis, there was a nonzero difference between these precursor states. This dependence could only be eliminated by assuming a very fast (instantaneous) rate of mixing of the S and T_0 states. The present approach shows that there is no such dependence. Moreover there are no terms corresponding to S−T_0 mixing such as the RPM for the geminate stage.

The initial condition for the exponential stage should be chosen in accordance with the geminate stage. Only the S and the T_0 parts of the RP can give rise to recombination products during the first stage. Let the fraction of RPs that react during the geminate stage be denoted $F^{(1)}$. The initial populations to be used for the second (exponential) stage is then

$$P_s + P_{T_0} = P_s^{(0)} + P_{T_0}^{(0)} - F^{(1)} \tag{37}$$

$$P = 1 - F^{(1)} \tag{38}$$

where superscript zero indicates the values of the populations of the precursor states, i.e. before stage one. Note that this expression is completely general and that for a polarized triplet state ($P_{T_0}^{(0)} \neq {}^1/_3$) only the distribution of the triplet between the T_0 state and the {T_+, T_-} manifold is important.

Experimentally the time dependence of the decay of the radical concentration is observed. This can be calculated by solving the time dependent version of the exponential SLE, eq 16, in the JM approximation, i.e.

$$\frac{d}{dt}\vec{\sigma} = -\mathbf{W}\vec{\sigma} \tag{39}$$

where $\vec{\sigma}$ is the diagonal matrix elements of the density matrix in the high-field basis, eq 26. The radical concentration is equal to

$$N(t) = \int_0^t \vec{1}\cdot\vec{\sigma}(t)\, dt \tag{40}$$

A general solution can be derived but it is rather lengthy and not very useful. Fortunately all that is needed for an analysis of the experimental results is the time constants. In general $N(t)$ can be written as

$$N(t) = \sum_{i=1}^{4} A_i\, e^{-\lambda_i t} \tag{41}$$

where λ_i are the eigenvalues of $\mathbf{W}$ and thus one should expect the decay to be given as a sum of four exponentials. This is indeed the case for a polarized triplet RP. However, for unpolarized initial states only two of the exponential terms remain and the decay constants of these terms are

$$k_s = w_d + w_r + w_s/4 - \sqrt{w_r^2 + (w_s/4)^2}$$
$$k_f = w_d + w_r + w_s/4 + \sqrt{w_r^2 + (w_s/4)^2} \tag{42}$$

where k_s and k_f are the decay constants of the slow and fast components, respectively. These expressions have also been obtained by the kinetic approach by incorporating an extra assumption of an infinitely fast mixing of the singlet and T_0

states.[14] If the relaxation rate (w_r) is much smaller than the rate of recombination (w_s), then eqs 42 reduce to the expressions derived by Hayashi and Nagakura[13]

$$k_s = w_d + w_r$$
$$k_f = w_d + w_r + w_s/2 \tag{43}$$

Similar to eq 34 for the recombination yield these decay constants are independent of the dephasing rate w_e and depend only on the total relaxation rate w_r. The situation is changed, however, if the initial state is a polarized triplet. Two extra exponentials will appear with decay constants

$$k_{e1} = w_d + w_r + w_e/2 - \sqrt{w_r^2 - 4w_r w_{r1} + 4w_{r1}^2 + (w_e/2)^2}$$
$$k_{e2} = w_d + w_r + w_e/2 + \sqrt{w_r^2 - 4w_r w_{r1} + 4w_{r1}^2 + (w_e/2)^2} \tag{44}$$

However, the experimental accuracy will probably not allow a decomposition of the decay curve into more than two exponentials. Moreover, a substantial polarization of the initial triplet state is needed for an observation of the extra terms.

Accuracy of Analytic Results. The analytic expression, eq 34, for the recombination yield during the exponential stage is very convenient for the analysis of experimental results. Below we will illustrate the predicted dependence on an external magnetic field and investigate the accuracy of the expression. Finally we will illustrate the importance of including the recombination yield from the geminate stage.

The relaxation is assumed to be caused by the rotational modulation of the anisotropic hyperfine (hfi relaxation) and Zeeman interactions (Δg relaxation). The relaxation rate is given by the usual expression

$$w_r = \frac{6\,\overline{(\Delta A)^2}\,\tau + 3\,\overline{(\Delta g)^2}\,\omega^2\tau}{40(1 + \omega^2\tau^2)} \tag{45}$$

where $\omega = g\beta B/\hbar$ is the transition frequency of the electron spin, τ is the rotational correlation time of the radical, and the anisotropy parameters are defined as[20]

$$\overline{(\Delta g)^2} = {}^1/_3(\mathbf{\Delta g}:\mathbf{\Delta g}) \quad \text{and} \quad \overline{(\Delta A)^2} = {}^1/_3(\mathbf{\Delta A}:\mathbf{\Delta A}). \tag{46}$$

Figure 1 shows the magnetic field dependence of the escape yield $Y(B)$ for a model system similar to one considered previously.[8] Radical a has one magnetic nucleus with spin $I = {}^1/_2$ and parameter values $A/g\beta = 10$ mT, $\Delta A/g\beta = 2$ mT, $\Delta g_a = 0.002$, and $\tau_a = 2.5 \times 10^{-10}$ s. The other radical, which has no magnetic nucleus, has $\Delta g_b = 0.003$ and $\tau_b = 1 \times 10^{-12}$ s. The value of the hyperfine constant A has no effect on the high-field curve, but it becomes important for small magnetic fields $B \approx A/g\beta$. The figure displays the results of three different levels of approximation: the full EM where the complete density matrix is used, the JMA approximation which uses only the diagonal elements of the density matrix in the basis of the true eigenstates of the free Hamiltonian, and the high-field approximation (hf-JMA) to the JMA where the high-field eigenstates are used for any field value.

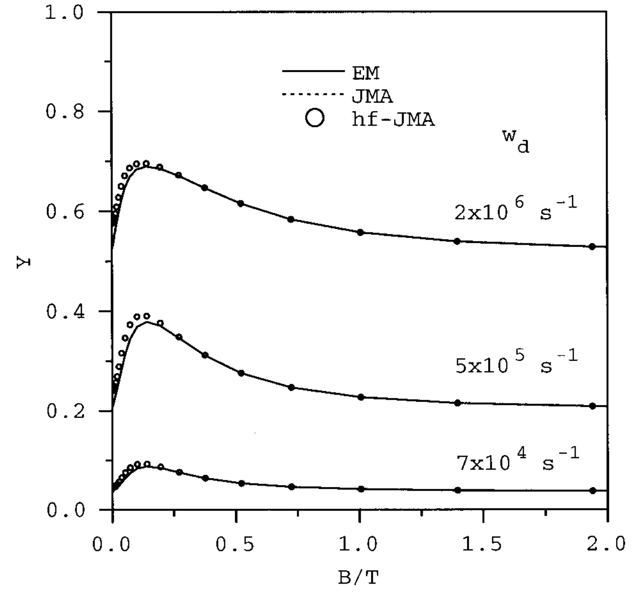

Figure 1. Magnetic field dependence of the escape yield of a RP in a micelle for three different values of the escape rate w_d. The RP has a single nucleus ($I = {}^1/_2$), $A = 10$ mT, and $g_a - g_b = 0$. The curves are the results of calculations using the exponential model (EM), the Johnson−Merrifield approximation (JMA), and the high-field approximation (hf-JMA) for a triplet precursor and the indicated values of w_d. Other parameters are $d = 5$ Å, $D_m = 10^{-6}$ cm^2 s^{-1} , $R/d = 5$, $D_s/D_m = 10$, $\alpha d = 10$, $J_0 d^2/D_m = 10^4$, $r_s = 1$, $\Delta A/g\beta = 2$ mT, $\Delta g_a = 0.002$, $\Delta g_b = 0.003$, $\tau_a = 2.5 \times 10^{-10}$ s, and $\tau_b = 1.0 \times 10^{-12}$ s.

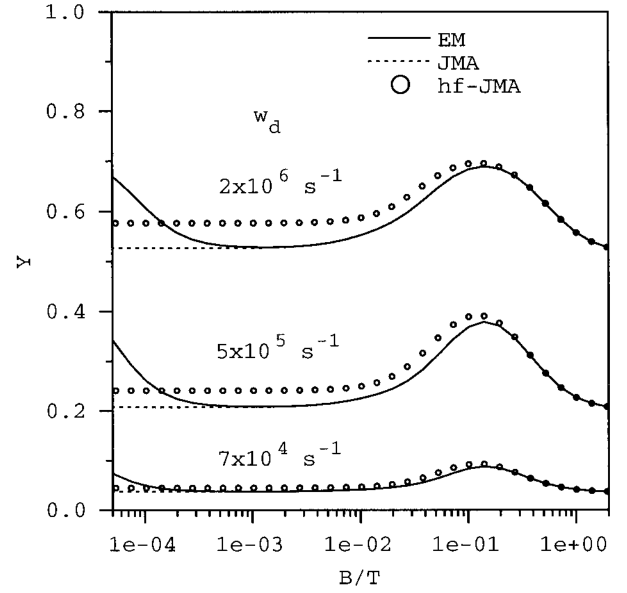

Figure 2. Same as Figure 1 but displayed on a logarithmic scale.

The behavior is easily understandable by noting that the hfi relaxation decreases with B while the Δg relaxation saturates for $\omega\tau \gg 1$. Radical a has a large (but typical) value of the correlation time τ, and on the linear scale the Δg relaxation appears to be saturated and the hfi relaxation started to decrease very close to the origin. Thus the initial maximum of $Y(B)$ at $B \approx 50$ mT is due to the decrease of the hfi relaxation. The following decrease is due to Δg relaxation of radical b which saturates at a much higher field since the correlation time τ_b is *very* short. The three different sets of curves illustrate the dependence of $Y(B)$ on the escape rate. It is remarkable how well the hf-JMA works. Almost down to fields of the order of the hyperfine interaction does it give results almost indistinguishable from the other two approximations (EM and JMA), and the error is probably smaller than the experimental accuracy.

Figure 2 is a replot of Figure 1 using a logarithmic scale for the magnetic field. The discrepancy of the hf-JMA at low magnetic fields is more clearly seen. The deviation between the JMA and the hf-JMA is due to the change of the eigenstates away from the high-field states. The deviation between the EM

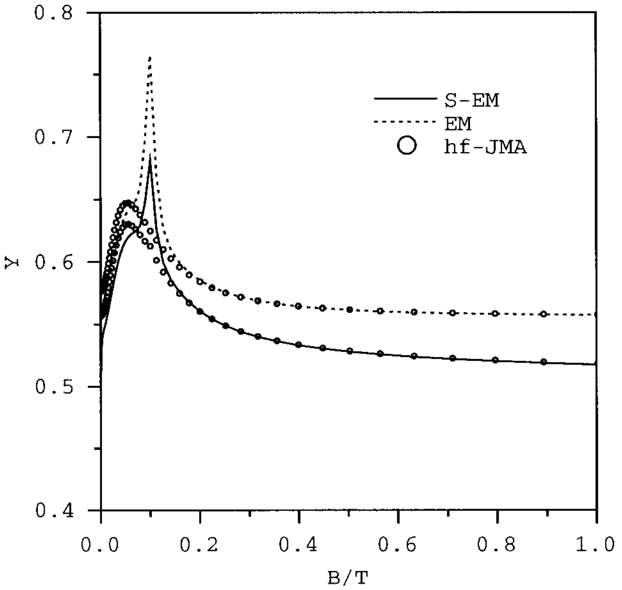

Figure 3. Comparison of the EM and its supercage extension (S-EM) with the corresponding high-field approximations (hf-JMA). The parameters are as in Figure 1 except for $A = 1$ mT, $g_a - g_b = 0.01$, and $\tau_b = 2.5 \times 10^{-11}$ s.

and the JMA is due to the appearance of degenerate states which the JMA cannot describe because condition 25 cannot be satisfied for nearly degenerate states. This is discussed in detail in ref 20.

Figure 3 shows the effect of including the geminate stage which obviously is present in an experimental situation. The parameter values are identical to those used in Figure 1 except that a difference in g-values of 0.01 has been assumed and the correlation time of radical b has been assigned a larger value. It is seen that the contribution from the geminate stage is important, especially for high magnetic fields where the difference in g-factors give rise to a large and increasing contribution via the RPM; cf. eqs 12 and 14. Thus the contribution from the geminate stage should always be included if the radicals have different g-factors. The spike is due to an accidental degeneracy, which is discussed in ref 20. For multinuclei systems the intensity of the spike is reduced.

In conclusion the analytic results obtained as the high-field limit of the JMA are very accurate down to fields of the order of the hyperfine interactions. The analytic results covered both the exponential stage and the combined geminate plus exponential stages. The contribution from the geminate stage is particularly important if the radicals have different g-values. The expressions for the rate constants of the radical decay during the exponential stage agree with the original expressions derived by Hayashi and Nagakura[13] assuming a fast singlet−triplet mixing.

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