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High resolution studies of the effects of magnetic fields on chemical reactions

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A simple and inexpensive experiment is described which detects magnetic field effects on chemical reactions with high signal-to-noise ratio and high resolution. It consists in applying a small modulation field to the sample, whilst the main field it experiences is varied, with optical detection at the modulation frequency. It consequently measures the derivative of the normal MARY spectrum. It is shown by theoretical analysis that when using this method it is better to monitor reaction intermediates than products. The method is demonstrated by application to known systems in which additional features are sometimes observed, in particular a low-field feature which is shown to vary as electron hopping occurs. MARY spectra obtained using modulated light excitation of the sample and pulsed excitation with laser-induced fluorescence detection are provided for comparison. The method represents a general technique for studying field effects in systems containing low stationary state concentrations of radicals, produced by any method.

1. Introduction

Even quite small magnetic fields may affect chemical reactions, particularly those involving free radicals [1–3]. In thermal and photochemical reactions radicals are invariably produced in pairs by reaction with spin conservation, so that the pair is created with the overall electron spin multiplicity of its molecular precursors. This spin-correlated radical pair (RP) is a reaction intermediate which exists briefly before its members subsequently react or diffuse apart. What occurs within it controls the amount of geminate product formed, and the concentration of free radicals escaping the geminate cage. It has been observed directly using flash-photolysis electron spin resonance [4, 5] and radical yield detected magnetic resonance (RYDMR) [6, 7]. However its presence can be inferred, and the geminate reaction manipulated, simply by studying the magnetic field dependence of the chemical reaction yield, the MARY pheonomenon [8].

The origin of MARY effects lies in the fact that the spin state of the RP evolves in time under the influence of different local magnetic fields at the two electrons of the pair. A triplet (T)-born pair, for example, acquires singlet (S) character in time; the S–T mixing is not instantaneous and the radicals separate before re-encountering at a later time, when they may react. The field-difference originates either in the Zeeman interaction with the applied field, the radicals in general having

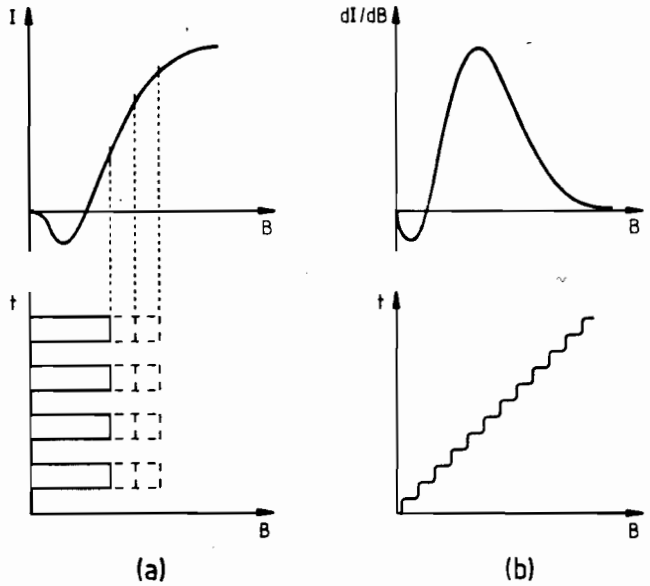


Figure 1. Two different strategies for observing MARY effects in magnetic-modulation experiments. (*a*) square-wave modulation of the total field as its amplitude is increased progressively yields the normal MARY curve directly, I being an absorption or fluorescence intensity monitored in the experiment. (*b*) sinusoidal modulation at small depth whilst the field is varied linearly gives the field-derivative of the spectrum shown in (*a*). The MARY effect depicted is for a system dominated by hyperfine state mixing, and shows a saturation characteristic; some systems also display a low-field feature of opposite phase, as shown.

different g values (of difference magnitude Δg), or in local hyperfine fields. At low fields the hyperfine interaction dominates and mixes all of the radical pair states S, T_0 and $T_{\pm 1}$. $S/T_{\pm 1}$ mixing is however suppressed in a field which is much greater than the hyperfine interaction. When this is so the field effect shows saturation characteristics, as illustrated in figure 1, and may be characterized by the value $B_{1/2}$ at which the effect reaches half of its saturation limit. In high fields the Δg effect becomes dominant but it mixes only the S and T_0 Zeeman states of the RP. If Δg processes control the overall behaviour, or if incoherent spin-relaxation competes with the coherent spin evolution in the RP, saturation behaviour is not observed.

A further characteristic of the field effect is that, as shown in figure 1, it is expected to exhibit a low-field feature of opposite phase to that observed at higher field; this has been reported rarely in experimental studies [9–11]. It can arise in two ways. Firstly, hyperfine-induced $T \rightarrow S$ spin evolution is a coherent process characterised by a spectrum of frequencies corresponding to differences between the eigenlevels of the system. Any accidental regular spacing favours a short $T \rightarrow S \rightarrow T$ recurrence time, and the singlet spin correlation is maintained for a relatively short period only. A small magnetic field may distort this regular spacing and increase the recurrence time, so that the kinetic consequences of hyperfine-induced mixing become more pronounced at low fields than in zero field. Secondly, S and T_{-1} hyperfine levels may become degenerate when the magnetic interaction equals the electron exchange energy $J(r)$ between the radicals in the pair, resulting in further mixing. This has been observed in chemically-linked radical pairs [9, 12] and would be interesting to confirm in freely-diffusing ones where information on the diffusional trajectories might result.

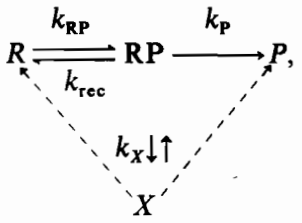
All the methods developed to study chemical kinetics may be used in MARY studies. At simplest, product yield analysis as a function of field strength represents a tedious and imprecise method, since often small changes are sought in an overall high yield. An improvement is to monitor stationary concentrations of reactants or products in a flow system [13]. In many reactions transient free radicals, triplets or excited singlets react to regenerate reactants with little overall product formation, and here the transients have been produced by pulsed laser excitation and MARY effects monitored using absorption spectroscopy or laser-induced fluorescence. If continuous irradiation is used the steady-state intermediate concentrations are very low but MARY studies have been made observing the radioluminescence [14] and photoluminescence [15, 16] produced by recombination of radical-ion pairs. A more general method using any detection technique is to modulate the formation of transients and to detect then in synchrony using phase-sensitive ('lock-in') detectors. This method is attractive for it can be applied in principle to any system, including thermal ones in which radicals occur, and opens the possibility, for example, of MARY studies in biological systems.

The MARY phenomenon offers an unusual opportunity for this type of experiment in that the stationary-state concentration can be varied by modulating the applied magnetic field. At its crudest, variation of the field at some modulation depth is formally equivalent to modulating the light source. To obtain the MARY spectrum, the variation in the signal observed as the intensity of the field is changed, various modulation strategies may be employed. Nath and Chowdhury [16] modulated the entire field sinusoidally and detected at twice the modulation frequency. The theoretical justification for this seems not to have been published although simple considerations suggest that any even harmonics would be suitable for detection. Square wave modulation of the total applied field as its magnitude is scanned (figure 1 (*a*)) has been used by Bube *et al.* [17], and yields the field-effect directly; a disadvantage is that the maximum modulation frequency is limited if the total field is to be changed.

A final method, which has inherently higher resolution than the above techniques and which permits optimisation of the signal-to-noise (S/N) ratio by proper choice of modulation frequency, is our subject here, and is analogous to modulation techniques used in spectroscopy to observe comparatively wide spectral lines. It consists of a sinusoidal modulation of low amplitude which is superimposed on a magnetic field ramp which is increased linearly at a rate of change much slower than used in the above experiments (figure 1 (*b*)). Phase-sensitive detection of the signal then yields the first derivative of the MARY spectrum. This makes the experiment particularly sensitive for observing changes of slope in the MARY spectrum, due possibly to changes in the origin of the magnetic field effect as the field is changed, and for investigating the low-field inversion feature. A further advantage is a high S/N, permitting investigations of systems which involve low radical concentrations. It has been applied once previously, by Frankevich [18], in a study of a very weak field effect in a luminol solution. Here we demonstrate the technique and analyse it in some detail as an efficient, and inexpensive, method for MARY spectroscopy.

2. Theory of the experiment

We discuss the application of MARY spectroscopy to chemical systems in terms of the generalized reaction scheme



where R and P are the reactants and products and X is an intermediate other than the geminate radical pair (RP). The RP is formed by thermal, photochemical or enzymatic processes with a rate constant k_{RP} and decays by recombination to R (rate constant k_{rec}), formation of diamagnetic product (P) (rate constant k_p) or transformation to an observable intermediate X (rate constant k_X). X may be a luminescent exciplex, an excited triplet state, a free radical or even a diamagnetic intermediate; it returns to the ground state R, may regenerate a new RP, or reacts to form products. All of the decay processes involving the RP are potentially field-dependent.

Normally product formation implies some irreversibility and long-term stationary conditions are attainable only in a flowing system where the stationary concentrations of any of the above species may be modulated. It is usually their average concentration within a flow cell which can be measured, although absolute reactant and product concentration changes can be measured at the outflow. The concentrations within the cell depend upon the amount of R introduced, the effective overall reaction rate constant and the average time that the solution spends within the cell. By choosing a modulation period $\tau_M \ll \Delta\tau_V < \bar{\tau}_V$, where $\bar{\tau}_V$ is the mean of the residence time of individual volume elements in the cell and $\Delta\tau_V$ its variance, the modulation of $[P]$ is strongly averaged out and not readily detectable. This is also true for $[R]$ if the average stationary concentration of radicals and intermediates $([RP] + [X])_{st}$ is smaller than the overall irreversible product formation, $\Delta[P]$. In the other extreme the modulation of $[R]$ follows that of the sum of the concentrations of the intermediates; this is completely reversible behaviour and flow is unnecessary.

We now consider the effect of magnetic modulation of $[RP]$ and $[X]$. The situation differs fundamentally from normal photolysis modulation experiments in which the rate of formation of the intermediates is varied; here it is one or more of their decay constants which is modulated. In the limiting case when the modulation frequency $\omega_m(=\tau_M^{-1}) \ll \tau_{RP}^{-1}$, the RP lifetime inverse, the stationary concentration is always in phase with the modulation and is given by

$$[RP] = k_P/(k_{rec} + k_X + k_P). \tag{1}$$

This is normally so since geminate radical pairs decay on the submicrosecond timescale whilst usually $\omega_m < 1$ KHz. With the highest radical concentrations available in irradiation using a cw laser beam, and with the assumption that the rate constants are not strongly field-dependent, this implies that $[RP] \leqslant 10^{-10}$ M, and the figure would be lower in thermal and enzyme reactions. It is not profitable in consequence to attempt to detect the RP directly in normal solutions.

However the situation is more favourable for observing the intermediate X. If this is formed in a luminescent state it can often be detected at a stationary concentration as low as that of the geminate RP. Otherwise if, as is usual, its lifetime $\tau_X \gg \tau_{RP}$, then its steady state concentration increases to about $(\tau_X/\tau_{RP})[RP]_{st}$. The

formation rate of X is given by

$$\left(\frac{d[X]}{dt}\right)_{\text{formation}} = k_X[RP], \tag{2}$$

and if k_X is field-independent, the rate of production will be modulated in phase with $[RP]$. This varies as

$$[RP]_t = [RP]_{st} + A_{RP} \cos(\omega_m t), \tag{3}$$

where A_{RP} is a proportionality constant. The concentration of $[X]$ varies at this frequency but with a phase-lag:

$$[X]_t = [X]_{st} + A_X \cos(\omega_m t + \phi) \tag{4}$$

where

$$[X]_{st} = \tau_X k_X [RP]_{st}, \tag{5}$$

$$A_X = k_X A_{RP} (\omega_m^2 + \tau_X^{-2})^{-1/2} \tag{6}$$

and

$$\tan \phi = -\tau_X \omega_m. \tag{7}$$

These are familiar relationships in modulation spectroscopy. When $\omega_m \ll \tau_X^{-1}$ the phase-shift ϕ is zero and $[X]$ and $[RP]$ vary together. As ω_m is increased ϕ increases and the modulation depth of $[X]$ decreases. In the limit no modulation is observed when $\omega_m \gg \tau_X^{-1}$ and $\phi \to -\pi/2$.

When k_X is itself field-dependent it too is modulated in time:

$$k_X = \bar{k}_X + A_k \cos(\omega_m t), \tag{8}$$

and,

$$\left(\frac{d[X]}{dt}\right)_{\text{formation}} = \bar{k}_X[RP] + (\bar{k}_X A_{RP} + [RP]_{st} A_k) \cos(\omega_m t) + A_{RP} A_k \cos^2(\omega_m t). \tag{9}$$

In consequence the rate of formation of the intermediate X varies at the modulation frequency ω_m in any situation and provides a convenient monitor of the effects of the field on the primary stages of the reaction. The final term in equation (9) represents oscillation at $2\omega_m$ and can be neglected to first order.

In conclusion, MARY effects in chemical reactions are most sensibly sought by observing an intermediate, X. If this is not produced in a luminescent state, the application of the magnetic modulation MARY technique depends critically upon its concentration accumulating in time to a stationary state value in excess of the radical pair concentration. This is normally the situation in chemical reactions. The intermediate should satisfy the lifetime conditions

$$\tau_{RP} \ll \tau_X \leqslant \tau_M < \tau_V, \tag{10}$$

the latter two of which can be varied experimentally over quite wide ranges. There is no restriction as to the nature of X, although free radicals are usually very suitable since their solution lifetime is often in the millisecond region; any convenient diamagnetic intermediate may also be usable. Although we have emphasized applications in the general case, the modulation technique is applicable, of course, to luminescent intermediates too.

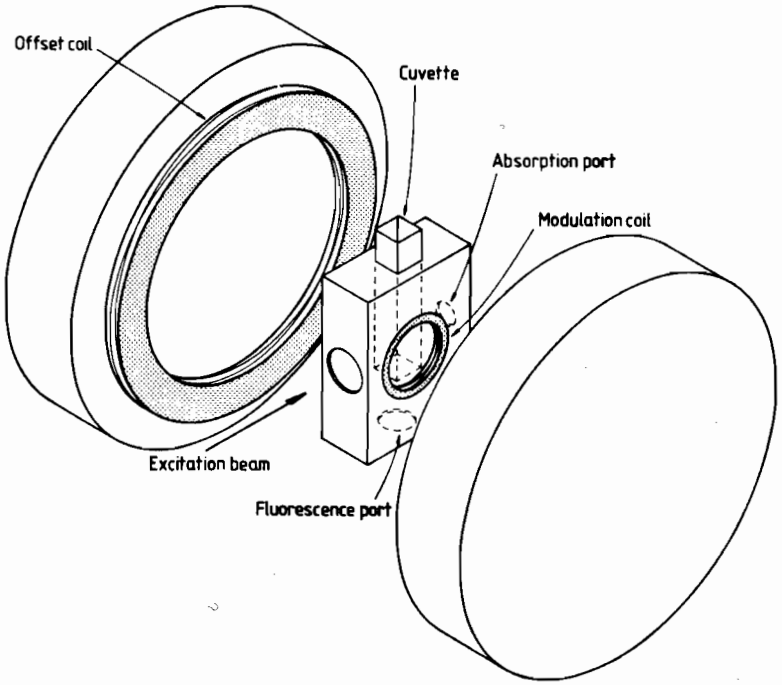


Figure 2. The irradiation cell sits within a thermal block drilled with light ports for excitation and for observation of absorbance (in line with the excitation port) and fluorescence (perpendicular to it). The modulation field is applied via coils recessed into the block whilst the whole is held within the pole caps of an electromagnet.

One important potential application of magnetic field studies involves enzymes, many of which are suspected to react via radical intermediates although often no free radicals appear. Rather radical-pair-like enzyme-bound states are often postulated as intermediates. The detection of any intermediate between the radical-pair type state and the eventual product of the reaction may be useful for probing MARY effects. The optimum condition would occur if the enzymatic reaction was fast enough to yield a considerable reaction turnover during the flow through the observation cell. The low stationary-state concentrations of radical pair intermediates militate against their direct observation, and pulsed methods cannot be applied to normal enzyme reactions. Furthermore only the magnetically-modulated MARY technique is specific, amongst general modulation techniques, to the existence of the radical pair state. The work reported here is an intermediate stage in proceeding to studies of such systems (although preliminary results have been obtained). These have potential use in mechanistic work and in assessing the effects on biological systems of exposure to magnetic fields, particularly in the low-field regime.

3. Experimental

In this section we describe a simple apparatus which may be used to detect field-modulated MARY effects, according to the scheme shown in figure 1 (*b*), via measurements of fluorescence from an intermediate or by its absorption at a specific wavelength. A standard UV flow-cuvette holds the solution within a sample block designed both to minimise stray light, whilst allowing excitation and detection, and to provide thermal stability, figure 2. The sides of the holder are recessed and hold

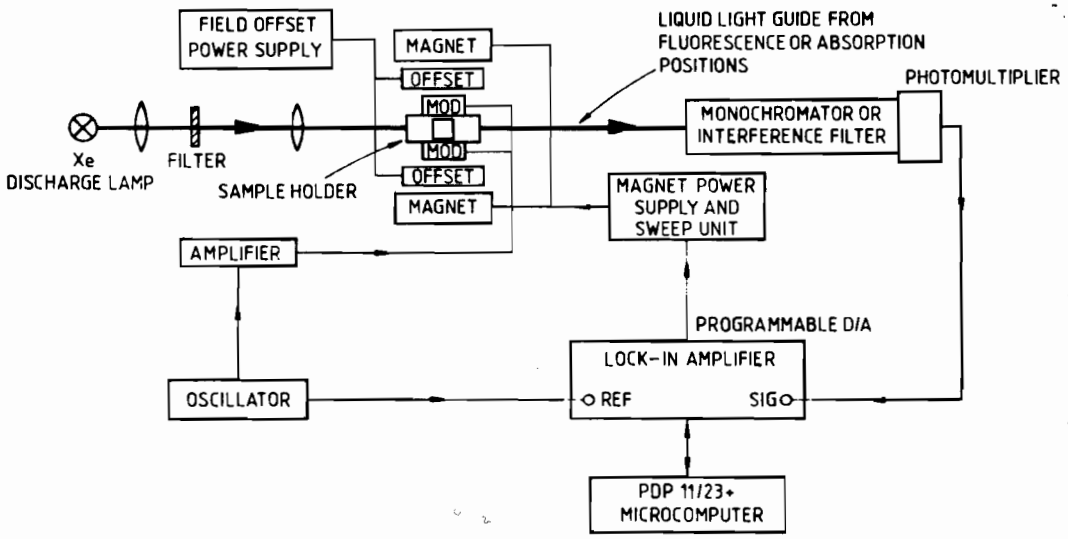


Figure 3. A block diagram of the whole apparatus, described in the text.

the coils via which the modulation is applied, with the excitation light beam focused to yield radicals close to the axis of the Helmholtz pair. The whole device is held within the field of a small electromagnet.

The overall apparatus is shown in figure 3. Light from a 150 watt high pressure xenon discharge lamp is collimated and, for the fluorescence measurements, passed through a UV bandpass filter (usually centred at 340 nm) before being focused onto the sample. A liquid light guide is plugged into one of two light exit ports to select absorbance or fluorescence measurements, and the light is conducted either to a monochromator or to selected interference filters before falling on an IP28 photomultiplier tube. Its output is applied to a Stanford Research Ltd. SR 510 phase-sensitive detector which is fed with a reference signal from the oscillator which supplies current to the modulation coils via an amplifier. The detected signal is stored in a dedicated microcomputer (PDP 11/23+) which also controls the variation of the applied magnetic field via a programmable D/A converter on the phase-sensitive detector; the size of the field step between each measurement is computer-controlled; stepping the field allows optimisation of the time constant of the detector. The converter feeds a power supply and ramp generator with which a full field sweep of 0–2·5 kG can be obtained, although most experiments involve smaller ones. The computer also controls the detector settings.

Modulation frequencies in the range 200–700 Hz were used, induction degrading the wave-form at higher frequencies, and an amplitude of up to 20 G was obtainable. As ever in a modulation experiment, this needed careful adjustment to avoid modulation broadening of spectral features.

To define the field zero of an experiment accurately a third magnetic field was applied to the sample, one which was in the opposite sense to the main field. This allowed field sweeps through zero, starting at fields down to -70 G; a true modulated MARY feature possesses inversion symmetry about the zero since the unmodulated characteristic would be related about zero by a plane of symmetry. The magnetic field magnitudes were measured using a commercial Hall effect probe.

To test the superiority of magnetic-field modulation in MARY experiments as compared with photolysis-modulation methods, and to provide a calibration of the

effects observed, some experiments were performed using a mechanical chopper placed within the photolysis beam, with light modulation frequencies up to 250 ± 2 Hz, no field modulation, and using the same settings of filters etc. on the phase-sensitive detector as in the above experiment. This was possible for the fluorescence experiments only. It allows, for example, the zero-field concentration of the excited species to be monitored, although the signal may contain a background contribution from the solvent. This information is necessary since the field-modulated experiment measures the first derivative of the change in concentration with applied field only. By using identical optical pathways and components, together with accurately reproduced reference and photomultiplier voltages, the magnitude of the field effect can be calculated from the relation

$$\text{Per cent field effect} = \frac{\int_0^B (dI/dB)\, dB}{(I_{zf} - I_s)} \times 100 \approx \frac{\int_0^B (I_{mod}/B_{mod})\, dB}{(I_{zf} - I_s)} \times 100. \quad (11)$$

Here (dI/dB) is the intensity change with field and is measured as the ratio of the lock-in output I_{mod} to the field modulation amplitude B_{mod}. I_{zf} is the absolute intensity observed in the light-modulated experiment from the solution held at zero-field and I_s is the background signal from the solvent, usually measurable with limited accuracy in a separate experiment on the pure solvent. Band overlap between intermediate and solvent spectral features constitutes a further source of error.

Similar, but worse, problems are encountered in a pulsed MARY experiment which we have used also for comparison purposes; it is based upon one we described previously [11] but this has been changed greatly in detail and will be the subject of a forthcoming paper. This experiment involves observation of laser-induced fluorescence from radicals produced in excimer laser flashes, which occur alternately with the magnetic field turned on and off. The laser-induced signal is recorded on a fast home-built transient recorder consisting of a close-coupled 250 MHz oscilloscope and video camera enhanced with an image-intensifier; the information from each raster scan is digitized and stored using a dedicated microcomputer. The experiment is repeated at several Hz to allow signal averaging. To improve S/N further it is the integrated areas, A, of the ca. 5 nanoseconds fluorescence pulses which are measured and compared in the field-on and field-off situations. With an obvious nomenclature, here

$$\text{Per cent field effect} = \frac{(A_{off} + A_s) - (A_{on} + A_s)}{(A_{off} + A_s)} \times 100, \quad (12)$$

with a background signal, A_s, included as before. Comparison with the result from the modulation experiment, equation (11), shows that the effect of the background contribution should be to cause the field effects to appear larger in that case than in the pulsed experiment. The background signal can be measured reasonably accurately in the modulation experiment, but it cannot be measured in real time in the pulsed one.

4. Results and discussion

MARY effects are enhanced if the lifetime of the spin-correlated radical pair is prolonged (up to a certain level) or if radical re-encounter probabilities can be

Figure 4. A field-modulated MARY spectrum of an acetophenone/dimethylaniline mixture in a micellar solution observed in absorbance; the vertical axis is in arbitrary units.

increased after a requisite amount of S–T mixing has occurred. Two experimental situations have consequently been investigated in detail: radicals in micellar solution and systems involving exciplexes, in which the Coulombic attraction tends to keep the charged species together. We illustrate our method with examples of each. In no case did the sample flow.

In figure 4 is shown the field-modulated MARY spectrum observed by monitoring the intermediate ketyl radical in absorption at 475 nm during the irradiation of a solution consisting of 0·01 M acetophenone and 0·01 M dimethylaniline in 0·1 M sodium dodecyl sulphate in aqueous solution at room temperature; this is basically a well-known system [19]. The spectrum was obtained with a field modulation of 10 G, to optimize S/N without distorting the peak, and is the average of five separate experiments on the same solution. It consists of a single broad peak, there being no discernible low-field feature, and at first sight seems to represent the behaviour shown in figure 1(*b*) in which the spectrum corresponds to a system dominated by S–T mixing from the hyperfine mechanism. However closer inspection shows that this is not so. In the first place, the signal does not return to zero at the higher magnetic field values shown, implying that the unmodulated MARY spectrum does not show saturation behaviour. Secondly the peak occurs at 27 ± 2 G, a considerably different value from the $B_{1/2}$ value calculated for the radical pair concerned (49·6 G). This accentuates the important point that the modulation experiment detects the point of inflexion in the MARY spectrum rather sensitively, and this equals the calculated $B_{1/2}$ value only if a single mechanism of spin-mixing is involved. The method has considerable potential for detecting the contribution from different mechanisms.

We now turn to systems involving exciplexes, initially that involving pyrene (Py) and dimethylaniline (DMA) [16, 20–22]. In figure 5(*a*) is shown the spectrum obtained from observation of fluorescence at 550 nm from a 6×10^{-3} M solution of

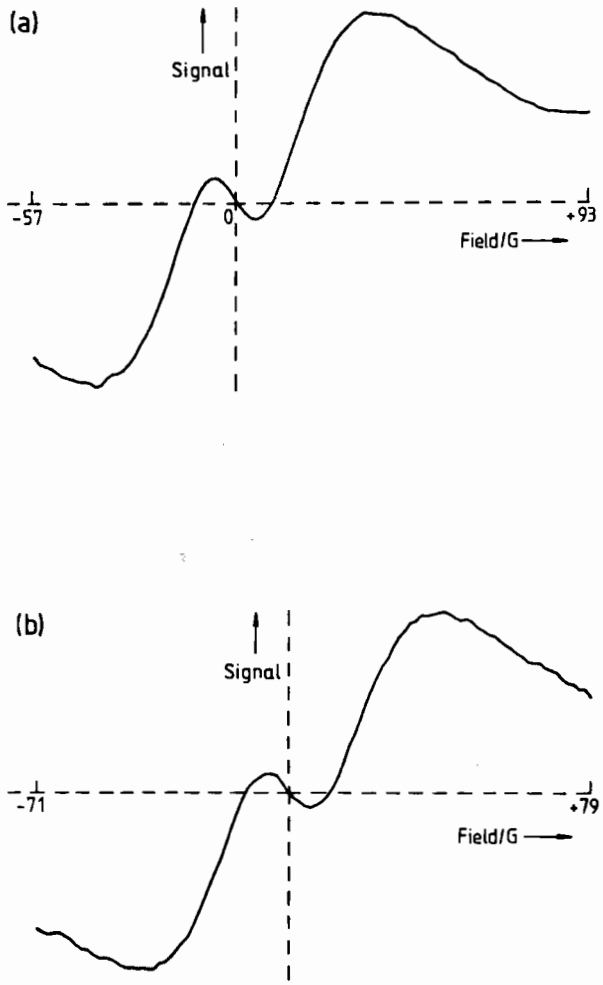


Figure 5. Field-modulated MARY spectra from exciplex fluorescence in the pyrene-dimethylaniline system (*a*) in a cyclohexanol/methanol mixture and (*b*) in pure methanol. Here the field sweep starts from strongly reversed values and the spectrum has inversion symmetry about the zero-field position; the vertical scale is arbitrary. A pronounced low-field feature is evident.

Py with 6×10^{-2} M DMA in a 7 : 3 cyclohexanol : methanol mixture by volume, using a modulation depth of 20 G. The conditions were chosen to optimise S/N and the diagram is of a single scan. The field sweep now starts from a reversed field value and the zero-field position can be identified via the inversion symmetry of the effect about it. The most notable feature is now a very clearly defined period in which the signal at low absolute field values is opposite in sign to that at higher ones; its origins were indicated in the introduction. The experiment detects two points of inflexion, with the signal passing through zero at the minimum of the unmodulated MARY spectrum.

Similar behaviour is exhibited in figure 5(*b*), obtained from a 10^{-4} M solution of Py in the presence of 10^{-2} M DMA in methanol alone; here the modulation depth was only 10 G, to avoid distortion of the low-field feature, and the diagram is also of a single scan. The position of the peak maximum in each of these figures (42 G) again does not correspond to the calculated $B_{1/2}$ value of the system (50 G) although

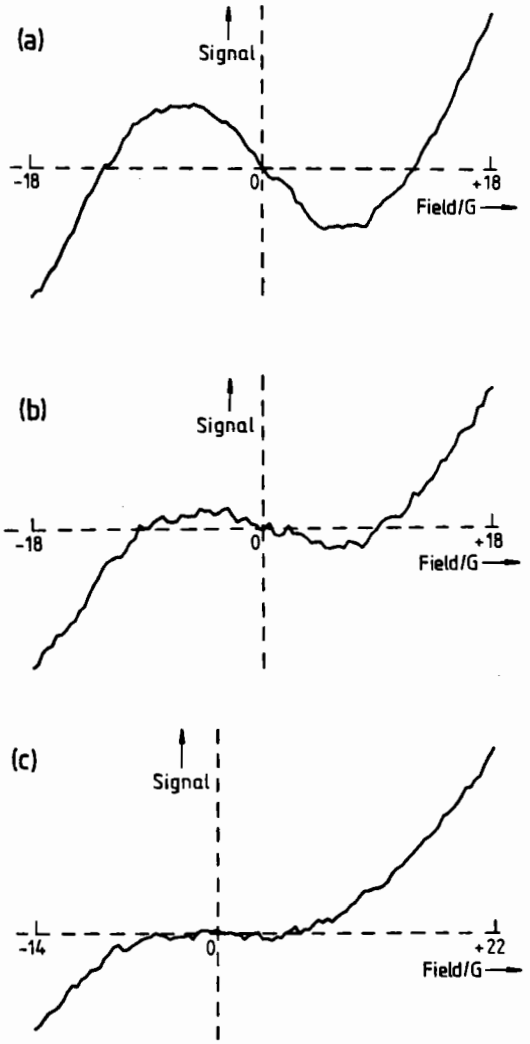


Figure 6. The low-field and field-reversed region of the system depicted in figure 5, investigated under conditions of different DMA concentration whilst keeping the pyrene concentration constant; see the text. The electron transfer rate increases from (*a*) to (*c*) and the low-field feature is attenuated.

the signal does return to zero at a field of *ca.* 300 G, above that shown in the figure. The field effect was measured to be 2 per cent in each case.

The concentrations in figure 5(*b*) were chosen to investigate the use of a high-resolution experiment in a system previously reported to be sensitive to electron transfer effects in its MARY behaviour [16, 17]; similar effects have been reported with diethylaniline [23]. In the former study this was deduced by observation of a change in $B_{1/2}$ as transfer occurred whilst in the latter it was inferred from a kinetic analysis. Its origin is that in either chemical or Heisenberg exchange the nuclear hyperfine couplings experienced at each electron in the radical pair are modulated as the electron hops between molecules in which the nuclear states are uncorrelated. Depending upon the rate of exchange this may cause partial averaging of the hyperfine interactions, so as to affect the $B_{1/2}$ observed [21], or direct relaxation effects; both may affect the spin-evolution in the radical pair. We now report the

new observation that the low-field feature in the spectrum is particularly dependent upon this process.

Figures 6(*a*)–(*c*) show the appearance of the modulated MARY spectrum (10 G modulation) about zero field for solutions containing 10^{-4} M Py with (*a*) 10^{-2} M DMA, (*b*) 6×10^{-2} M DMA, and (*c*) 10^{-1} M DMA. The full spectra (not shown) exhibit no variation in the intensity of the spectrum in each case and no variation in the position of the peak: any effective change in $\langle B_{1/2} \rangle$ in this concentration range is small. However it is apparent that the low-field feature is observed very clearly in figure 6(*a*), at the lowest DMA concentration and electron exchange rate, and less clearly in figure 6(*b*). At the highest concentration it is highly attenuated. This represents a completely new, and quite sensitive, method for detecting electron hopping between initial molecules and related radical ions present as members of an exciplex pair.

In terms of the origins of the low-field feature discussed in the introduction such behaviour would be expected. Due to electron hopping the spin motion is slower and less coherent [24, 25] and this obviates the low-field effect of decreasing the $T \rightarrow S \rightarrow T$ recurrence time. Also it causes lifetime broadening of the hyperfine levels with the consequence that the field region in which $S - T_{-1}$ level crossing occurs is also broadened, and the phase inversion feature of the low-field MARY spectrum becomes blurred. Both possible origins of the low-field feature are expected to produce qualitatively similar effects and unfortunately cannot be distinguished readily.

Having seen the features and S/N available in the magnetic-field modulated experiment it is interesting to compare them with results obtained using modulation of the light source with no field modulation. Figure 7(*a*) shows the MARY spectrum obtained in fluorescence, as an average of 5 scans, from observation of a solution of 10^{-4} M Py and 6×10^{-2} M DMA in methanol, scanning from -50 to $+250$ G. This was obtained in chopped single-beam mode with detection at the chopping frequency. The S/N can be compared directly with that of figure 5(*b*) in the field-modulated experiment, and the superiority of the latter experiment is evident. In particular the important low-field feature cannot be recognized. Some improvement in S/N in chopped-beam experiments can be achieved by turning to dual-beam methods in which the difference in absorbance between samples inside and outside a

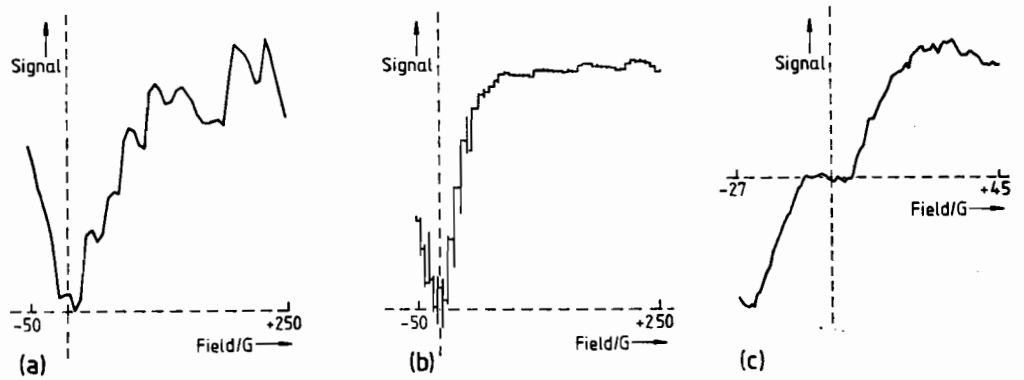


Figure 7. MARY experiments carried out with photolysis-light, rather than field, modulation (*a*) of the pyrene/DMA system in fluorescence using a single beam method and (*b*) of the acetophenone/DMA system in a micelle using a dual beam method. The S/N of both compare badly with the field-modulation results, shown for the second system in (*c*), on an extended field scale. This also demonstrates some structure is present.

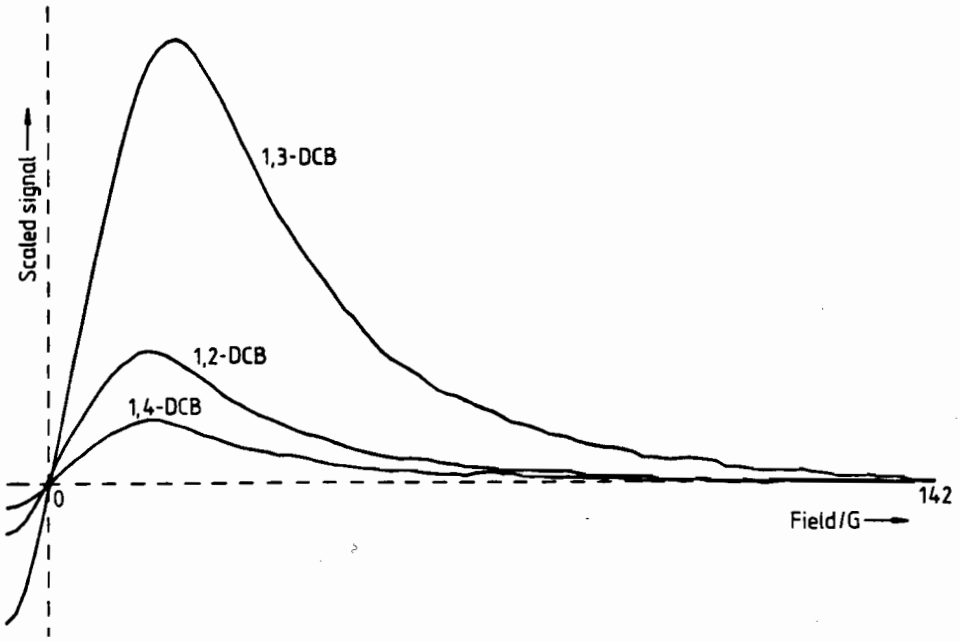


Figure 8. Field-modulated MARY observations of the fluorescence from solutions of pyrene with 1,2-dicyanobenzene, 1,3-dicyanobenzene and 1,4-dicyanobenzene, all sweeps starting from slightly negative values whilst the vertical scale is in the same arbitrary units for each isomer.

magnetic field is measured directly. An example is shown in figure 7(*b*) in which the sample consisted of a solution consisting of 0·01 M acetophenone and 0·01 M DMA in a sodium dodecyl sulphate micellar solution. The S/N on this single scan has been optimised and the field step is coarse to allow long time constants to be used at each field value. Nevertheless the S/N is less than in the much simpler field-modulation experiment and is inadequate to detect any structure which does occur in the curve, as shown in figure 7(*c*).

Finally we turn to a study involving a second exciplex system, pyrene and the isomers of dicyanobenzene (DCB), in which the hyperfine mixing parameters can be changed in a systematic way. We show results from both our modulated and our pulse MARY experiments. These were conducted with $5{\cdot}6 \times 10^{-5}$ M Py and 3×10^{-2} M DCB in a 5 : 3 cyclohexanol : acetonitrile mixture by volume. The modulation experiments were performed with 20 G modulation and the spectra (figure 8) are averages of 5 scans; as before excitation was with a 340 nm pass filter

Isomer	$B_{1/2}$(calc)/G	$B_{1/2}$(obs, mod)/G	$B_{1/2}$(obs, pulse)/G	% Effect
1, 2	17	15	20·6	0·5
1, 3	20	19	27·6	1·7
1, 4	17	15	20·6	0·2

where (26)

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

and

$$B_n = [\Sigma_n a_{nk}^2 I_k(I_k + 1)]^{1/2}, \quad n = 1, 2$$

in the beam whilst a 550 nm broad-band interference filter was placed before the photomultiplier. The spectra from all of the isomers are of the simplest form, showing a single maximum and returning to zero amplitude at the higher fields. The peak positions now occur at the $B_{1/2}$ values calculated from the values of the hyperfine coupling constants [26], as is shown in the table which also lists the sizes of the effects observed.

The direct MARY spectra obtained using our much more complicated pulse experiment are shown in figure 9, normalized to the same intensity in figure 9(*a*) and shown in absolute form in figure 9(*b*). The $B_{1/2}$ values are difficult to obtain due both to the S/N of the observations and to the shape of the signal, and their direct measurement shows some discrepancy with those expected (table). This demonstrates a further advantage of the modulation in that the peak position is better defined; in both experiments calibration of low fields remains difficult.

Both experiments demonstrate that the 1, 2 and 1, 4 isomers have the same $B_{1/2}$ values, as is expected from calculation [26]. However both also show that the

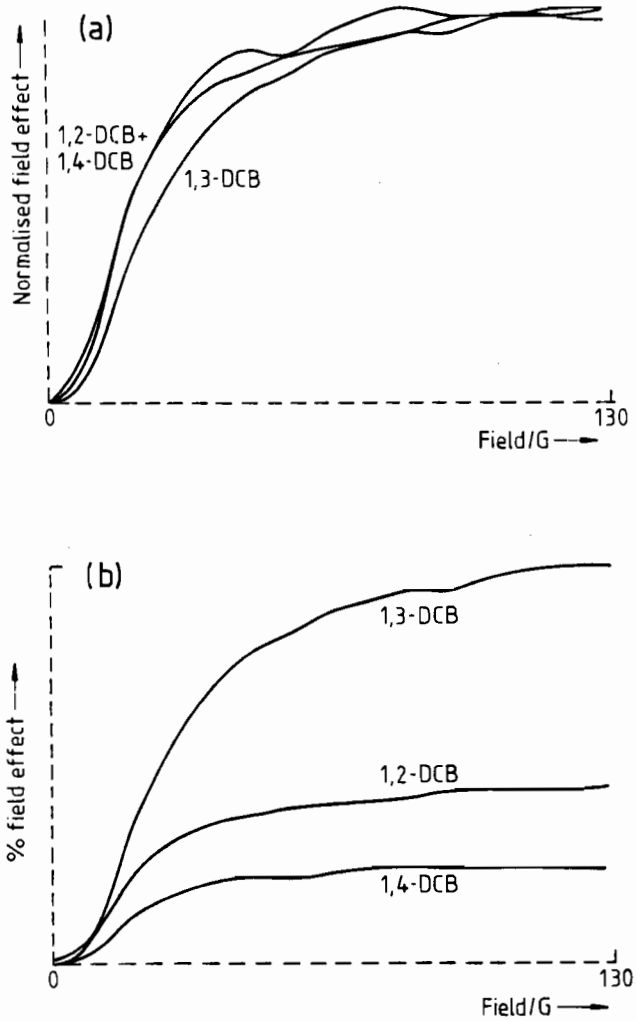


Figure 9. Pulsed MARY experiments using laser-induced fluorescence of the same systems as used in figure 8. (*a*) plotted with the same amplitude to demonstrate that the 1, 2 and 1, 4 isomers have identical $B_{1/2}$ values, different from that for the 1, 3 isomer and (*b*) plotted on an absolute scale.

field-effect of the 1, 2 isomer exceeds that of the 1, 4 one, and this cannot be explained in terms of spin-mixing alone. Here it must be remembered that the effect is influenced also by the molecular diffusion within the geminate cage and the origin of the discrepancy is probably in different interactions within the two different exciplex pairs. The isomer with the largest $B_{1/2}$ value, 1, 3 DCB, does however show the largest effect as would be expected at first sight. In experiments performed on identical solutions the pulse experiments gave slightly lower values for the magnitudes of the effects, as expected (see above).

5. Conclusion

In this paper we have described a little-used method for detecting MARY effects in high S/N and with high resolution. Low-field features whose mere existence has sometimes been questioned have been shown to exist and to be sensitive to the effects of electron transfer. The method appears capable of further development along lines apparent from studying the form of the theoretical equations given above. There appear to be considerable cost and accuracy advantages over previous pulsed experiments and large S/N advantages as compared with light-modulated experiments. The detection of the point of inflexion of the MARY spectrum, which does not necessarily occur at $B_{1/2}$, is of considerable interest.

The method was designed specifically to detect MARY effects in systems in which radicals are observed at stationary-state concentrations rather than being detected in a pulse-correlated fashion. This makes it applicable to thermal and enzymatic reactions as well as photochemical and radiochemical ones. An important consequence of the analysis provided has been to conclude that observations should be made on reaction intermediates, of any nature, rather than on the stable products of the reaction. It has been shown that the characteristic of reactions involving intermediates, that their concentration can be optimised by judicial choice of conditions, can be exploited in detecting MARY effects. This may be of particular importance in enzyme studies.

Above all the experiment is inexpensive and very simple to set up, and it has positive advantages over more complicated ones. What it lacks is the time-resolution which allows the kinetics of very fast processes to be studied in pulse experiments.

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