ENVIRONMENTAL PERTURBATION OF THE MAGNETIC FIELD EFFECT IN RADICAL PAIR REACTIONS: A REVIEW

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Radical pair (RP) reactions where the total electronic spin is not conserved exhibit sensitivity to external magnetic field. The dependence of the field effect on the surroundings of the RP has been reviewed. In particular, the influences of viscosity, which dielectric constant and microheterogeneity of the medium, of chain-length, prevents free diffusion of two radicals and of proximity of a second donor molecule and/or paramagnetic ions in the medium are discussed.

Key Words: Magnetic Field Effect; Radical Pair Reactions

INTRODUCTION

The possibility of a magnetic field influencing the course of a chemical reaction, although conceived as early as 1908, has been established beyond doubt only in the seventies. This break-through has been possible because of the availability of new experimental techniques and theoretical concepts, such as noise-free time-resolved flash photolysis experiments, newer methods of generation and detection of radical pairs, novel kinetic schemes involving micellar phase and lastly, new concepts originating from Chemically Induced Dynamic Nuclear Polarisation (CIDNP) theories. The eighties have witnessed the development of finer aspects of the magnetic field effect so that it can now be considered as a rather mature science. The field has recently been reviewed by Turro and earlier by Atkins, Atkins and Lambert, Sagdeev, Buchachenko, Lawler and Evans, and Turro and Kraeutler. In the present article, we shall confine the discussion to the environmental perturbation of the magnetic field effect.

BASIC PRINCIPLES

The current concepts stem from Wigner's explanation of ortho-para hydrogen conversion which has been boosted further by the discovery of CIDNP.\textsuperscript{10-14} It is now realised that the effect originates through the pre-exponential term in the rate expression, rather than the energy exponent.\textsuperscript{16} The angular moment conservation principle influences the pre-exponential term in the following way.

Homolytic cleavage of single bond leads to a radical pair (RP). Whether the RP, \( R_1 \) and \( R_2 \) will be initially in a singlet state or in a triplet state will be determined by the spin-multiplicity of the parent electronic state in which cleavage of the molecule takes place. In solution they will diffuse apart with time.
and correlation between the spins of the partners might be lost. If they encounter
again, a bond will be formed only if the RP electron spin corresponds to a singlet
state; this type of radical recombination is called ‘geminate recombination’. Encounters involving triplet state RPs are unproductive. During the diffusional
excursion process the exchange interaction falls off rapidly. Beyond a certain
distance (\(\sim 10 \, \text{Å} \) for a typical organic RP) \(J\) becomes negligible and the singlet
and triplet states become energetically degenerate. At this point inter-system cross-
ing (ISC) may take place converting singlet RPs into triplets RPs and this prevents
geminate reencounters from forming recombination product. When the singlet
RP transforms itself to the triplet RP non-geminate or random encounters become
more probable as the rate of escape of either radical from the initial solvent cage
increases. Products which arise from non-geminate encounters are termed as
escape products. It is obvious that the product distribution will depend on the RP
ISC rate if it can effectively compete with the dynamics of other parallel
physico-chemical processes.

There are two principal mechanisms which govern the RP ISC process:

1) The electron-nuclear hyperfine \((hf)\) coupling mechanism \((a\)-mechanism\): It induces ISC from singlet \((S)\) to three triplet \(T\) states \((T_0, T_{+1}, T_{-1})\) in zero
external field through the interaction of local nuclear magnetic fields with the
electron spin via the hyperfine coupling. The rate of hyperfine-induced inter-
system crossing \(K_{\text{ISC}}\) is \(\sim 3 \times 10^6 \, a^4\) where \(a\) is the hyperfine constant. Since
typical values of \(a\) (for a single nucleus) fall in the range 10–100 G, \(K_{\text{ISC}}\) is in the
range \(3 \times 10^7\) to \(3 \times 10^8 \, \text{s}^{-1}\) which can effectively compete with the escape
rate. This scheme has been successfully employed for separation of isotopes
differing in \(a\).\(^{16}\)

2) \(\Delta g\) mechanism: It arises if the individual components of a RP possess
differ in \(g\)-factors (i.e. \(\Delta g \neq 0\)). This mechanism operates only to induce
\(S \rightarrow T_0\) ISC. The rate of \(\Delta g\)-induced \(K_{\text{ISC}}\) is \(\sim 3 \times 10^6 \, \Delta gH\).\(^{16}\) In strong
laboratory magnetic fields \(\sim 10^5 \, \text{G}\), the values of \(K_{\text{ISC}}\) for carbon-centered RPs
fall in the range of \(10^8\)–\(10^9 \, \text{s}^{-1}\); this can interfere with the cage recombination
processes.

3) It is possible to modulate the hf-induced ISC transformation by a small,
externally applied, magnetic field. In presence of a low \(\sim 50 \, \text{G}\) external
magnetic field of the order of hf-coupling, there is a competition between the
external field and the field provided by the magnetic nuclei in controlling the
spin-rephasing rate of RPs. While hyperfine interaction causes \(S \rightarrow T_{\pm 1}, T_0\)
transformation equally amongst three triplet components, an externally applied
magnetic field will reduce \(S \rightarrow T_{\pm 1}\) transition rate due to the loss of degeneracy
between \(S\) and \(T_{\pm 1}\) states (Fig. 1). It can be shown that for a two-level system,
\(K_{\text{SR}} \approx 1/\hbar \langle ME \rangle^2/\Delta E, ME\) representing the matrix element coupling the two
states and \(\Delta E\) their energy gap.\(^2\) A magnetic field as low as 100 gauss causes the
Zeeman splitting to be greater than hf-interaction and thus cuts down the RP
Energy levels (above) and corresponding vectorial representation (below) of degenerate singlet ($S$) and three triplet ($T_0$, $T_+$ and $T_-$) states in absence of external magnetic field ($H$) and exchange interaction ($J$). $S_1$ and $S_2$ are the vectorial representations of spin moments of two electrons in RP precessing around the laboratory $Z$-axis. $S_+\rightarrow T_0$ and $S_+\rightarrow T_+$ or $T_-$ transitions occur through the interaction of nuclear spin moment (I) with the electron spin ($S$) via the hyperfine coupling ($a I S$, where $a$ is hyperfine coupling constant).

(b) Energy levels of $S$ and $T$ states in presence of magnetic field (applied in $Z$-direction). Energy differences between $S$ and $T_\pm$ suppress $S \rightarrow T_+$ or $T_-$ transition rate.

The IS rate to one-third of its zero-field value. The field at which the magnetic-field-induced change is half of the value at saturation, may be taken as a measure of hyperfine couplings present in the two radicals and can be expressed by the relation (1)

$$B_{1/2} = \frac{2(B_1^2 + B_2^2)}{2B_1 + B_2}$$

Here $B_i = \Sigma a_{ik}^2 [I_k (I_k + 1)]^{1/2}, a_{ik}$ and $I_k$ being the hyperfine coupling constant and the nuclear spin of the $k$th nucleus of the $i$th radical respectively and the sum extends over all the nuclei of the radical.

**Environmental Influence**

The observation of significant magnetic field effect requires a proper balance between the rates for diffusion-controlled chemical and spin evaluation processes. The magnitude of the effect of an external magnetic field may be increased or decreased by tinkering with the spatial motion of the RP and/or allowing electron exchange. Following environmental factors influence the interplay of spin and spatial motions.
Viscosity and Dielectric Constant of Solvent

The significant role of ubiquitous solvent molecules arises principally through viscosity and dielectric constant of the medium, the first affecting the thermal motion and the second the motion caused by the force field (or potential surface) of the charged RP. Specific non-Coulombic interaction can also modify the potential energy curves at short inter-radical distances. In addition, if the solvent relaxation rates are comparable to RP diffusion rates, dynamical properties of solvents need to be taken into consideration.

For a neutral RP the diffusive excursion time and length depend on the solvent viscosity. The simple exponential model for the decay of the caged RP predicts that an increase in viscosity should increase the residence time; the increased residence time will allow more spin evolution to occur and hence increase the magnetic field effect. Brocklehurst\(^4\) observed that the fluorescence yield from singlet recombination from fluorene cation and anion (produced by \(\gamma\)-irradiation) is maximum for most viscous solvent, squalane, and vanishes for least viscous benzene. Similar increase in the magnitude of the effect has been reported for triplet-born RP from fluorenone and biazabicyclo-octane.\(^4\)

Petrov et al.\(^5\) were the first to observe the influence of dielectric constant on the magnetic field effect of pyrene-diethylamline (Py-DEA) exciplex system in alcoholic solvent mixtures. They found that the field effect is small at low and high dielectric constants and peaks at a dielectric constant of about \(\sim 26\). Nath et al.\(^6\) and Basu et al.\(^8\) studied the shape of the magnetic field—induced change vs dielectric constant curve as a function of the exciplex system and solvent composition. In alcoholic solvents, pyrene-dimethylanline (Py-DMA) system\(^6\) and 9-cyanophenanthrene-trans-anethole (CNP-AN) system\(^8\) exhibit maximum magnetic field effect at \(\varepsilon = 28\) and \(\varepsilon = 40\), respectively; but in non-alcoholic solvents, both the systems exhibit the maximum effect at \(\varepsilon = 18\) irrespective of the choice of components of non-alcoholic solvent mixtures.\(^7\) Moreover, the absolute magnitude of the per cent magnetic field effect (\(\Delta\phi/\phi\%\)) is much greater in non-alcoholic media compared to that in alcoholic media\(^7\), although the exciplex luminescence yields and the lifetimes are larger in alcoholic media.\(^7\)\(^8\) The variation of exciplex luminescence \(\phi\) and relative change of exciplex luminescence (\(\Delta\phi/\phi\)) in presence of magnetic field with dielectric constant (\(\varepsilon\)) is shown in Figs. 2–4.

Qualitatively the influence of dielectric constant on field effect can be understood from the potential energy diagrams\(^7\)\(^8\) shown schematically in Fig. 5. The exciplex luminescence, \(\phi\) is proportional to \(\beta\), where \(\beta\) is the fraction of the initially generated solvent-separated ion pairs (SSIP) that crosses an activation barrier to form the luminescent contact ion pair (CIP) or exciplex. On the other hand, the magnetic field-modulated luminescence, \(\Delta\phi\) can be shown\(^8\) to be proportional to \((1 - \beta) \delta\delta\), where \(1 - \beta\) is the fraction of the SSIP which diffuses outward and \(\delta\) is the fraction of thus escaping RIP's which recombine to form SSIP. Therefore, \(\Delta\phi/\phi \approx (1 - \beta) \delta \approx (1 - \phi) \delta\). For low dielectric media,
Fig 2 Change in saturated relative magnetic field effect on exciplex luminescence ($\Delta \phi/\phi$) with variation in dielectric const ($\epsilon$) using various solvent mixtures of varying compositions. Curve 1 to curve 4 stand for the Py/DMA exciplex, $[\text{Py}] = 10^{-4}\text{M}, [\text{DMA}] = 6 \times 10^{-4}\text{M}$, tetrahydrofuran (THF)/N,N-dimethyl formamide (DMF), ethylacetate/DMF, ethylacetate/acetonitrile, 1-propanol/methanol mixed solvents respectively. Curve 5 stands for CNP/AN exciplex system, $[\text{CNP}] = 10^{-3}\text{M}, [\text{AN}] = 8 \times 10^{-3}\text{M}$ in THF/DMF mixed solvents.

$1 - \phi$, and hence $\Delta \phi/\phi$, is small; for high dielectric media, the potential energy curve is flat and hence $\delta$ is small. The $\Delta \phi/\phi$ therefore peaks at an intermediate $\epsilon$.

The drastic difference between the curves obtained from the alcoholic and non-alcoholic solvents essentially originates from the difference of potential energy curves at short distances in the two cases. From an analysis of the observed results, Basu et al. and Nath concluded that hydrogen bonding alters the height of the activation barrier and the depth of the CIP potential minima in alcoholic medium. Also, the shift in $\epsilon_{\text{max}}$ in alcoholic medium between the two exciplex system has been explained by Basu et al. as due to lower charge transfer character of the CNP-AN exciplex compared to the Py-DMA system.

Numerical calculation of the effect of viscosity and dielectric constant on RIP system have been carried out by Schulten et al. An analytical formalism based on Smoluchowski's diffusion equation has been developed by Nath et al. to explain the features of $\phi$ vs. $\epsilon$ and $\Delta \phi$ vs. $\epsilon$ plots. Assuming the spin and the spatial motion as independent and using the semi-classical numerical results of
Fig 3 Comparison of the theoretical $\Delta \phi/\phi$ vs. $\epsilon$ and $\phi$ vs. $\epsilon$ curves (dotted lines) for Py/DMA exciplex with the experimental curves (solid lines) in THF/DMF mixed solvents. Curve-3 and 4 are the $\Delta \phi/\phi$ vs. $\epsilon$ curves while curve-1 and 2 represent variation of $\phi$ with $\epsilon$. Parameter values for the theoretical curves are $R = 6 \, \text{Å}, \, r_g = 8 \, \text{Å}, \, \kappa = 1000 \, \text{i.e.} \, h = 1 \, \text{cm/s}$

Schulten et al. for spin-evolution dynamics and the Hong and Noolandi's exact analytical solution of Smoluchowskis's equation with Coulombic field for spatial dynamics, Nath et al. deduced the following expressions for $\phi$ and $\Delta \phi/\phi$:

$$\phi = \frac{1 - \frac{r_c}{r_g} e^{-r_c/r_g}}{1 + \left(\frac{\bar{u} r_c}{R^2} - 1\right) e^{-r_c/R}}$$

where $\bar{u} = D/h$

and

$$\Delta \phi/\phi = \text{Constant} \times \frac{r_c}{1 - \frac{r_c}{r_g} e^{-r_c/r_g}} \frac{(\frac{\bar{u} r_c}{R^2} - 1) e^{-r_c/R} - \frac{r_c}{r_g} e^{-r_c/r_g}}{1 + (\frac{\bar{u} r_c}{R^2} - 1) e^{-r_c/R}}$$

where

$r_c$ = Onsagar radius

$r_g$ = radius at which direct transition to the r.i.p. state is assumed to take place from the initial ($^1A^* + D$) state.

$R$ = reaction radius

$D$ = mutual diffusivity of the two radicals
Fig 4 Comparison of the theoretical $\Delta \phi / \phi$ vs. $\epsilon$ and $\phi$ vs. $\epsilon$ curves (dotted lines) for Py/DMA exciplex with the experimental curves (solid lines) in 1-propanol/methanol mixed solvents. Curve-3 and 4 are the $\Delta \phi / \phi$ vs. $\epsilon$ curves while curve-1 and 2 represent variation of $\phi$ with $\epsilon$. Parameter values for the theoretical curves are $R = 2.5 \AA$, $r_\theta = 4 \AA$, $\bar{a} = 900$ i.e. $h = 1.1$ cm/s.

$h$ = an adjustable parameter which is given by $k \nu_0 / 4$ where $\nu_0$ is an effective velocity of crossing the potential barrier at the reaction radius and $K$ is a transmission coefficient

$\bar{a} = 10^3 / h$ assuming $D = 10^{-5}$ cm/S.

Theoretical best fits (assuming constant $D$) to the experimental $\Delta \phi / \phi$ vs. $\epsilon$ curves in alcoholic and non-alcoholic solvents are shown in Figs. 3, 4, 7. In the theoretical curve $\Delta \phi / \phi$ drops more slowly with increase in $\epsilon$ in comparison to the experimental one, presumably due to the assumption that the spin-evolution rate is independent of $r$ for $r$ greater than $R$.

**Micro-heterogeneity of the Medium**

If the medium is heterogeneous as in micro-emulsions or micelles, the radical pair diffusing out may suffer a reflection at the boundary leading to a greater geminate recombination. The size and nature of the micelle may be adjusted to optimise the field effect. The residence time of a geminate RP which is generated by homolytic cleavage of a molecule and solubilized in a micelle, is $\sim 10^{-5}$s,
Fig 5 Schematic potential energy diagram of the exciplex system in non-polar (---) and polar (—) media, (...) represent the case where the charge transfer is less than 1. P and C correspond to the distance at which exciplexes are formed. Model structures of ion-pair at different positions of PE diagram are shown. Two potential energy minima corresponding to the two forms A (contact ion pair or CIP) and C (solvent shared ion pair or SSIP) are separated by a potential hump at B. Point D represents the energy of free ions and E represents the point beyond which J assumes values of the order of hyperfine splitting.
while in homogeneous non-viscous solvent it is $\sim 10^{-10}$ to $10^{-11}$ S. The volume of a solvent cage is roughly the size of the solvated pair, whereas the volume of the micellar cage is such that the component radicals of a pair are allowed to separate by distances where $J$ becomes negligible. Thus, micelle systems can provide a reflecting boundary to the geminate pair to allow ISC to compete with diffusive separation.

Nano-second laser photolysis studies of magnetic field effect on the primary photochemical processes of some carbonyl compounds (e.g. benzophenone, anthraquinone and their derivatives, dibenzylketone benzil etc.) in presence and absence of H-donors were carried out by Sakaguchi, Tanimoto, Turro Dutta and others in micellar medium and the mechanisms of the reactions were established.$^{11}$ The scheme has been employed for isotope separation as well.$^{11-13}$ Steiner$^{12}$ et al. reported that a drastic magnetic field effect in electron transfer reaction between aniline and thionine triplet can be observed in reverse micelles but not in homogeneous medium. Surprisingly, the $B_{1/2}$ values obtained in the above cases sometimes exceed the values expected from hyperfine coupling constants. As the time scale for geminate RP is greater in micellar system, other mechanisms (e.g. triplet mechanism, $T_- \rightarrow S$ mechanism, spin relaxation mechanism etc.) have been evoked to overcome the discrepancies.

Turro et al.$^{13}$ observed that in case of emulsion polymerization, molecular weight of polymer can be increased to a great extent in presence of magnetic field with proper photo-sensitized initiator of (R-R) type. If the radicals are in singlet state, one of the radicals will initiate the chain reaction, which will soon be terminated by the second radical of opposite spin present in the micellar medium, resulting in a low molecular weight polymer. If the radicals are in triplet state then the partner radical, being of same spin as the initiating radical, cannot terminate the chain through recombination; one of the radicals is likely to escape and long chain polymer is expected. In presence of a magnetic field the ISC rate from triplet to singlet should be decreased; consequently the molecular weight of the polymer will be increased if the initiating RP is born in a triplet state. In fact, it has been demonstrated that in dibenzyl ketone-photo-sensitized emulsion polymerization of styrene, the average molecular weight increases by about 400 per cent at a magnetic field of 0.1 KG.

*Chain Length between the Donor and the Acceptor*

Although micelles can provide a proper cage environment for maximising the magnetic field effect, location and motion of radicals in the micelle are rather ill-defined. Molecules where the motion of the partners of the radicals may be restricted by chaining them with insulating or conducting flexible bridges, offer themselves as ideal systems for the study of the effect of interradical distance on spin dynamics.

Weller et al.$^{14}$ were the first to observe magnetic field effects on intramolecular photoreaction of polymethylene-linked bi-chromophoric compounds. The
compound, Py\((\text{CH}_2)_n\) — DMA in acetonitrile\textsuperscript{14} was studied, when \(n\) varies from 2–16, by steady state and time-resolved magnetic modulation spectroscopy. An extremely large increase of exciplex luminescence intensity in presence of magnetic field was obtained for \(n = 16\); but the compounds with \(n = 2–8\) show negligible magnetic field effect. Similar result has been obtained by Tanimoto et al.\textsuperscript{15} who worked with the compound \(\alpha-(4\text{-dimethyl amino phenyl})-\omega-(9\text{-phenanthryl})\) alkanes where \(n\) varies from 2–10. It has been found that \(\varphi' (H)/\varphi(0)\) vs, \(B\) curve \((\varphi' (H) = \text{total luminescence in the presence of magnetic field } B; \varphi (0) = \text{total luminescence in the absence of magnetic field})\) shows a minima at small \(B\) which is more pronounced for small \(n\). This has been taken as evidence by Weller and by Tanimoto of increased exchange interaction at reduced internuclear distances for small \(n\).

Since the degeneracy of the singlet and the triplet of the RP seems to occur at a distance shorter than the estimated end-to-end distance of the stretched form, which is 11.3 Å for \(n = 8\) and 13.8 Å for \(n = 10\textsuperscript{15}\) and the field effect becomes appreciable only for \(n > 8\), it may be concluded that the distance below which exchange interaction \(J\) suppresses the field effect is of the order of 10 Å. The same conclusion has been obtained for the S-T degeneracy of the RP in studies of magnetic field effects on the hydrogen abstraction reaction of 1-(xanthene-2-carbonyloxy)-\(n\)(xanthene-2-carbonyloxy) alkanes\textsuperscript{16} and on the photoredox reaction of N-[\(\omega-(p\text{-nitrophenoxyl})\) alkyl] anilines.\textsuperscript{17} Nath et al.\textsuperscript{7(a)} investigated a polymer with pyrene as one end group and DMA the other, \textit{i.e.}, Py\((\text{CH}_2)_n\) — COCH\(_2\) CH\(_2\) — Polystyrene — CH — DMA. These polymers have more rotational and translational freedom compared to short-chain methylene-linked systems studied by previous workers. It is interesting to note that the behaviour of the flexible polymers with respect to the magnetic field perturbation is closer to unlinked Py-DMA system than to methylene-linked system, inspite of the fact that the lifetimes of the linked and the unlinked systems differ markedly.

**Concentration of Donor/s**

Addition of neutral donor molecules may cause electron hopping\textsuperscript{18} between donor radicals and the neutral species which might induce spin dephasing and/or uncertainty broadening.\textsuperscript{19} It has been reported that some exciplex systems having donors with large hfc exhibit concentration-dependent magnetic field effect.\textsuperscript{20,21} In case of very low donor concentrations, the \(B_{1/2}\) values can be well correlated with total hyperfine coupling calculated by equation (1)\textsuperscript{20,21} but the experimental \(B_{1/2}\) value increases as the concentration of the donor increases. For example, in case of (Py-DMA) exciplex in alcoholic medium several workers\textsuperscript{20,21} observed that the \(B_{1/2}\) value increases from 50 G to 70 G when concentration of DMA changes from 2.7 mM to 60 mM, while Py-DMA should have \(B_{1/2} = 55\) G from equation (1). It was suggested\textsuperscript{20} that electron hopping between different donors
in solution reduces the lifetime of a fixed nuclear environment and causes an uncertainty broadening of the energy levels which, coupled with hyperfine coupling and Zeeman interaction, increases the effective $B_{1/2}$. To verify the electron hopping theory, Nath et al.\textsuperscript{21} replaced half of the donor (DMA) at high concentration by DMT (Dimethyl Toluidine), another donor of similar hyperfine interaction. The idea was to decrease the exchange rate keeping the total donor concentration around the exciplex unchanged. It was found that the two-component (or single donor) system has the same $B_{1/2}$ as the three-component (or two donors) system at identical total donor concentrations. This result, along with the observation that lifetime of the exciplex does not influence its $B_{1/2}$, cast doubt on the explanation based on electron hopping. There is a possibility that the environment directly perturbs the spin-rephasing process.\textsuperscript{21} At low concentrations the decaying exciplex is in a cage formed by solvent molecules while at higher concentrations one or more of the solvent molecules in the cybotactic region are replaced by excess donor molecules having large hfs. If the surrounding molecules perturb the caged RP, nuclei of weakly-bonded molecules need to be included in the sum of the expression (1) for $B_i$; this will lead to an increase in $B_{1/2}$ when one or more of the solvent molecules with low $B_i$ are replaced by another donor having high $B_i$. The observation that isotopic replacement of non-bonded solvent molecules CH$_3$OH by CD$_3$OD, causes a small but definite decrease of $B_{1/2}$ indicates that perturbation by weakly bonded neighbours can indeed occur.\textsuperscript{21}

*Internal Field provided by Paramagnetic Species*

Spin rephasing dynamics of RP can be modulated by application of an external magnetic field, which in turn can be modulated by addition of magnetic particles\textsuperscript{22} or paramagnetic ions in the system.\textsuperscript{23–25}

The effect of paramagnetic lanthanide ions on spin evolution process of RPs has been thoroughly investigated.\textsuperscript{23–25} It has been observed that some photochemical reactions of Napthoquinone\textsuperscript{23} and dibenzylketone\textsuperscript{24} in micellar media are influenced by paramagnetic Ln$^{3+}$ ions (as LnCl$_3$) but not by diamagnetic La$^{3+}$ and Lu$^{3+}$ ions or Eu$^{3+}$ ions. The effect occurs only in presence of an external magnetic field.\textsuperscript{23,24} The rate of yield of cage product from initially formed triplet radical pair after ISC is suppressed by an external magnetic field but it increases again with the concentration of paramagnetic Ln$^{3+}$ ions. It was argued that paramagnetic Ln$^{3+}$ ion increases $S \rightarrow T$ transitions by reopening the channels, $S \rightarrow T_{\pm 1}$, blocked by the external magnetic field indirectly through increased $T_{\pm} \leftrightarrow T_0$ relaxation rate.\textsuperscript{23} The puzzling observation was made that the capacity of Ln$^{3+}$ ions to quench the magnetic field effect is proportional to its spin-only moment but not to the total moment.\textsuperscript{23,24} This could not be explained by the two groups of workers mentioned above. Recently, Basu et al.\textsuperscript{25} investigated the effect of Ln$^{3+}$ ions (as Lanthanum-acetyl acetonates) on magnetic field effect of exciplex luminescence in partially polar medium (acetone). The values of $\Delta \phi/\phi$ (as discussed before) were found to decrease with increase in concentration of paramagnetic Ln$^{3+}$ ions. Despite wide differences in the medium, the charges of the radicals, the structure of the
lanthanide complex and the method of studying spin-rephasing rate in the three studies, the same dependences of the quenching rate constants on spin-only moments of Ln$^{3+}$ ions (except Eu$^{3+}$) were observed. This showed that the spin moment dependent relaxation behaviour is an inherent characteristic of Ln$^{3+}$ ions.

This spin-moment dependent phenomenon, which parallels closely magnetic transition temperature,$^{26}$ has been explained by Basu et al. on the basis of Heisenberg exchange interaction between a paramagnetic Ln$^{3+}$ ions and the RP system.$^{25}$ The exchange hamiltonian takes a simple isotropic form, $H_{ex} = \beta \vec{S}_1 \cdot \vec{S}_2$, for one electron on each interacting system. For many-electron systems, $H_{ex} = \beta \vec{S}_1 \cdot \vec{S}_2$ where $S_1$ and $S_2$ are the total spin of the subsystems 1 and 2 respectively.$^{26}$ For rare earth ions, the exchange or the crystal field interaction is smaller than the spin-orbit coupling, so the spins can be further projected on to $J.$$^{26}$ Assuming $S \sim (g - 1) J$ where $g$ is the Lande 'g' factor, $H_{ex} = (g - 1) \beta J_1 J_2$; assuming $\beta$ constant along the Ln$^{3+}$ series, $H_{ex}$ is proportional to $(g - 1) [J (J + 1)]^{1/2}$ or the square root of the de Gennes factor $G$ which is known to play a pivotal role in determining the magnetic transition temperatures in rare earths and alloys.$^{26}$ The variation of $G^{1/2}$ along the Ln$^{3+}$ ion series is shown in Fig. 6 and all the interesting features of the observed curve including the dip at

![Graph showing quenching rate constants and Ln$^{3+}$ ions](attachment:image.png)

Fig 6 Plot of the quenching rate constants ($Q$) of [Py-DMA] exciplex ($\square$), [CNP-AN] exciplex ($\triangle$) and square root of the de Gennes factor, $G^{1/2}$ ($\bigtriangleup$) versus Ln$^{3+}$ ions. Pm$^{3+}$ and Lu$^{3+}$ were unavailable for testing.
Eu$^{3+}$ are qualitatively reproduced. Generally the magnetic dipole-dipole interaction, and not the exchange interaction, is the long-range one, but it is evident from the correlation that the latter one dominates the coupling between the Ln$^{3+}$ ion and the RP system. Presumably superexchange through the ligands or the medium extends the range of exchange interaction. The long-tailed 65 orbital of Ln$^{3+}$ ions might be involved in the interaction.

Another point to note that Ln$^{3+}$ ions, though capable of turning the total spin-vector of the RP through terms like $J_{1}^{\pm} S_{2}^{\mp}$ in the presence of a field, are incapable of bringing about a change in $S \rightarrow T$ transition rate in RP in the absence of a magnetic field. This means that the two partners of the RP must have equal coupling constants with Ln$^{3+}$ ion; this can happen if the distance of the Ln$^{3+}$ ion from the RP is long compared to the inter-radical separation within the RP.

**CONCLUSION**

The brief overview summarises some of the rapid strides made in this area in recent years. However, more concrete conclusions require further substantial effort. Time-resolved magnetic field experiments are needed to throw new light on the central problem of CIP $\Leftrightarrow$ SSIP dynamics. Experiments with donor-acceptor pairs at fixed distances in rigid matrix or crystal are likely to simplify the complication of coupling between spin and spatial motion. The intrinsic complexity of the problem offers greater challenge to the theoreticians who are yet to develop a working analytical formulation. We believe that the magnetic field effect can be used as a sensitive probe for static and dynamical role of solvents, and can throw new light on the emerging views of ion formation and ion motion in liquids.

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