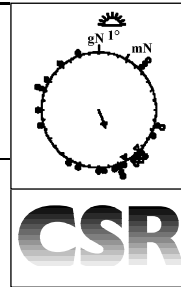


Magnetic fields and radical reactions: recent developments and their role in nature



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Recombination of pairs of radicals is exceptional in being affected by magnetic fields. The mechanism has been known for some thirty years, but recently new applications have appeared and research has been extended to very high fields (up to 30 Tesla). Claims that low electromagnetic fields damage health have led to extensive medical, chemical and physical research: no firm evidence of hazards has emerged; on the other hand, migrating birds orient themselves in the earth's field (50 μ T): radical pairs may provide the mechanism.

1 Introductory

Magnetic field effects (MFEs) are now studied over a very wide range: superconducting magnets provide fields of more than ten Tesla for industry, for research (spin resonance, NMR and EPR) and for magnetic resonance imaging (MRI). At the other extreme, over the last ten years concerns have arisen about potential hazards due to environmental electromagnetic (EM) fields of a few microTesla. For comparison, the field between the poles of a horseshoe magnet might be 100–200 mT and the earth's field is $\sim 50 \mu$ T. At first sight, effects on chemical reactions appear very unlikely; even a field of 1 T produces a splitting of the electronic energies of a radical of only 11.2 J mol⁻¹; for comparison, kT is ~ 2500 J mol⁻¹ at normal temperatures; heats of typical chemical reactions are ~ 10 –100 kJ mol⁻¹. Indeed there is no effect at all on most ground state reactions. The exception is provided by the rates (not the equilibria) of recombination of free radicals and radical ions in solution and in solids; this is the subject of this review.

The behaviour of radical pairs in mobile liquids at moderate fields (~ 1 –100 mT) is particularly simple: it depends on the relative magnitudes of the interactions of electron spins with an

applied field (Zeeman splitting) and with magnetic nuclei, the isotropic hyperfine couplings, a . (Many important nuclei are not magnetic, e.g. ¹²C and ¹⁶O.) Hyperfine couplings are familiar from EPR spectroscopy and range from 0.1 to 2–3 mT for common organic radicals. Radical pair (RP) theory has found the bulk of its applications in spin resonance research; spin evolution in RPs differs between the nuclear spin states which leads to 'spin-selective reactions'. Since conventional spin resonance measurements depend on differences in the Boltzmann distribution among the energy states of a few parts per thousand (EPR) or per million (NMR), such processes can give spectacular effects. Chemically induced dynamic polarisation (CIDEP and CIDNP) has become a very large research area in its own right; there is not space to include it here. Nor is it possible to do justice to many well-developed areas, e.g. much of the older solution work and studies of micelles and photosynthetic reaction centres. Other MFEs not covered are magnetic isotope effects which also result from radical pairs, processes involving triplet excited states,¹ gas-phase dissociation of excited molecules,² and bulk effects of fields such as orientation of liquid crystals.

The next section sets out the basic ideas of RP theory; for mobile liquids its predictions have been borne out by experimental work spanning nearly 30 years. The amount is now very large: in a thorough review in 1992, Steiner and Ulrich¹ listed some 774 papers and 34 earlier reviews. Section 3 contains examples chosen to illustrate the principles and the types of experiments used. Most space is given there to radioluminescence: this is the author's own interest but arguably it provides the best illustrations of the basic phenomena and research in this area is very active at present.

Later sections describe recent developments including a wider range of experiments and the study of low field effects, LFE, where the Zeeman interaction is less than the hyperfine couplings, necessitated by the possibility of health hazards. Sections 4 and 5 describe work on electron transfer processes and radical reactions in solids and biological materials. These are more complicated because the anisotropic components of hyperfine coupling no longer average to zero. No final conclusions about health hazards are yet possible, but while the positive evidence is weak there can be no doubt that birds make use of the geomagnetic field to aid migration over long distances, while many organisms use it to orient themselves (sections 6 and 7). The S.I. unit the Tesla has replaced the gauss, G, (1 T = 10000 G) but the latter still appears widely in the literature so both are used as needed.

2 Concepts

2.1 Spin correlation

Most molecules have singlet ground states. The spin behaviour of the electron pairs in each orbital is said to be correlated: the

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two spins are oriented in opposite directions and their phases are also related: this is another way of saying that there is no resultant spin momentum. In a triplet state, the two unpaired spins are also correlated but now they are parallel and their phase relation gives a total spin of one. In a molecule, this correlation is dictated by the powerful electron exchange interaction, J . If a bond is broken to produce two radicals or an electron is transferred to a neighbouring molecule to produce radical ions, J becomes zero or very small.

An important concept is the distinction between stationary and non-stationary states. The solutions of a particular wave equation are stationary states or eigenfunctions; the singlet and triplet states of a molecule provide an example. When a bond is broken forming radicals, momentarily the spin wavefunction becomes a non-stationary state of the RP, because the hamiltonian has changed; suddenly J is very small, less than or comparable with the electron–nuclear hyperfine interactions. The result is that the wavefunction will oscillate back and forth between singlet and triplet. In wave-mechanical terms, the non-stationary state can be treated as a superposition of the true stationary states which are solutions of equations like (1) for each radical. A parallel can be found in the vibration of molecules: spectroscopy deals with the stationary states, called normal vibrations, but a collision between two molecules may lead to a superposition of such motions in which energy flows back and forth between different bonds.

‘Correlation’ is used here to describe the connection between two electron spins. It is retained despite conversion between the spin states which is said to be coherent. Eventually the correlation is lost by spin relaxation (section 2.6), a random process very familiar in EPR where it dictates the width of the lines; typically it takes a few microseconds for radicals in solution.

2.2 Spin evolution: the simple case

The interaction between an electron, magnetic nuclei such as those of hydrogen (simply called protons here for convenience), and an external field, B , is given by

$$H = g\mu_B \mathbf{B} \cdot \mathbf{S} + \sum_j a_j \mathbf{S} \cdot \mathbf{I}_j + \sum_j \mathbf{S} \mathbf{A}_j \cdot \mathbf{I}_j \quad (1)$$

The second and third terms correspond to the two parts of the hyperfine interactions summed over the various nuclei; a is the contact term which is independent of orientation; \mathbf{A} is used for the classical, dipolar interaction of two magnets which is orientation dependent. The Zeeman interaction between the field and the electron spin is represented by the first term; that with the nuclei can be neglected. μ_B is the Bohr magneton. g is commonly called the g -factor: departures from the free electron value, g_e , of 2.0023 are due to contributions from the orbital angular momentum, usually small for organic radicals; it too may be anisotropic. Eqn. (1) is about energies but both frequency and field units are commonly used for energy levels; 1 mT \equiv 28.0 MHz. Here field units have been used as far as possible so that a and B can be readily compared. S and I are the operators for electron and nuclear spin. For spin-resonance experiments, $B \gg a$, eigenvalues of S and I are $+\frac{1}{2}$ and $-\frac{1}{2}$ for α and β spins. This meaning of S is not needed further: in the remainder of the review, S and T are used as shorthand for singlet and triplet states; T_+ , T_0 and T_- are components of T .

In mobile liquids rapid molecular rotation simplifies matters because the \mathbf{A} term and the anisotropic part of g average to zero. Eqn. (1) can then be solved analytically in many cases, notably when $B \gg a$. It is also possible at any field provided that only one type of nucleus is present (one value of a). Fig. 1 shows the field dependence of the energy levels of one electron and one proton. The EPR transitions (at right) at high field are separated

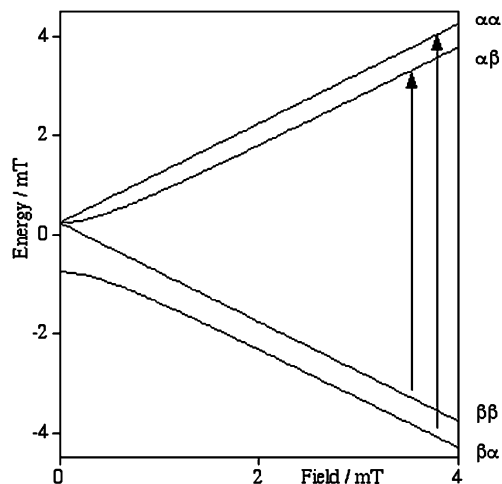


Fig. 1 Energy levels of one proton, one electron (Breit-Rabi diagram); $a = 1$ mT.

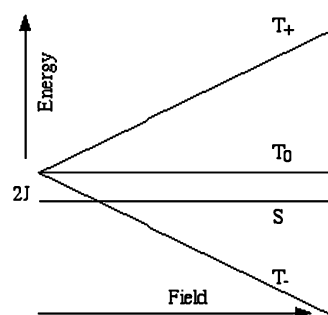


Fig. 2 Energy levels for two electrons; exchange interaction, $J \neq 0$.

by a , the two pairs of levels each by $a/2$. Fig. 2 shows the field dependence of the spin states for two electrons; for clarity the case of a small J is shown. When $J = 0$, T_0 and S are degenerate at all fields. When magnetic nuclei are present, these lines are replaced by close bands of levels. In a strong field, electrons and nuclei are decoupled and both precess round the field direction as shown in Fig. 3. The rate for electrons is determined by the sum of the external field and the local field of the nuclei. Interconversion between singlet and triplet is most easily understood using a vector model of angular momentum; Fig. 3a shows the T_0 and S states for two electrons. The field differs slightly between different nuclear spin orientations, so the two electrons may precess at slightly different rates. If so, the overall state oscillates between S and T_0 through mixed states. The other two triplet components are not involved, Fig. 3b; this can be understood in terms of the splittings in Fig. 2. For a single proton, it is a simple matter to derive an equation describing this behaviour.³

$$\rho_S(t) = \left(1 + \cos(\Delta g B t) \cdot \cos(a t / 2)\right) / 2 \quad (2)$$

$\rho_S(t)$ is the probability of an initially pure singlet remaining so after time, t ; simply related to $\rho_S(t)$ are the yields of triplet from triplet or triplet from singlet (T from S); e.g. the latter is $(1 - \rho_S(t))$ so some of the plots in the figures may appear to be upside down. Δg is the difference between the (isotropic) g -values of the two radicals. The second factor contains $a/2$ (in units of radians per second) corresponding to the $a/2$ splittings in Fig. 1. An important result is that the time-average value of ρ_S , $\langle \rho_S \rangle$, is one half.

At zero field the three triplet components become indistinguishable (Fig. 2); if $J = 0$, one might expect a limiting value of $\langle \rho_S \rangle$ of one quarter and a field effect, ratio field on/field off, of two or 100% increase, but this is seldom reached.³ One reason is that at zero field electrons and protons precess round

their resultant. The vector diagram for one electron and one proton (Fig. 3c) is symmetrical; though their magnetic moments are very different, the particles have the same angular momentum. As a result the changes in the electron orientation are smaller; however the two electrons now see local fields with different orientations, provided both interact with nuclei then the overall result is that $\langle \rho_S \rangle$ is less than one half, though it may not reach the possible limit of one quarter. In the simple case the oscillating term contains $\cos(at)$ corresponding to the splitting at the left of Fig. 1, so spin evolution is faster than at high field. For low fields the behaviour becomes still more complicated, but the time-dependence of S is still represented by equations with cosine terms and a constant term. When eqn. (1) cannot be solved analytically (more than one type of proton and low or zero field), it is still possible to calculate ρ_S using computer programmes or approximations such as the 'semi-classical method'.¹ Magnetic field effects are then given by the ratio of ρ_S or $\langle \rho_S \rangle$ in a field to that at zero field. Fig. 4 shows results of some computer calculations.

2.3 Spin changes and diffusion

When radical ions recombine, the product may be an excited state: observation of fluorescence makes possible time-resolved measurements of the ratio of the ρ_S values down to one nanosecond (section 3.1, also 4). Spin evolution can be followed and the limiting field effect measured directly. More commonly, effects on the overall yield are measured. Neutral radicals (section 3.3) usually correlate with an attractive ground state singlet and a repulsive anti-bonding triplet. Only singlet pairs can react; triplet pairs must separate. Re-encounter of unreacted pairs has a high probability which leads to a complicated situation in which both molecular diffusion and spin evolution must be considered. Further complexities arise for neutral radicals from the exchange and dipolar interactions between the unpaired electrons. Detailed theoretical treatments are numerous because of the importance of CIDNP, *etc.* However, for a qualitative description of the MFEs, one simply wants to illustrate the expected dependence of $\langle \rho_S \rangle$ on field and on reaction time; oscillating curves (Fig. 4) are not very informative. It is convenient to use the 'exponential model'¹ to simplify description; it is assumed that singlet and triplet pairs decay by first order processes with the same rate constant. Then

$$\langle \rho_S \rangle = \tau^{-1} \int_0^{\infty} \rho_S(t) \cdot \exp(-t/\tau) \cdot dt \quad (3)$$

where τ is the mean lifetime of the RP. This is especially useful in illustrating the importance of the relation between lifetime and spin evolution: the smaller the field, the more time it takes for a field effect to develop.

When $B > \Sigma a$ the time taken for high field effects to develop is $\sim 1/a$, typically a few nanoseconds; when $B < \Sigma a$, the time

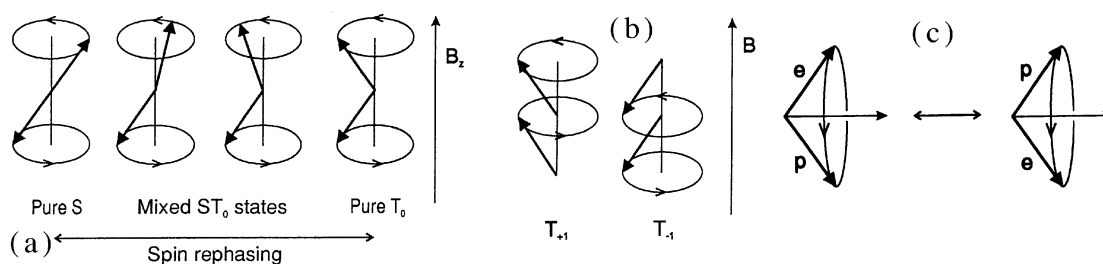


Fig. 3 Vector representations of spin motion: (a) and (b), two electrons at high field, (a) showing the conversion between S and T_0 ; (c) electron and proton at zero field.²⁸ Reproduced from *Int. J. Radiat. Biol.*, vol. 69, B. Brocklehurst and K. A. McLauchlan, 'Free Radical Mechanism for the Effects of Environmental Electromagnetic Fields on Biological Systems', pages 3–24, copyright 1996, with permission from Taylor and Francis, Ltd.

is $\sim 1/B$, $0.7 \mu\text{s}$ for the geomagnetic field of $50 \mu\text{T}$. Relaxation times seldom exceed a few microseconds; 50–60 Hz and other oscillating fields up to 1 MHz are essentially constant over such times. Only the effects of static fields are considered in most of this review.

Once $B \gg a$, the hyperfine effects level off. It is useful to define a characteristic field at which half the limiting effect is reached. Using the semi-classical method, it can be shown¹ that

$$B_{1/2} = 2(B_a^2 + B_b^2) / (B_a + B_b) \quad (4)$$

where $B_{a,b} = \left(\sum_i I_i(I_i + 1)a_i^2 \right)^{1/2}$

Here I is the spin quantum number for the each type of nucleus, *e.g.* 1 or 0 for two protons, 1 for one deuteron; suffixes a and b indicate the two radicals. This result is valid providing the radical decay by reaction, electron transfer or relaxation is sufficiently slow compared to spin evolution. In strong fields, the Δg factor (eqn. (2)) may become important: if τ is short then loss of initial spin character by this means can lead to reduction in the field effect.

In non-polar solvents the final approach of recombining ions is very fast; there is no barrier to reaction and both singlet and triplet states are accessible so it is reasonable to suppose recombination rates are equal and exchange and electron–electron interaction can be neglected. Radical ions in polar solvents (section 3.2) provide an intermediate case between ions in hydrocarbons and neutral radicals: both singlets and triplets can react, but their rates may well be very different because ion solvation produces barriers. For example, triplet pairs may react more readily if excited singlets are not accessible and the large energy release of ground state formation puts it in the Marcus 'inverted region' (where reaction rates are reduced by the Franck-Condon principle). The same is true of charge transfer in

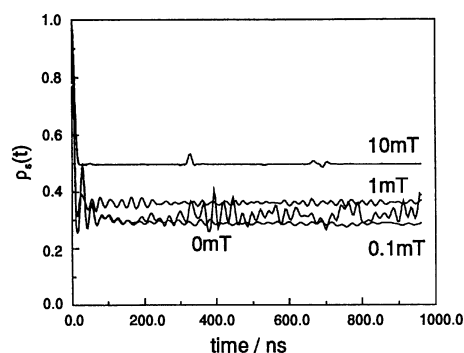


Fig. 4 Calculations of the evolutions of the singlet character in the pyrene/1,3-dicyanobenzene system from an initial pure singlet.²⁸ At long times the zero field curve rises above that for 0.1 mT. Reproduced from *Int. J. Radiat. Biol.*, vol. 69, B. Brocklehurst and K. A. McLauchlan, 'Free Radical Mechanism for the Effects of Environmental Electromagnetic Fields on Biological Systems', pages 3–24, copyright 1996, with permission from Taylor and Francis, Ltd.

large organic molecules and assemblies, notably photosynthetic reaction centres (section 5.1).

2.4 Low field effect

In general, vector models and other physical descriptions should be used with care; it is best to solve the wave equations first and look for a model afterwards. The author accidentally came across the LFE in this way.³ Because of concerns about EMF and health in recent years the need to understand low field effects has grown. Their mechanism is less obvious than at high fields. The cosine terms in the equations reflect the splittings between energy levels: when levels are degenerate, there will be cosine terms with zero argument, which contribute to the fixed term, and so to $\langle\rho_S\rangle$. The existence of a degeneracy at zero field (Fig. 1) accounts for the failure of $\langle\rho_S\rangle$ to reach the limiting value of one quarter. It follows that further causes of splitting will be important. In particular, a small field suffices to split the zero field levels and $\langle\rho_S\rangle$ decreases. In terms of the vector model, fields $< a$ do not uncouple electron and proton but the resultant (Fig. 3c) can precess round them. The LFE is illustrated by the numerical calculations in Fig. 4, which also emphasises the point that the lower the field, the longer the time required for the effect to take place; only at long times is it clear that ρ_S at 0.1 mT is less than the zero field value.

Detailed calculations⁴ show that, for mobile liquids, the LFE can be quite large at long times, between 10 and 40%. An interesting point which emerged, again accidentally, is that the relative sign of different a values in the same radical has an effect at low fields (reducing the LFE) though not at high. The same is true in EPR where the signs of a cannot be determined directly at the fields normally used. Alkyl radicals typify such behaviour: α - and β -protons have a values of ~ -2.2 and $\sim +2.7$ mT respectively.

The LFE provides a first illustration of Kramers' theorem which states that the lowest state of an odd number of spin-one-half particles (one must include the electron here) must be at least doubly degenerate: this degeneracy can only be split by a magnetic field, not by an electric field, *i.e.* not by any valence interaction.

2.5 Anisotropy effects

Radical reactions can take place in solids *via* electron transfer; ions and neutral radicals may recombine in viscous liquids. In both cases the anisotropy of hyperfine and Zeeman interaction can no longer be neglected. The effects become very complicated: a tour de force⁵ for the alkylcob(m)alamin system (section 5.2) illustrates this, though it should be noted the authors set a long relaxation time limit of 50 μ s which exaggerates the low field effects. Here one and two proton systems are used for illustration.

The effect of anisotropy, A , is another case of Kramers' theorem. A single spin-half particle can reduce ρ_S to one quarter by splitting the zero field levels, but this is not the case for two, or any even number of spin-one-half nuclei or, *e.g.*, one deuteron³ because of the remaining degenerate 'Kramers' doublets'. For two protons and one electron, a alone gives one quartet and two doublets: A splits these levels into four doublets, and the conditions for seeing a LFE remain.

Even for a single proton the outcome at low fields depends on the orientation of the field and the symmetry of the situation.⁴ In many radicals, A is axial, *i.e.*, two of the principal values are equal. Fig. 5 provides an example; demonstrating the complexity of the results. Even when an average over all orientations is taken, the LFE remains, though much smaller than in the case of fast rotation. When the asymmetry is greater, $A_{xx} \neq A_{yy} \neq A_{zz}$, the LFE decreases further but does not disappear entirely. The

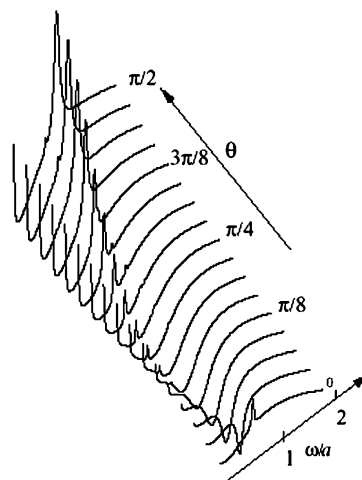


Fig. 5 Effects of low fields and orientation (θ) on the singlet recombination yield for a single proton radical pair; ω is the electron Larmor frequency; singlet and triplet decay rates are $0.1a/2\pi$. Anisotropy values were taken as $A_{xx} = A_{yy} = 0.3a$, $A_{zz} = -0.6a$.^{4b} Reproduced from *Chem. Phys. Lett.*, vol. 334, C. R. Timmel, F. Cintolesi, B. Brocklehurst and P.J. Hore, 'Model calculations of magnetic field effects on recombination reactions of radicals with hyperfine interactions', pages 387–395, copyright 2001, with permission from Elsevier Science.

'bumps' or resonances are remarkable (Fig. 5) and again are not lost on averaging. These are due to curve crossings where the arguments of some cosines again equal zero. Such behaviour can occur in other cases, *e.g.* when the $\Delta g.B$ term matches an a factor at high field; *e.g.* for a single proton (eqn. (2)) when $\Delta g.B = a/2$, $\langle\rho_S\rangle = 3/4$ not $1/2$.

2.6 Spin relaxation

There are many contributions to spin relaxation; EPR textbooks provide more details. For radicals in solution, relaxation times are typically a few μ s, so that coherent processes are much faster but this is not always true; also, relaxation is sometimes field dependent, so it must be considered briefly here.

The two types of relaxation are characterised by T_1 and T_2 . T_1 , the spin-lattice relaxation time, is concerned with re-orientation of the spin, $\alpha \leftrightarrow \beta$, *i.e.* conversion between the T_+ or T_- and T_0 or S (Fig. 2) states in this context; T_2 , the spin-spin relaxation time, changes the phase relation between the spins, interconverting T_0 or S (*cf.* Fig. 3). The distinction disappears at zero field, but since T_1 and T_2 may differ in a field, this can produce MFEs in radical pairs. Typically the two times are comparable in mobile liquids but become distinct at higher viscosities. Spin-lattice relaxation results from fluctuating local fields, usually due to re-orientation of the radical itself; the contribution of the anisotropy, A , is field independent, but that of g anisotropy increases with the square of the field, producing a further field dependence. In some radicals, solvent-induced fluctuations of the orbital contribution to the g -value itself produce fast relaxation: notably the \cdot OH radical relaxes in < 1 ns in solution because fluctuations in hydrogen bonding modulate the g -value; no field effects on its reactions are observed.

3 Reactions in solution: experimental results

3.1 Radioluminescence of hydrocarbons

Ion recombination in pure alkanes is extremely fast; it can be slowed from picoseconds to nanoseconds by addition of aromatics which trap both electrons and positive charge, allowing time for development of field effects. One can assume that the product yields reflect the singlet and triplet contents of

the RP wavefunction (section 2.3) and another advantage is that nearly all the ion pairs undergo geminate recombination because of coulombic attraction; RPs are initially separated by ranges of distances with mean values of 5–10 nm, much larger than the range of J , but much less than the Onsager escape distance, ~ 30 nm at room temperature.

An early test of RP theory of MFEs was provided by isotope studies⁶ (Fig. 6). Hyperfine couplings to protons are ~ 6 times

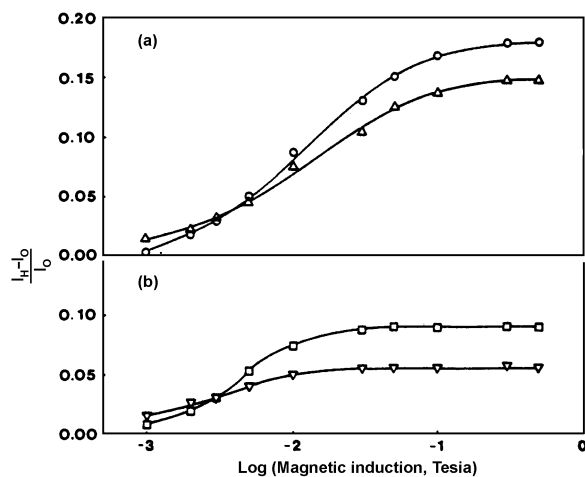


Fig. 6 Field effect on fluorescence intensity of γ -irradiated 10^{-2} M solutions in (a) squalane and (b) cyclohexane; circles, naphthalene; triangles, naphthalene-d8.⁶ Reproduced from *Chem. Phys. Lett.*, vol. 47, R. S. Dixon, F. P. Sargent, V. J. Lopata and E. M. Gardy, 'Fluorescence from γ -irradiated solutions of naphthalene-d8. Effect of an applied magnetic field.', pages 108–112, copyright 1975, with permission from Elsevier Science.

larger than to deuterons. The MFE for deuterated species is smaller when B is large, because spin evolution is slower; the recombination rate itself is unaffected by the field. In contrast, at low field the Zeeman interaction more easily overcomes the weaker deuterium hyperfine coupling (*cf.* Fig. 1).

Squalane (2,6,10,15,19,23-hexamethyltetracosane) is a convenient solvent for many purposes, when higher viscosities are needed. It extends ion recombination into the microsecond region,⁷ but solute rotation is still fast enough to average out anisotropy effects. The initial sharp rise shown in Fig. 7 arises

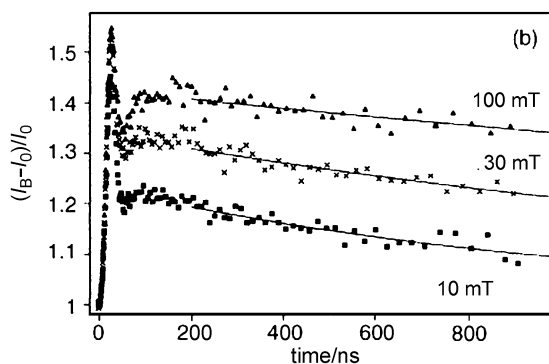


Fig. 7 Field effect on fluorescence decays of p -terphenyl in squalane excited by ^{90}Sr β -particles. Reproduced from *J. Chem. Soc., Faraday Trans.*, vol. 93, B. Brocklehurst, 'Ion recombination luminescence in squalane solutions: spin relaxation effects', pages 1079–88.

because spin evolution is faster at zero field (section 2.2). The plateau region, around 100 ns, is followed by field-dependent spin relaxation which finally destroys the spin correlation. The extent of the limiting effect, 40% enhancement in the plateau region, is smaller than the 50–100% expected for initial singlets. This reflects the complications of radiolysis: in short tracks and

in spurs containing two or more ion pairs, an electron may return to its initial partner, or to a different cation where there is no spin correlation; MFEs have been used to investigate this.^{7,8}

In principle, the field effect oscillates in time (Fig. 4); but this is not easy to observe: the positive 'hole' usually spends a significant time in the solvent. (This explains the larger effect in squalane in Fig. 6.) Also, the numbers of nuclei and values of a are usually large: *e.g.*, p -terphenyl cation and anion both have 14 protons with 4 hyperfine couplings. Use of partial deuteration and separate scavengers for hole and electron can produce a system with just one large coupling. Spectacular oscillations then become visible. This has been demonstrated by Molin and his collaborators at Novosibirsk, who have used field effects on fluorescence and related measurements for a wide range of studies^{8b} of oscillations due to a and g -value differences between the solutes (Fig. 8a). The results agree well with EPR

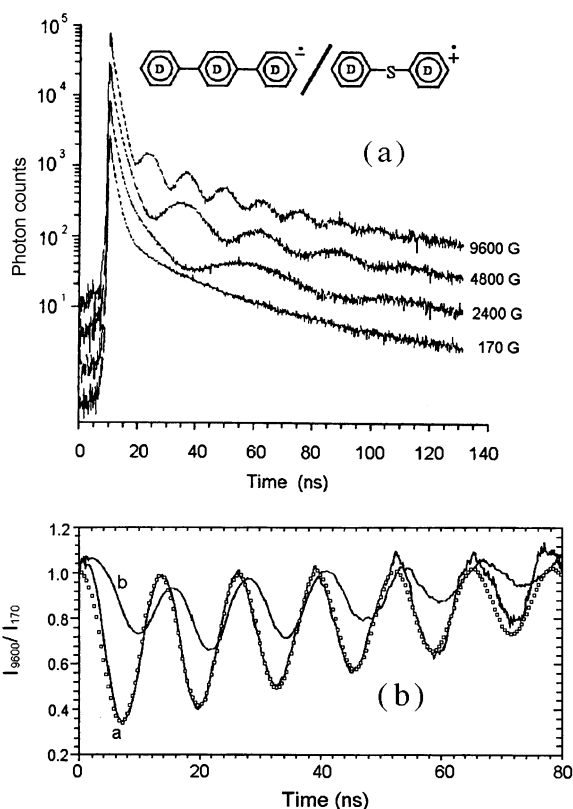


Fig. 8 (a) Decay of radio-luminescence from solutions of deuterated p -terphenyl (10^{-3} M) and diphenyl sulfide (3×10^{-2} M) in iso-octane; (b) the curve at 170 G is used as a reference curve for the oscillating component: curves A and B, 0.12 and 0.012 M respectively. Points are theoretical.^{8b} Reproduced from *Chem. Phys. Lett.*, vol. 246, V. M. Grigoryants, B. M. Tadjikov, O. M. Usov and Yu. N. Molin, 'Phase-shift of quantum oscillations in the recombination luminescence of spin-correlated radical-ion pairs', pages 392–398, copyright 1995, with permission from Elsevier Science.

measurements of a and g ; in some cases parameters have been obtained which are not otherwise accessible. The rate of hole scavenging can be determined from the phase-shifts observed at low concentrations (Fig. 8b).

Molin's group have made a number of observations of the LFE in radioluminescence⁷ and this has been applied to the study of distribution of ion separations:⁹ a spectacular demonstration is shown in Fig. 9. The range of the LFE reflects the strength of the fluorine hyperfine coupling ($a = 13.7$ mT) in C_6F_6^- . The bump at $3a$ is due to a curve-crossing: the maximum at $B = 0$ can be understood in the same way of course; their weakness (curve B) is due to charge exchange between anion and neutral hexafluorobenzene. The shift in the LFE minimum

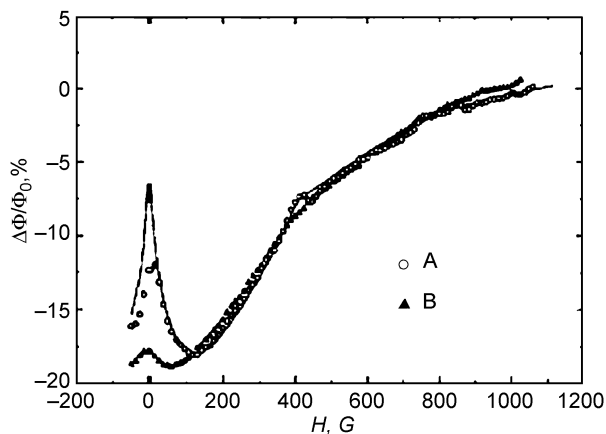


Fig. 9 Field-induced changes in fluorescence yield of 0.086 M hexafluorobenzene in perdeutero-isooctane- d_{18} relative to the high field value: excitation by (A) 123.6 nm photons, (B) β -particles: full line is a theoretical prediction.⁹ Reproduced from *Chem. Phys. Lett.*, vol. 264, V. O. Saik and S. Lipsky, 'Magnetic field effects on recombination fluorescence: comparison of VUV and fast electron excitation', 649–654, copyright 1997, with permission from Elsevier Science.

is due to wider distribution of ion pair separations for irradiation with β -particles.

The complexities of radiolysis can be simplified by using vacuum UV photons >8 – 10 eV to produce single ion pairs or very small groups of ions: at lower energies (e.g. Fig. 9), the solute is ionised not the solvent. Synchrotron light sources (such as Daresbury's SRS) which are now widely available, provide photons over a wide range in the VUV and X-ray regions. Experimentation is difficult and the data in Fig. 10 required use

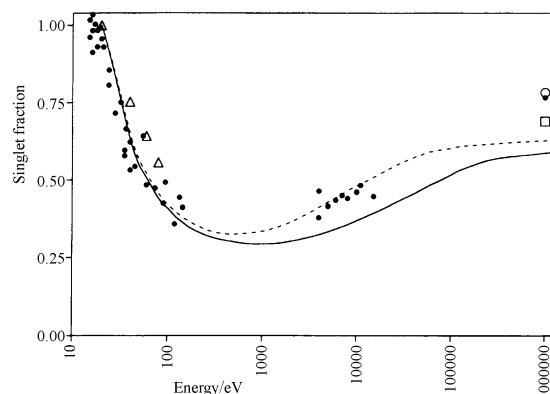


Fig. 10 Initial singlet fractions calculated from MFEs for *p*-terphenyl in squalane: closed circles, data from 3 stations of the SRS and for ^{90}Sr β -particles (far right); open symbols and lines from theoretical predictions. Reproduced from *Chem. Phys. Lett.*, vol. 211, B. Brocklehurst, 'Radioluminescence of Alkane Solutions: Comparison of Experiment and Simulation over a Wide Energy Range', 31–35, copyright 1993, with permission from Elsevier Science.

of three stations for different energy ranges. Single ionisations produce the maximum at left; the minimum is due to cross-recombination when many ion pairs are close together: the particle tracks become more sparse for high energy electrons (fast β -particles or from γ -rays). MFEs have also been used to study luminescence from tracks of fast protons and helium ions.⁷ As expected, the extent of the effect decreases with increasing LET (linear energy transfer) but it does not disappear entirely, showing that some correlation between ions remains in the penumbra of a very dense track.

These results illustrate the usefulness of MFEs in radiation chemistry.⁷ They do not provide very detailed information but they have the unique feature of detecting the presence of spin correlation between two radicals. Measurements of this type

lend themselves to computer modelling and a start has been made in this direction. Puzzles remain however: the extent of the effect has been found to decrease near the ionisation threshold in aliphatic solvents, and it is always smaller in aromatics than in alkanes. Published work on aromatics is limited; a very detailed study of crystalline anthracene has been made and field effects have been seen in VUV-excited DNA.⁷

3.2 Ultraviolet photo-ionisation

Photoionisation in the UV requires donors with a low ionisation potential and acceptors with a high electron affinity; aromatic amines and cyano compounds are commonly used with hydrocarbons. Polar solvents are needed to facilitate ionisation; provided the solvation energy is not too high, recombination into singlet excited states is possible; observation of fluorescence is especially convenient since recombination usually leads to an exciplex which emits at longer wavelengths than the parent neutral molecules. Whereas radiolysis is indiscriminate, initial ionisation taking place in the solvent, UV photons are absorbed specifically by the solutes; so only two ions are involved, though at higher concentrations charge exchange effects are found.

MFEs in such systems were extensively studied in the late '70s and the '80s by Weller and his colleagues, their experimental work complemented by Schulten's theoretical work.¹ Good agreement was found, notably field dependences agree well with eqn. (4). Fig. 11 illustrates an interesting

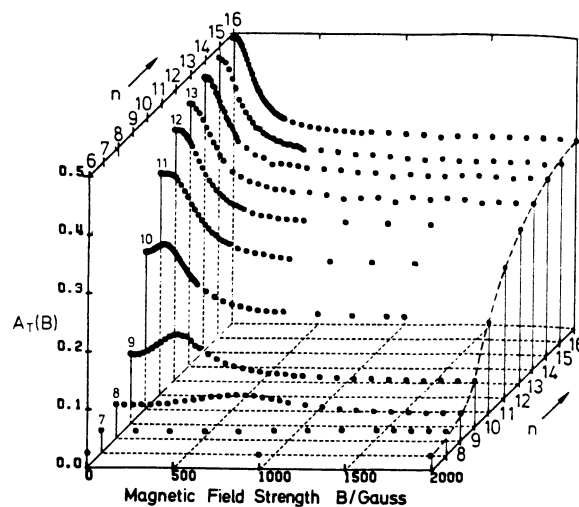


Fig. 11 Field dependence of triplet yields in acetonitrile solutions of dimethylaniline donor–pyrene acceptor pairs linked by a $(\text{CH}_2)_n$ chain.¹⁰ Reproduced from *J. Phys., Chem.*, vol. 97, U. Werner, W. Kühnle, and H. Staerk, 'Magnetic-field dependent reaction yields from radical-ion pairs linked by a partially rigid aliphatic chain', pages 9280–9287, copyright 1993, with permission from the American Chemical Society.

development, the study of the dynamics of linked pairs of donors and acceptors;¹⁰ lower concentrations can be used, obviating charge exchange. The link is usually a flexible chain, $(-\text{CH}_2-)_n$; at some values of n a 'J-resonance' is observed; it follows that for most of the life of the ion pair there is a small and nearly constant exchange interaction; the resonance occurs when the Zeeman interaction matches this (Fig. 2). All these systems were also studied in Japan by groups associated with Nagakura, Hayashi and Tanimoto² (see below). Surprisingly, only a few time-resolved measurements have been reported¹¹—a pity in the author's view because the dynamics of these pairs are less simple than in radiolysis. Solvation provides barriers to recombination so the rate constants for singlet and triplet formation may be different.

3.3 Neutral radicals

MFEs are normally very small for neutral radicals meeting at random; 25% (the singlets) can react directly; initial triplets require time for spin evolution and then a re-encounter—much less probable. Large couplings would help; *e.g.* study of H + H recombination (where the *ortho/para* ratio would change) is feasible because $a = 50$ mT for hydrogen atoms, but this has not been done.⁷ The effects remain small even when pure triplet RPs are produced by photolysis unless radical separation is restricted in some way, paralleling the coulombic attraction of radical ion pairs. The work of Turro *et al.* on the emulsion polymerisation of styrene produced spectacular results: application of a field increased the average molecular weight fivefold by reducing the rate of radical recombination. In connection with health hazard work, Scaiano *et al.*¹² showed that MFEs on RPs derived from triplet benzophenone could be enhanced by addition of bovine or human serum albumen which restrict radical diffusion. Similar but smaller enhancement was obtained with DNA.

Far more work (some hundreds of papers) has been done on RPs in micelles, typically detergents of the type $H(CH_2)_nSO_4^-Na^+$. The spins of RPs produced photochemically can remain correlated until the radicals escape into the bulk solution and so significant effects have been seen.^{1,2} Micelle radii are typically 2–3 nm, so that electron exchange and, possibly, dipolar interaction between the radicals complicate the spin evolution. Large effects require competition, usually between recombination and escape. This remains a very active area;² here we concentrate on the LFE since micelles can be regarded as simple models of biological systems (*cf.* sections 3.4 and 6.2).

Shkrob *et al.*¹³ studied reactions of radicals produced in micelles by photo-dissociation of deoxybenzoin derivatives. They found three types of field dependence, (i) due to hyperfine interaction and exchange, (ii) due to spin relaxation and (iii) an intermediate case. Type (i) was shown by small radicals and these produced an LFE: Fig. 12 illustrates the usefulness of isotopic substitution; the fully deuterated radicals probably also show a LFE but the appropriate fields would be much smaller. The field dependence obeys eqn. (3) very well. The crossing point (change of sign of the field effect) obeyed a similar relation, but interpretation of the LFE is complicated by the likely involvement of exchange. Larger radicals produced by abstraction from the surfactant by triplet benzophenone did not show a LFE; there was also a striking difference in the field dependence; these were classified as type (ii).

In comparable work¹⁴ on benzophenone in a range of micelles small LFEs have been found; results are shown in Fig. 13. The reason for the discrepancy is not known, but the later experiments are time-resolved (*cf.* Fig. 14), the earlier results are total yields. Both groups agree that size and structure of the micelles play an important role. Internal viscosity decreases with increasing size: both size and viscosity decrease with temperature. The largest effects were found for sulfates with n

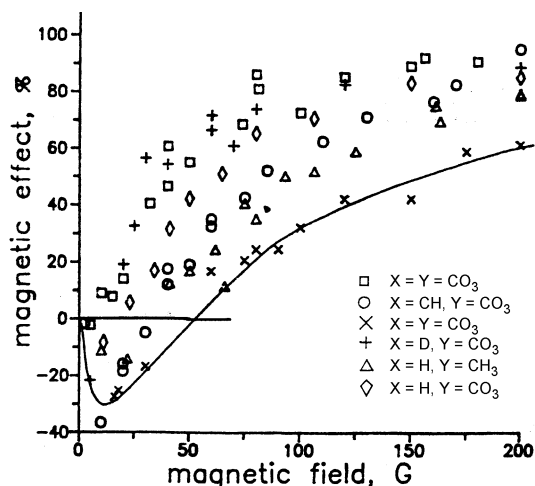


Fig. 12 Field effects on product yields from photodissociation of derivatives of deoxybenzoin, $C_6H_5CO.CXY.C_6H_5$, in SDS micelles. Results scaled to 100% of effect at 1.74 kG, which is ~ 10 –20%.¹³ Reproduced from *Chem. Phys.*, vol. 153, I. A. Shkrob, M. F. Tarasov and A. L. Buchachenko, 'Electron-spin exchange in micellized radical pairs. 2. Magnetic-field and magnetic isotope effects in multinuclear pairs', copyright 1991, with permission from Elsevier Science.

= 10 which probably corresponds to equal rates of recombination and escape. The structural effects, differences between ionic and neutral micelles and sulfates and sulfonates are not yet understood. More experiments and modelling are required.

3.4 Very high fields

Micelles and linked pairs have also been used to study effects of very high fields. Several laboratories now routinely use superconducting magnets.^{2,15} Ten T constant fields are available and measurements up to 30 T with pulsed fields have been reported. In a number of experiments a 'reversion' is observed at high fields where the hyperfine effect has become constant; Fig. 14 shows an example of this; benzophenone reduction in SDS behaves similarly.¹⁶ Two factors are probably involved, the Δg effect (*cf.* eqn. (2)) which increases the rate of interconversion between S and T_0 and spin relaxation due to anisotropy of the g -values which leads to conversion between T_+ and T_- and the other components. In these fields, Δg effects become significant even for organic radicals where Δg is small. When the orbital contribution is large, Δg may be very large as the next example shows.

Studies of MFEs at normal fields tend to be outshone by time-resolved EPR which provides detailed spectroscopic information about the radicals involved. However, this technique is limited to times greater than 10 ns. When optical detection is used, MFEs are limited only by the rate of spin evolution. This has been demonstrated recently in study of ion recombination over a few ps:¹⁵ the oxazine cation has a normal g -value but the

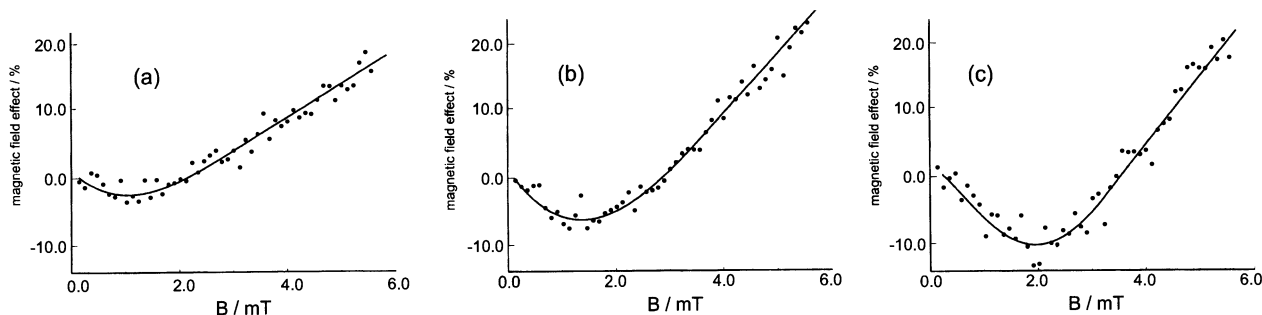


Fig. 13 Temperature dependence of LFEs on $(C_6H_5)_2COH$ radicals in sodium dodecyl sulfate: (a) 296 K, (b) 312 K, (c) 328 K.¹⁴ Reproduced from *Int. J. Radiat. Biol.*, vol. 76, R. W. Eveson, C. R. Timmel, B. Brocklehurst, P. J. Hore and K. A. McLauchlan, 'The effects of weak magnetic fields on radical recombination reactions in micelles', pages 1509–22, copyright 2000, with permission from Taylor and Francis.

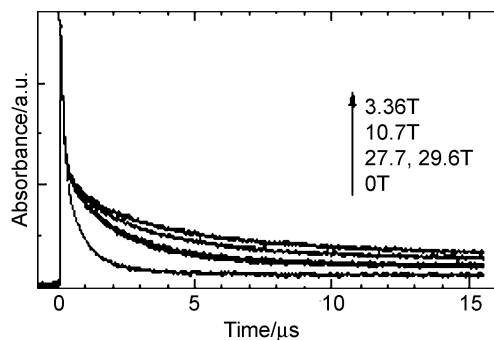


Fig. 14 Decay of $(\text{C}_6\text{H}_5)_2\text{COH}$ radicals at very high fields: benzophenone solutions in Brij 35.¹⁶ Reproduced from *Chem. Phys. Lett.*, vol. 267, K. Nishizawa, Y. Sakaguchi, H. Hayashi, H. Abe and G. Kido, 'A laser flash photolysis study of the effects of ultrahigh magnetic fields up to 29.6 T on dynamic behaviour of radical pairs in micellar solutions', pages 501–506, copyright 1997, with permission from Elsevier Science.

Zeeman interaction in the ethyl ferrocene anion is highly anisotropic, g ranging from -0.7 to 2.4 ; the average Δg is ~ 1 corresponding to a spin evolution time of 1 ps at 10 T. Experiment agreed well with theory; spin relaxation is fast too but does not compete on this time-scale. Extension of this technique to other fast processes will be very useful.

4 Viscous liquids and solids

Since the discovery of the electrical properties of polyacetylene which earned a Nobel prize in 2000 a great deal of research has been devoted to the applications of conducting polymers, especially electroluminescence. Typically, electrons and holes are injected into a thin layer of a conducting polymer such as polyphenylenevinylene, PPV; the resulting 'polarons' react to produce fluorescence. Initially it was supposed that spin considerations would limit the efficiency of this process to 25% but recent measurements of relative singlet and triplet yields have shown this to be incorrect.¹⁷ While the spin restriction should perhaps be reconsidered (*e.g.* recombination may be slow unlike that in alkane solutions), it may be that unreacted pairs are able to separate: the charge of a polaron is spread over a number of monomers, reducing the coulombic attraction. Another experimental approach is to use photoionisation; the initial pair is spin correlated and small MFEs have been observed on both the photocurrent^{18a} and fluorescence.^{18b} More work using time-resolved field effects on luminescence could help unravel the mechanisms.

The observation of magnetoplasticity, the effect of field on the ease of deforming crystals appears extraordinary, but it is now well established.^{19a} It can be understood in terms of dislocations; typically these are centres involving an impurity atom such as Ca in NaCl; during deformation layers of atoms move past the impurity. A weak bonding interaction (singlet), impedes this process where a triplet would not; singlet–triplet conversion leads to field dependence. This mechanism^{19b} has been confirmed by optically detected magnetic resonance measurements.^{19a}

A more doubtful area involves the extensively studied effect of fields on precipitation of calcium carbonate from hard water; related work claims to show memory effects in liquids involving fields.²⁰ This is very hard to accept but one can speculate that these phenomena, if real, involve dislocations; crystal growth during precipitation and dissolution of particles in suspension depend on dislocations. RF radiation leads to the formation of aragonite in addition to calcite but there appears to be no corresponding work on MFEs.

Surprisingly, little work has been published on viscous liquids. Basu *et al.*²¹ studied exciplex emission from solutions of diphenylhexatriene and 1,4-dicyanobenzene in dimethylfor-

amide/tetrahydrofuran mixtures. When the viscosity was increased by adding cellulose acetate, the MFE became greater when the exciting light was polarised parallel to the field than when it was polarised at right angles. The exciting light selects different molecular orientations.

5 Biological systems

5.1 Photosynthetic reaction centres

Charge separation is of immense importance in nature. The photosynthetic reaction process is essentially the foundation of life on earth. Its mechanism has evolved to prevent wasteful charge recombination by transferring the electron very quickly. If this process is blocked by removing or reducing the quinone acceptor this does not happen and recombination into the ground state or the triplet of the chlorophyll dimer takes place. MFEs are observed and have been studied since the 1970s²² though the larger part of the research uses CIDEP and time-resolved EPR. An early remarkable demonstration of the role of hyperfine coupling came from algae grown in D_2O which survived long enough to show an isotope effect.

Fig. 15a shows measurements on a suspension of quinone-depleted reaction centres of triplet yields. Initially the low field

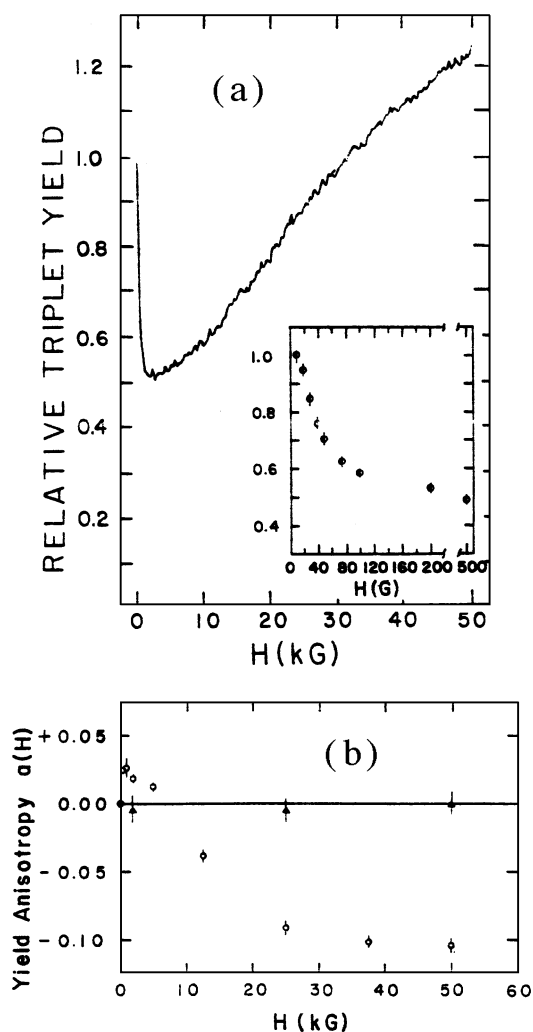


Fig. 15 (a) Relative yields of triplets in quinone-depleted photosynthetic reaction centres; (b) relative yield anisotropy in non-viscous buffer (triangles) and in viscous glycerol/buffer (circles).^{22a} Reproduced from *Ann. Rev. Phys. Chem.*, vol. 34, S. G. Boxer, C. E. D. Chidsey and M. G. Roelofs, 'Magnetic-field effects on reaction yields in the solid-state—an example from photosynthetic reaction centers', pages 389–417, copyright 1983, with permission from *Annual Reviews*.

fall and the high field rise in yield were ascribed to hyperfine interaction and the difference in g -value between the two ions, respectively. Later it was found that the electron–electron dipolar interaction was also involved. Increasing the viscosity slows rotation of the centres (the relative position of the radical ions is fixed) and the quantum yield becomes anisotropic (Fig. 15b). The change in sign is very striking, clearly demonstrating that two different effects are involved.

5.2 Enzyme reactions

MFEs have been demonstrated for enzyme reactions which require co-factors related to vitamin B₁₂, cyanocobal(III)amin: the field dependence shows that an RP mechanism is involved. There is a number of such reactions and a theoretical study of the possible LFE has been made.⁵ Grissom has reviewed his detailed experimental work on the B₁₂ systems^{23a} and concludes that those important for human health will be insensitive to magnetic field; he also surveys the possibility of MFEs on other enzyme reactions. Fig. 16 shows some of his later work on

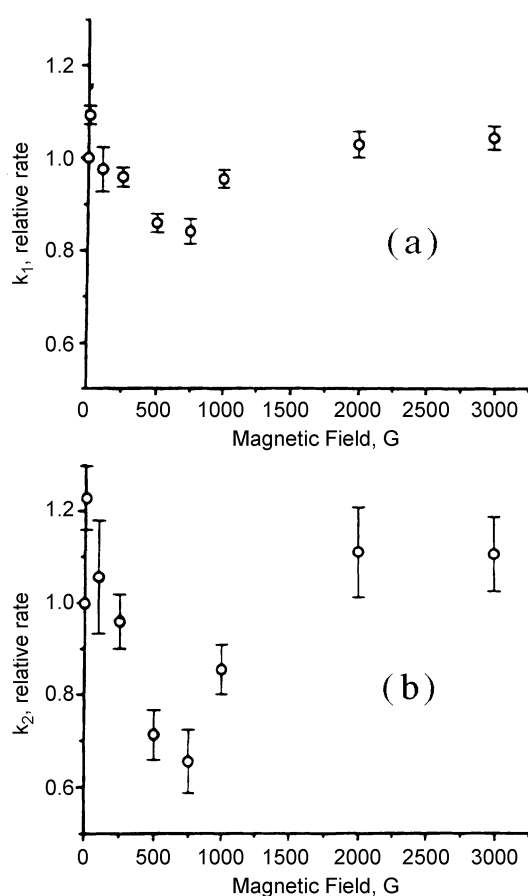


Fig. 16 Field dependence of fitted rate constants of the two stages of reduction of horseradish peroxidase after oxidation.^{23b} Reproduced from *J. Am. Chem. Soc.*, vol. 119, M. B. Taraban, T. V. Leshina, M. A. Anderson and C. B. Grissom, 'Magnetic Field Dependence of Electron Transfer and the Role of Electron Spin in Heme Enzymes: Horseradish Peroxidase', pages 5768–5769, copyright 1997, with permission from the American Chemical Society.

horseradish peroxidase,^{23b} one of a family of haem-containing enzymes; again, these are *in vitro* experiments. The central iron atom is first oxidized with hydrogen peroxide and then reduced back in two stages by an enolate which forms a radical; fitting to a kinetic model shows that both steps have similar field dependences, though details of the radical pair step are not yet known; both hyperfine interactions and Δg effects are involved as expected from the EPR data of the haem and the oxy-radical;

notably there is evidence for an LFE (the high points at left almost on the axis are at 10 gauss).

6 Hazards of environmental fields

The rise in prosperity in the industrial nations has been paralleled by increases in the incidence of a number of illnesses.^{24–28} The use of electricity has been put forward as a possible cause. Effects might be direct, involving chemical processes, or indirect, *via* some synergism with hazardous materials such as carcinogens. Physicists have pointed to ionisation of the air below power lines and its ability to concentrate radon decay products and chemical carcinogens.²⁴ Another hypothesis is that 'light at night' (LAN) interferes with circadian rhythms and so reduces the production of melatonin in the pineal gland; this hormone may prevent the development of cancer cells.²⁵ These concerns have led to a great deal of research, which can be roughly classified as epidemiological, empirical (laboratory work on animals or biological materials) and chemical.

6.1 Epidemiological studies

If it occurs at all, EM field-induced damage to human health is not a common process, so statistical work is particularly important. Exposure varies widely from place to place and from time to time, so studies of electrical workers are of special interest: women are few in this profession, but evidence has been reported for a higher level of breast cancer among *male* workers.²⁵ Most work has been devoted to childhood cancers, especially acute lymphoblastic leukaemia, which has been the subject of legal actions. Early surveys appeared to show slight correlations, not statistically significant individually but mostly in the positive direction. Later studies have not confirmed an effect. A great effort went into the UK Childhood Cancer Study of all cancer types in Britain over seven years; 350 people including Sir Richard Doll (who first associated lung cancer with smoking) contributed to the report;²⁶ it found no evidence of association for average fields < 0.4 μ T, in agreement with similar work in other countries. Numbers of cases exposed to higher fields were too few for definite conclusions to be drawn.

6.2 Biological systems—low fields

A great variety of work on biological materials²⁷ has produced many claims, but no clearcut pattern has emerged and attempts to reproduce results in other laboratories are often unsuccessful. Work with typical environmental fields on biological systems is very difficult and researchers tend not to report negative results. Regarding LAN, there are reports that induction of tumours in laboratory animals by chemical carcinogens is speeded up both by exposure to light and to EM fields;²⁵ again these are controversial.

6.3 Chemical studies

An alternative approach is to start from known or proposed effects on chemical reactions. Among many suggestions only the RP mechanism is well-established but it is not yet clear whether it is relevant to human biology.²⁸ There is also the question of the direction of the effect: a visit to a pharmacy will suggest that radicals are harmful and this assumption is adopted here though it is not always true.²⁹ Where radicals are useful the following arguments should be reversed.

Two cases arise: (a) two radicals generated by radiation or light or as byproducts encounter at random, reacting if they are

singlets, the remaining 75% triplets unable to react at once; (b) in some specific process involving temporary formation of RPs from a singlet precursor, decay into a triplet state enhances the escape of radicals. Case (a) must involve the normal or high field effect which hinders triplet to singlet conversion; for (b) singlet to triplet must be enhanced (increasing the escape of radicals)—the LFE. Case (a), sometimes at least, will occur in unconfined surroundings where encounters will be short-lived and the MFE very small at low fields, especially compared to the 25% of singlet encounters. Case (b) looks more likely: the effects are larger, pairs are more likely to be constrained but small fields need very long times; that implies constrained systems where anisotropy effects may reduce the magnitude of the LFEs.

However, chemists should remember that biological systems are full of surprises. Reaction mechanisms are far from simple and it is possible that very small effects can be amplified. Only static fields have been considered so far: while oscillating fields (up to 1 MHz) are not likely to affect the chemical process, it has been proposed that the complexity of enzyme kinetics could lead to considerable amplification.³⁰ At higher frequencies (microwaves), absorption of radiation among the spin states can interconvert singlet and triplet levels; this phenomenon is familiar in strong fields (optically detected magnetic resonance) but observations at zero or low field have only been made very recently.³¹

Laboratory work has only demonstrated effects of fields down to ~ 0.1 mT. Provided the radical lifetimes are long enough similar effects at lower fields are possible and numerical calculations have been used to investigate them in more detail.⁴ It must be remembered that fields of ~ 10 μ T correspond to spin evolution times of several μ s. Only in a few cases are spin relaxation times equal to or much longer than this and those of reactive oxygen species, common causes of biological damage, are generally much less. Finally, true zero field is irrelevant in nature because of the geomagnetic field and local fields in an organism. For this reason, bumps or resonances are of special interest.

6.4 Conclusions

One certain conclusion is that effects of exposure to fields are not proportional to field strength; those of us who have experienced MRI scans can be thankful for that, because they may require some 20 minutes exposure to fields of a few T which are quite strongly modulated. Fields due to electrical equipment which affect the population at large are very small, usually smaller than the geomagnetic field, but oscillating at 50 Hz; data can be found in the reviews.^{27,32} Field strengths are rarely proportional to power because of cancellations due to the wiring type; often they are larger for electrical gadgets than for mains cables. Clearly much more work is needed. One might well conclude that small fields cannot possibly be dangerous but one must not forget that birds navigate using the geomagnetic field (0.05 mT) and many other organisms use it to aid orientation.^{33–35}

7 Animal orientation and navigation

The commonest magnetic material found on the earth's surface is magnetite. The magnetic interactions between iron atoms are such that small crystals, between 0.05 and 1 μ m in length, consist of single domains³⁴ if needle-shaped; all the spins are oriented the same way and they produce strong fields for their size; multiple domains are more stable in larger crystals and fields largely cancel out. Many organisms, including fish³⁵ and some bacteria (including those claimed to come from Mars), use magnetite crystals to orient themselves in the geomagnetic field;

remarkably they always synthesize crystals below the single domain limit. However, this is not the whole story: some organisms need light for navigation using magnetic fields;³³ in newts, the detectors are in the pineal gland, in birds, in the eye.

A plausible mechanism for the avian compass must provide large changes with orientation and account for its properties: (i) birds cannot detect the polarity of the field but distinguish north/south using the inclination. Their sensitivity is extraordinary: Fig. 17 shows recent observations on captive birds taken to sites

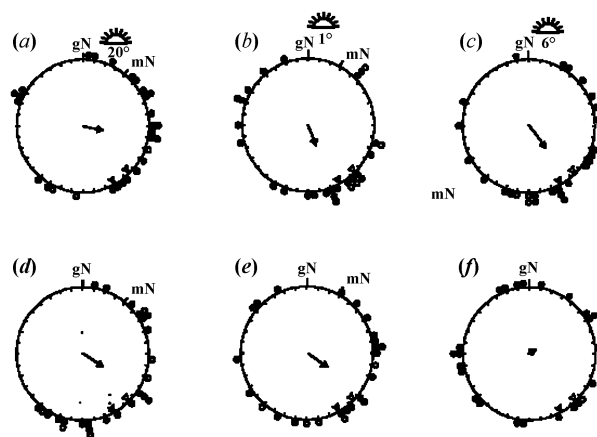


Fig. 17 Take-off orientations of white-crowned sparrows in Arctic Canada: gN and mN mark directions of geographic and magnetic north; (a–c) under natural clear skies, (d–f) under simulated overcast sky; magnetic inclinations —(a,b) 87.1° , (b,e) 88.6° , (c,f) 89.7° . Arrows mark mean orientations.³⁶ Reproduced from Proc. R. Soc. London, Ser. B, vol. 268, S. Åkesson, J. Morin, R. Muheim and U. Ottosson 'Avian orientation at steep angles of inclination: experiments with migratory white-crowned sparrows at the magnetic North Pole', pages 1907–1913, copyright 2001, with permission from The Royal Society.

in the Arctic;³⁶ navigation at the magnetic north pole is impossible of course but birds moved to sites very close to it, where the inclination is 1.4° from the vertical, can still locate their migration direction. (ii) Their response is quite sharply tuned to the strength of the field though they are able to adapt to artificial changes. (iii) The involvement with light is demonstrated by wavelength effects; birds utilise the earth's field if exposed to white, blue or green light but not to red; salamanders use red too. Natural magnets such as magnetite do not readily explain features (i) and (iii); the latter in particular led Schulzen to postulate a RP mechanism.³⁷ In this case, hyperfine anisotropy must be involved, and the RP would probably consist of fixed radical ions formed by charge transfer. Since light detection in the eye is highly developed one might postulate ionisation of rhodopsin itself, but rods can rotate about their long axis; recent work on cryptochromes suggests they are more likely candidates.³⁷ Field effects on electrical signals from the optic nerve have been detected³⁸ but the full range of physical techniques has not yet been applied to this.

8 Future developments

In 1976, Peter Atkins wrote in *Chemistry in Britain*,³⁹ 'The study of the effects of magnetic fields on chemical reactions has long been a romping ground for charlatans'. Outside chemistry this is still true though some claims (dowsing?) may yet be correct and there can be no doubt about bird navigation. In the early '70s, work on MFEs on radical pairs had just begun. Now the study of RPs is well-developed though the applications are not fully exploited, partly because of CIDEP and CIDNP; these are powerful techniques for spectroscopy but MFEs have many uses as I have hoped to show. Much more can be done: more practical use could be made of magnetic isotopes⁴⁰ and field

variations; biologists might do well to use stronger fields, a few mT rather than μT initially. Chemists need to put more effort into studying resonances. Finally the great advantage of MFEs is simplicity: strong or well-defined fields are not needed; any magnet will do!

9 Acknowledgments

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