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Second generation of magnetic effects in chemical reactions

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Abstract. Spin selective chemical reactions must also be magnetically sensitive. The susceptibility of chemical reactions to magnetic interactions produces two generations of magnetic effects: the first includes the magnetic field effect, the magnetic isotope effect, and the chemical polarisation of nuclei, all induced by external or internal magnetic fields. The second generation effects are stimulated by external electromagnetic fields interacting with the chemically active spin systems. The bibliography includes 31 references.

I. Two scenarios of chemical reaction

Any chemical event, including its feasibility and its result, is traditionally rationalised according to its energy scenario: how much energy is required, how to pump this energy into the reacting species, and how efficiently is this energy exploited in the chemical system.

However, another physical property besides energy is of paramount importance in chemistry: the angular momentum (spin) of the electrons and nuclei of the reagents. The fundamental ruling principle of chemical reactions is that both the spins and their projections remains unchanged in elementary chemical events. The conservation of the total spin has important consequences: the chemical reactions are spin selective, they are allowed only for spin states of the products whose total spin is identical to that of reagents, and they are strictly forbidden if they require spin change. For example, the transformation of the radical pair into the molecule (through recombination or disproportionation) is allowed only from the singlet spin state of the pair, and forbidden from the triplet one. The reaction $H + O_2 \rightarrow HO_2$ takes place in the doublet spin state of the reagent ($H\cdots O_2$) since the total spin of the pair in this state is identical to that of the reaction product, but it is forbidden in the quartet spin state of the pair. Of the nine possible spin states of the pair of triplet carbenes Ph_2C:, each having spin $S = 1$, only one can undergo a spin allowed reaction and produce the recombination product tetraphenylethylene. The spin of the other eight states ($S = 1$ and 2) is not equal to that of the reaction product ($S = 0$), and therefore these states are chemically nonreactive.

In general the spin selectivity of chemical events implies that chemically identical but spin different intermediates (the reaction product precursors) have different, spin dependent chemical reactivities. The only interactions which can alter the spin of reaction precursors and transform nonreactive, spin forbidden into the reactive, spin allowed states are magnetic interactions. Their contribution to the total energy is insignificant, but they control the spin behaviour of the chemical species, they modify their chemical reactivity, and they establish a new, magnetic scenario of chemical reactions.[1–4]

Spin selectivity (and therefore also the magnetic sensitivity of chemical reactions) gives rise to two generations of magnetic effects, illustrated in Fig. 1 for the particular but widely met case of a radical pair (RP). The nonreactive, triplet spin state RP can be transformed into the reactive, singlet spin state pair either by magnetic interactions, characteristic of the reaction itself, or by external radiofrequency or microwave (mw) magnetic fields. The triplet-singlet spin conversion induced by 'native' magnetic interactions is responsible for the magnetic effects of the first generation, or native magnetic effects, while the triplet–singlet conversion stimulated by rf or mw magnetic fields induces the magnetic effects of the second generation. The former includes Magnetic Field Effect (MFE), Magnetic Isotope Effect (MIE) and Chemically Induced Dynamic Nuclear Polarisation (CIDNP) — three effects originating from the dependence of the reaction probability P in RP on the magnetic field H, hyperfine (Fermi) electron-nuclear interaction, and nuclear spin orientation I_z. The latter are the basis of Reaction Yield Detected Magnetic Resonance (RYDMR), Radio Induced Magnetic Isotope Effect (RIMIE) and Stimulated Nuclear Polarisation (SNP). The relation between these two generations of magnetic effects is schematically shown in Fig. 1*b*.

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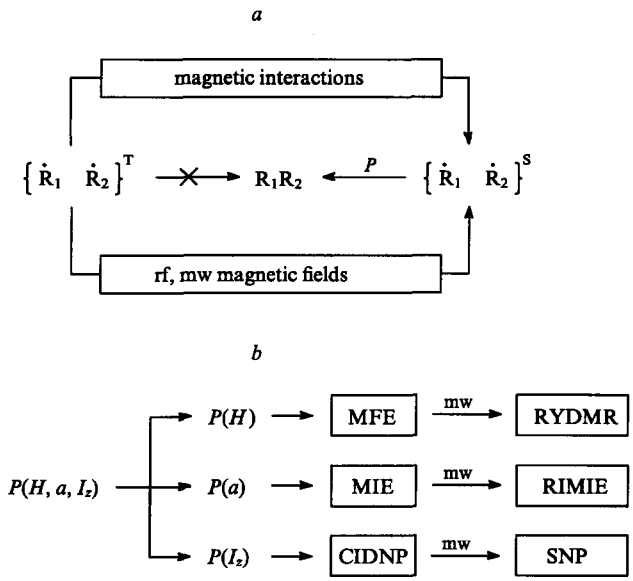


Figure 1. (*a*) Transformation of an unreactive triplet radical pair into a chemically active singlet pair under the influence of magnetic interactions and electromagnetic fields (radio-frequency or microwave); (*b*) relationship between first and second generation magnetic effects.

II. Spin dynamics of the radical pair

A radical pair is a dynamic intermediate or chemical microreactor from which the partners can diffuse without reacting, travel randomly in space and time, and then return and reencounter. The time between partner contacts, or repeated encounters, is used by the pair for its own spin conversion which is driven by magnetic interactions in the radicals resulting either in triplet–singlet transformation of the pair (if its starting spin state is triplet) or in singlet-triplet conversion (for pairs with singlet starting state).

To transform the triplet RP into a molecule at least four simultaneous events are required.

Firstly, the radicals leaving the RP at time $t = 0$ should return and reencounter at some time t. This process of regeneration of the contacts between RP partners is described by molecular dynamics. Secondly, at the same instance t the pair must have completed its triplet–singlet conversion and be ready to form a molecule. This process is controlled by spin dynamics. Thirdly, during their diffusional travels the radicals must not undergo chemical transformations: for the primary molecule to be reformed the initial pair must survive to time t. The probability of this event is determined by the chemical dynamics. Fourthly, the RP now ready to react (i.e. having survived to time t and being in a singlet state with the partners in contact) will recombine into a molecule only if a favourable orientation of the partners is achieved by rotational dynamics. Thus, the birth of a molecule from the RP is a result of the collective and coordinated efforts of three dynamics: spin, molecular and chemical.

The key act of the chemical interaction is spin conversion, controlled by the magnetic interactions, among which Zeeman and electron–nuclear (Fermi) hyperfine interaction (HFI) are the most important. Spin dynamics are modulated by molecular dynamics, which produce random variations of the distance between radicals and therefore of the exchange interaction potential. This, in its turn, influences the rate of spin conversion and ultimately the spin dynamics of the RP. The chemical reactions of RP partners destroy the pair, so that the spin dynamics are controlled by chemical dynamics.

The extended spin dynamics of the RP are the combination of all three dynamics considered cooperatively. The rate of triplet–singlet conversion is directly related to the matrix element Q of the RP spin Hamiltonian evaluated with the spin wave functions of triplet (T) and singlet (S) states.

For the multinuclear RP these Q_{ab} values are

$$Q_{ab}(T_0 - S) = \tfrac{1}{2}\left[\Delta g\mu_B H + \sum_i i m_i^a - \sum_j j m_j^b\right], \quad (1)$$

$$Q_{ab}(T_+ - S) = -\left(\tfrac{1}{8}\right)^{1/2} a_i\left[I_i(I_i+1) - m_i(m_i-1)\right], \quad (2)$$

$$Q_{ab}(T_- - S) = \left(\tfrac{1}{8}\right)^{1/2} a_i\left[I_i(I_i+1) - m_i(m_i+1)\right], \quad (3)$$

where the first describes the contribution of the T_0-S transition to the total rate of T–S conversion, the other two give the contributions of T_+-S and T_--S transitions; T_0, $T_\pm$ are the substates of the triplet spin state, with different electron spin projections: 0 for T_0 and ±1 for $T_\pm$ respectively. The term $\Delta g\mu_B H$ is the difference of Zeeman energies of the radical partners; Δg is the difference of their g-factors, $\Delta g = g_1 - g_2$; μ_B is the Bohr magneton; H is the strength of magnetic field; a_i and a_j are the HFI constants for the i-th and j-th kind of nuclei, with spins I_i and I_j: m_i^a are the quantum numbers of the projections of the nuclear spins I_i in the first radical of the pair and m_j^b are those for its partner.

It follows from Eqns (1)–(3) that the rate of triplet–singlet conversion (and consequently the probability of chemical reaction in the RP) depends firstly on the magnetic field strength H through the difference in electron Zeeman energies $\Delta g\mu_B H$; secondly on the nuclear magnetic moments through the HFI constant a, since $a = (8\pi/3)\mu_e\mu_n|\psi(0)|^2$, where μ_e and μ_n are the magnetic moments of the electron and nucleus, $|\psi(0)|^2$ is the electron spin density at the nucleus; thirdly on the nuclear spin orientation I_z through the quantum numbers m_i^a and m_j^b.

The reaction probability of the RP may be represented in the closed form as $P = F(H, a, I_z)$. This compact formula embodies the three main magnetic effects of the first generation (see Fig. 1*b*).

III. First generation of magnetic effects

1. Magnetic field effect

The modern theory of the MFE, based on the extended spin dynamics, identifies two main MFE sources.

1. In zero and in very low magnetic fields the S and T spin states are almost degenerate and the spin conversion involves all four states (S, T_0, $T_\pm$). In high fields the degeneracy of triplet substates is lifted and the $T_\pm$ levels are separated from the S state by Zeeman interaction and excluded from the spin conversion, so that the rate of the triplet–singlet RP transformation is reduced to approximately one third of the rate in zero field.

If the starting spin state of the pair is singlet the magnetic field closes the $S-T_\pm$ channels and partly locks the pair, increasing its chance to react. Conversely, if the starting state is triplet the magnetic field switches off the T–S conversion and partially suppresses (by about 60%) intra-pair chemical reactions.

The $T_\pm-S$ spin conversion is induced by HFI (usually in the 1–150 G range),† and therefore even these low magnetic fields ($H \approx a$) are sufficient to decouple electron–nuclear spin subsystems and produce marked and even multiple changes in reaction rates.

† 1 G = 10^{-4} T.

2. The rate of spin conversion by the T_0-S channel is magnetic field dependent according to Eqn (1). As in the previous case, the sign of the MFE is a function of the starting spin state: the magnetic field enhances the leakage of the reactive singlet pairs into nonreactive triplet pairs, and has the opposite effect on triplet pairs. As a result the magnetic field accelerates the reactions starting from triplet pairs (and triplet RP precursors) and hinders the reactions in singlets and in their precursors.

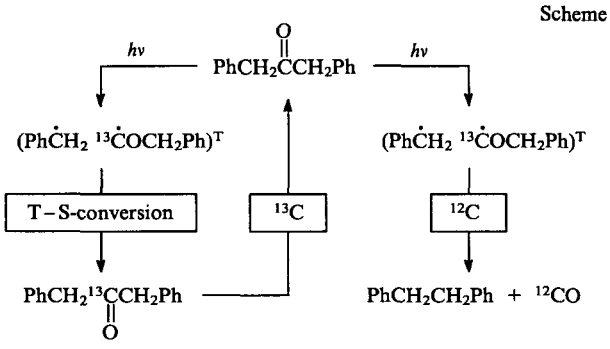
These two sources of MFE are easily distinguished because of the difference in their response to changes in the magnetic field: the field dependence for the MFEs originating from $T_{\pm}-S$ spin conversion channels reaches saturation at $H \gtrsim a$, while the magnitude of MFEs induced by T_0-S conversion varies monotonically with the magnetic field. For the RP with short-lived radicals (life-time $\tau \ll |Q_{ab}|^{-1}$) the effect is proportional to $(\Delta g \mu_B H)^2$, whereas for long-lived RPs ($\tau \gg |Q_{ab}|^{-1}$) the effect is proportional to $(\Delta g \mu_B H)^{1/2}$.[5] Furthermore it is evident that the signs of MFEs arising from these two sources are opposite; this provides an important criterion for identifying the spin states of the RPs and their precursors through the sign of the MFE.

2. Magnetic isotope effect

The coupling between chemical species or spin carriers (between radicals, in particular), being electron spin selective, must also be nuclear spin selective, since the two spin subsystems (electronic and nuclear) are coupled by Fermi HFI interaction. The nuclear spin system affects the magnetic behaviour of the electron spin system, thus influencing the chemical reactivity. The nuclear spin selectivity of chemical reactions produces a difference between the reaction rates of radicals (or, in general, of any other spin bearing chemical species) having magnetic or nonmagnetic nuclei. The name magnetic isotope effect (MIE) has been suggested by the present writer for this phenomenon, in contrast to the well known classical isotope effect (CIE) which follows from the nuclear mass selectivity of chemical reactions.[4,7]

A striking result of the MIE is the chemically induced separation of magnetic from nonmagnetic isotopes. MIE-induced isotope selectivity may be clearly exemplified by the photolysis of dibenzylketone (DBK), which is known to occur via the fragmentation of the excited triplet molecule and generation of a triplet RP (Scheme 1). The triplet RP can either undergo triplet–single spin conversion (driven by HFI) and recombine, recreating the starting ketone, or it can dissociate into the separate radicals $Ph\dot{C}H_2$ and $PhCH_2\dot{C}O$; the latter decomposes into $Ph\dot{C}H_2$ and CO. The main reaction products are dibenzyl $(PhCH_2)_2$ and carbon monoxide (Scheme 1).

Scheme 1



The rate of triplet–singlet conversion for magnetic RPs (i.e. the pairs with magnetic ^{13}C nuclei in benzoyl or benzyl radicals) is higher than that for nonmagnetic pairs (with nonmagnetic ^{12}C nuclei). Therefore the magnetic RPs will preferentially recombine and regenerate the starting ketone molecules, while the time lag of the triplet–singlet conversion in nonmagnetic RPs makes dissociation more likely for these pairs. As a result ^{13}C magnetic nuclei are accumulated in the ketone molecules, while carbon monoxide and dibenzyl are enriched in the ^{12}C nonmagnetic isotope. Thus, because of the difference in the rates of triplet–singlet spin conversion, the RPs can separate the nuclei according to their magnetic moments: they dispatch the magnetic and the nonmagnetic nuclei into the different chemical products.

MIE is a phenomenon of fundamental importance. It establishes a new chemical principle of isotope separation, it provides a new method of detection and identification of paramagnetic intermediates in chemical and biochemical processes, and it offers new ideas and approaches to problems in geochemistry, space chemistry, and molecular biology.[4,6,7]

3. Chemical polarisation of nuclei

Chemically induced dynamic nuclear polarisation (CIDNP) is the result of the nuclear spin selectivity of chemical reaction. The rate of T–S spin conversion according to Eqn (1) is a function of nuclear spin orientation, and therefore RPs which differ in nuclear spin orientation have different chemical reactivities. Hence the RP as a chemical reactor can not only separate magnetic from nonmagnetic nuclei (as it does in the MIE), but it can also assign differently oriented magnetic nuclei to different reaction products.

This is the first mechanism of CIDNP, which operates in high magnetic fields where the T_0-S channel of spin conversion is predominant. It selects the magnetic nuclei with respect to their orientations according to Eqn (1), and therefore the CIDNP is directly related to Δg and to a_i and to a_j.

The second CIDNP mechanism operates in low fields ($H < a$), where the $T_{\pm}-S$ channels also contribute to the RP spin evolution. The $T_{\pm}-S$ spin transitions are accompanied by reorientation of the nuclear spins, unlike the T_0-S transition which selects only the oriented nuclei without changing their alignment.

An excess of nuclear spins oriented with or against the field in the product molecules corresponds to overpopulation of the lower or the upper Zeeman nuclear levels respectively (for ^1H, ^{13}C, and ^{31}P nuclei with a positive magnetic moment). This non-equilibrium population manifests itself in the NMR spectra of the molecules as an anomalously strong absorption or emission, the latter corresponding to population inversion of Zeeman levels.

CIDNP is a well-known phenomenon, widely used as an efficient method of identifying reaction mechanisms and of detecting radicals and radical intermediates. CIDNP is a powerful means of defining the spin multiplicity of the radical pairs and of their molecular precursors, it can be used to separate radical from nonradical reaction pathways and to identify unstable intermediate products and reversible radical stages which cannot be detected by other methods. From the CIDNP kinetics we can determine the reaction rate constants, including those of fast reactions (10^8-10^9 s^{-1}). CIDNP can determine the signals of HFI constants in radicals in radicals and the spin-spin coupling constants in molecules, and it can also detect the hot, energy-rich radicals. The mechanisms of many types of chemical reaction have been studied by CIDNP and much valuable information has been collected.[8,9]

IV. Principles of chemical reception of microwaves

We should stress that the magnetic interactions do not influence the chemical reaction itself, i.e. that they do not affect the motion of chemically reacting atomic systems along the potential energy surface. Their effect is to switch the reaction from the spin-forbidden channels into spin-allowed ones, controlling the spin behaviour of the reactants (or vice versa, depending on whether the starting spin state of the reactants is spin-forbidden or spin-allowed). This statement applies to both the magnetic interactions (Zeeman, Fermi, dipolar, spin-orbital), specific to the reaction itself, and to the external electromagnetic fields and their influence on the spin-carrying reaction precursors (radical pairs in particular).

The principles of chemical reception of microwaves will be demonstrated by considering the RP example. The scheme of Zeeman energy levels of the RP is shown in Fig. 2. Let the pair be produced in a singlet spin state strongly coupled (for example, by HFI) with the triplet T_0 substate, so that the population of the mixed, ready-to-react ST_0 state is much higher than that of the T_+ or T_- substates. Resonant transitions between the T_0 and $T_\pm$ levels stimulated by an electromagnetic field (EMF) depopulate the reactive ST_0 mixed state and suppress the intrapair reactions, lowering the yield of reaction product from the singlet reaction channel. Conversely, if the starting spin state of the pair is triplet the reaction along the singlet channel depletes the population of the mixed ST_0 state: however, the $T_\pm - T_0$ pumping induced by the EMF additionally populates the reactive ST_0 state and increases the yield of reaction products. In general the EMF rearranges the spin system, switching the reaction between channels of different spin multiplicity and modifying the chemical reactivity of the RP as is found with other magnetic interactions.

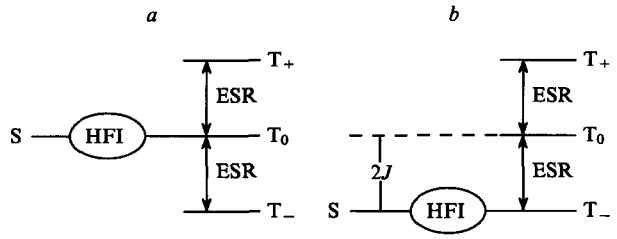


Figure 2. Microwave pumping of the Zeeman levels of a radical pair: (*a*) without exchange interaction ($J = 0$) the $T_\pm - T_0$ transitions stimulated by the EMF populate or depopulate (by hyperfine interaction) the ST_0 state; (*b*) in the presence of exchange interaction ($2J \approx g\mu_B H$) microwave pumping populates or depopulates the reactive mixed ST_- state. Possible ESR transitions are shown by arrows.

The exchange interaction J which appears at small inter-radical distances splits the S and T_0 levels, so that the T–S mixing now occurs only in the level crossing region (Fig. 2*b*), where $g\mu_B H \approx 2J$. However, in the spin evolution of the RP with distant partners the exchange interaction can be ignored. This situation is often met because the RP spends most of its lifetime in the state with remote partners.

Microwave pumping of the spin transitions modifies the rate of spin evolution of the RPs and therefore also their chemistry, providing a new principle of resonant, frequency-tuned chemical reception of microwaves. The change of the yield of products is the true chemical response to the perturbation of the reacting spin system by the EMF. (The frequency spectrum of the response is equivalent to the microwave absorption spectrum of the RP, and is therefore identical to its ESR spectrum.) Varying the external magnetic field H_0 allows us to detect the ESR spectrum of the RP by monitoring the yield of any product related to the reaction in the RP. Frankevich, who discovered the phenomenon, suggested the name Reaction Yield Detected Magnetic Resonance (RYDMR) for it.[10]

In order to visualise the spin transition induced by the EMF we shall consider the vector representation of spin dynamics in the radical pair.[2] To extract magnetic energy from the electromagnetic wave a particular polarisation is required: the magnetic vector $\vec{H}_1$ of the wave should lie in a plane normal to the permanent external magnetic field $\vec{H}_0$ (Fig. 3). The magnetic moment $\vec{M}_1$ of the spin carrier [assumed to have a spin $S = (1/2)\hbar$, so that $M_1 = (1/2)g_1\mu_B$] precesses with a Larmor frequency $\omega = \gamma H_0$ round the $\vec{H}_0$ magnetic field directed along the Z axis; $\gamma = g_1\mu_B/\hbar$ is the gyromagnetic ratio. The $\vec{H}_1$ vector of the EMF is directed along the Y axis: its value is $2\vec{H}_1 = 2H_1 \cos \omega t$. The total motion of the vector $2\vec{H}_1$ can be

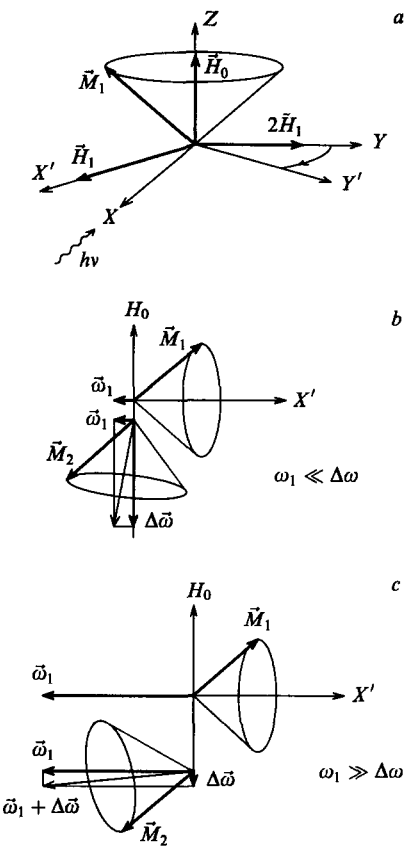


Figure 3. Vector diagram of the spin dynamics of a radical pair developed under the influence of the microwave field $\vec{H}_1$ (symbols defined in the text).

resolved into two circularly polarised vectors $\vec{H}_1$ rotating with a frequency ω in the XY plane in mutually opposite directions (Fig. 3*a*). One of these vectors, $\vec{H}_1$, rotating in phase with the Larmor precession appears to be motionless in a new frame of coordinates X', Y', Z chosen to rotate with the magnetic moment $\vec{M}_1$.

In this new, rotating frame the vector $\vec{M}_1$ experiences only the magnetic field $\vec{H}_1$ which is now permanent, and rotates round its direction with a frequency $\omega_1 = \gamma H_1$. This motion is equivalent to a periodic reorientation of the $\vec{M}_1$ vector with respect to the Z axis and therefore to $\vec{H}_0$. The magnetic moment $\vec{M}_2$ of the partner behaves similarly if the Larmor frequency of its precession is also equal to ω. These orientations are easily seen to correspond to $T_\pm - T_0$ spin transition.

We shall now assume that the magnetic moments $\vec{M}_1$ and $\vec{M}_2$ are not equivalent, owing to the difference Δg between their g-factors or to the hyperfine coupling a_2. Then the difference in the precession frequencies of the $\vec{M}_1$ and $\vec{M}_2$ vectors, $\Delta\omega$, is equal to $\Delta g\mu_B H_0/\hbar$ or $g_2\mu_B a_2/\hbar$ respectively. In the X', Y', Z frame rotating with the Larmor frequency of M_1 this vector is again motionless. However, the vector $\vec{M}_2$ now precesses with respect to $\vec{M}_1$ with a frequency $\Delta\omega$. This motion is equivalent to a $T_0 \rightleftarrows S$ spin evolution (Fig. 3*c*).

Switching on an EMF small enough (H_1) to satisfy the condition $\omega_1 \ll \Delta\omega$ stimulates the $T_0 \rightleftarrows T_\pm$ transitions responsible for the RYDMR phenomenon. At higher values of H_1, when $\omega_1 \geqslant \Delta\omega$, the vector $\vec{M}_1$ precesses round the vector $\vec{H}_1$ (or $\vec{\omega}_1$) as before, but the magnetic moment $\vec{M}_2$ now precesses round a total vector $(\vec{\omega}_1 + \Delta\vec{\omega})$ with a frequency $(\omega_1^2 + \Delta\omega^2)^{1/2}$ (see Fig. 3*c*). This means that the singlet–triplet spin mixing now takes place with new difference frequency

$$\Omega = (\omega_1^2 + \Delta\omega^2)^{1/2} - \omega_1 \approx \frac{\Delta\omega^2}{2\omega_1},$$

which is less than $\Delta\omega$ itself. This implies that at high enough EMF amplitudes the mw irradiation alters the spin behaviour of the radical pair: instead of stimulating triplet–singlet transitions it begins to suppress them. The spin state of the pair at high EMF amplitudes when $\omega_1 \gg \Delta\omega$ (see Fig. 3*c*) appears to be locked, so that the phenomenon is called spin locking. It manifests itself in distortion and ultimately in phase inversion of the RYDMR spectra.[11]

The jump of the $S-T_0$ mixing frequency from $\Delta\omega$ to $\Delta\omega^2/\omega_1$ can influence the properties of the mixed ST_0 state only under conditions such that the lifetime of the pair τ satisfies the relation $\tau < \omega_1/\Delta\omega^2$. Conversely, for $\tau \gg \omega_1/\Delta\omega^2$ the ST_0 mixing as well as the chemical properties of the pair will not depend on ω_1 and, therefore, on H_1 (spin scrambling). By varying ω_1 over wide limits and studying the dependence of the RYDMR spectra on ω_1 (or H_1) we may determine both $\Delta\omega$ and the lifetime τ of the radical pairs.[2]

V. Reaction yield detected magnetic resonance

The frequency spectrum of the chemical response to mw pumping is essentially the RYDMR spectrum, which may be recorded by monitoring any parameter of the chemical system under investigation providing that it is kinetically related to the RP reaction (and therefore to the population of spin substates of the pair). Among the most easily and precisely measurable parameters used to detect RYDMR spectra are the luminescence intensity, optical absorption, electric conductivity and radical concentration.

Electronically excited molecules able to emit from their singlet or triplet states (fluorescence or phosphorescence respectively) are usually produced by the recombination of ion-radical pairs (or, more precisely, by electron transfer reactions between partners). For example, the reaction between the ion radicals $D^{\cdot+}$ and $A^{\cdot-}$ may occur along singlet or triplet channels:

$$D^{\cdot+} + A^{\cdot-} \longrightarrow {}^1(D^{\cdot+}\,A^{\cdot-}) \longrightarrow {}^1D + A_0 \longrightarrow$$
$$\longrightarrow D_0 + A_0 + h\nu \qquad \text{(fluorescence)}$$

$$D^{\cdot+} + A^{\cdot-} \longrightarrow {}^3(D^{\cdot+}\,A^{\cdot-}) \longrightarrow {}^3D + A_0 \longrightarrow$$
$$\longrightarrow D_0 + A_0 + h\nu \qquad \text{(phosphorescence)}$$

The mw pumping of the singlet pairs stimulates their singlet–triplet conversion, thus suppressing the fluorescence in favour of the phosphorescence. Conversely, the mw pumping of triplet pairs induces the opposite effect. However, the intensity of fluorescence is usually small, and therefore fluorescence is seldom used to detect RYDMR spectra. Most of the RYDMR experiments are based on fluorescence intensity measurements.

Fig. 4 shows the RYDMR spectrum for the ion-radical pair $(M^{\cdot+}\ M^{\cdot-})$ generated by positron irradiation of a solution of naphthalene in squalane.[12] The reactions resulting in the formation and recombination of aromatic ion-radical pairs are:

$$S \longrightarrow S^{\cdot+} + e,$$
$$M + e \longrightarrow M^{\cdot-},$$
$$M + S^{\cdot+} \longrightarrow M^{\cdot+} + S,$$
$$M^{\cdot+} + M^{\cdot-} \longrightarrow M^* + M,$$

where S and M are solvent and aromatic molecules, respectively, $M^{\cdot+}$, $M^{\cdot-}$, $S^{\cdot+}$ are their cation and anion radicals, and M^* is the excited aromatic molecule (the fluorescence emitter). The pairs $(M^{\cdot+}\ M^{\cdot-})$ are mostly formed in the Onsager sphere and in the singlet spin state, so that their reaction product along the spin-allowed channel is an excited M^* molecule in the singlet spin state.

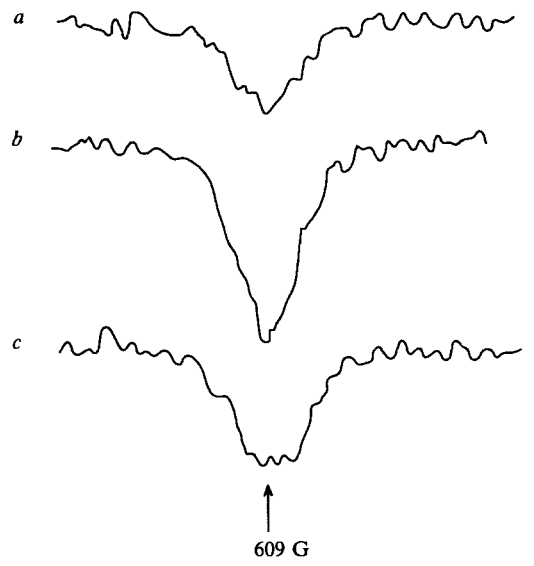


Figure 4. RYDMR spectra of an ion-radical pair [(naphthalene)$^+$/(naphthalene)$^-$] for a microwave pumping power of 1.3 (*a*), 3.8 (*b*), and 7.6 W (*c*).[12]

In order that the mw pumping may influence the spin evolution of the pair, two dynamic requirements must be satisfied:

$$\tau_{S-T_0} \lesssim (\gamma H_1)^{-1} \quad \text{and} \quad \tau_{RP} \approx (\gamma H_1)^{-1},$$

where H_1 is the amplitude of the mw field, $(\gamma H_1)^{-1}$ is the characteristic time of the mw-stimulated $T_0-T_\pm$ transitions, τ_{S-T_0} and τ_{RP} are the characteristic time of the $S-T_0$ spin evolution and of the lifetime of the ion-radical pair respectively.

The first relation ensures the fast $S-T_0$ transition and efficient chemical leakage of ion-radical pairs along the singlet channel, the second ensures that the pair undergoes mw-stimulated $T_0-T_\pm$ transitions before its disappearance.

The RYDMR signals (Fig. 4) are a single line with a halfwidth of 14 G, evidently due to the unresolved hyperfine structure of positive and negative naphthalene ion radicals, since the total HFI splitting is comparable to the width of the line. The centre of the RYDMR spectrum lies at 609 G, which corresponds to the *g*-factor of aromatic ion radicals at an operating frequency of 1704.6 MHz.

The optically detected RYDMR spectrum with resolved HFI splitting shown in Fig. 5 belongs to the ion-radical pair $(M^{\cdot+}\ M^{\cdot-})$, where M is biphenyl, generated under conditions similar to those used to generate the naphthalene ion-radical pair.[13]

As well as the radical–radical interactions, the chemical and physical processes in triplet–triplet and triplet–doublet pairs can be studied by the RYDMR technique in liquids and in molecular solids. The dynamics and mechanism of the triplet exciton annihilation and the quenching of triplet molecules by radicals and other spin carriers can also be elucidated by this technique. The mw pumping changes the population of the Zeeman spin levels in T–T or T–D pairs (as it does in D–D pairs) and thus controls the intensity of the prompt or the delayed fluorescence.[14]

The scheme of spin levels and mw-stimulated interlevel transitions in a pair of triplet excitons is shown in Fig. 6 as an example. In a strong magnetic field H two of the nine spin states of the pair (SQ_1 and SQ_2) include singlet components with amplitudes equal to $\frac{1}{2}$ and $\frac{2}{3}$ respectively. The singlet components of these states are mixed with the components of the quintet state, but the other states of the two-triplet pair ($Q_{\pm1}$ and $Q_{\pm2}$) are pure triplets and quintets.

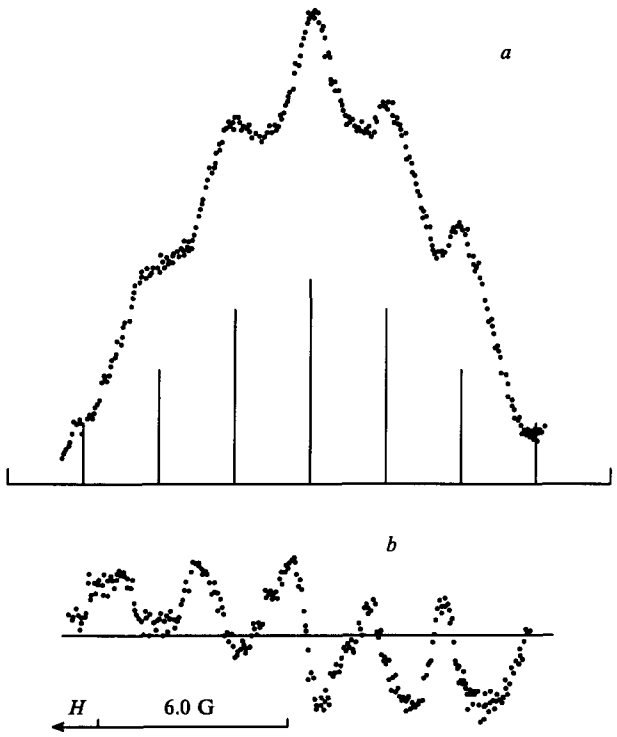


Figure 5. RYDMR spectrum of the (biphenyl)$^+$ – (biphenyl)$^-$ radical pair (*a*) and its first derivative (*b*).[13]

Upon exposure to a resonant mw field, transitions involving a change in the projection of the magnetic quantum number m by $\Delta m = \pm 1$, with the total spin S preserved ($\Delta S = 0$) are allowed. These transitions, shown by arrows in Fig. 6, increase the population—the SQ_1 and SQ_2 states which generate the annihilation product: the excited molecule which emits the fluorescence.

The mw-stimulated spectrum of the triplet exciton pair detected by the prompt fluorescence of the tetracene molecule in a tetracene single crystal is shown in Fig. 7 for

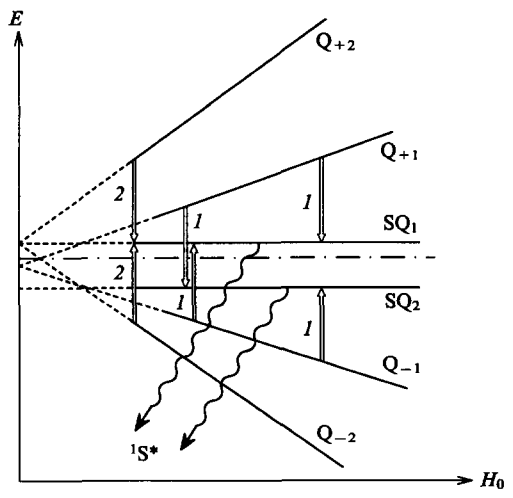


Figure 6. Energy level diagram of a triplet molecule pair: the Q levels are pure quintet states, SQ_1 and SQ_2 are levels of mixed quintet – singlet states. Triplet-levels do not contribute to the spin transitions and are not shown in the diagram. The arrows indicate transitions which populate the mixed SQ states and the formation of a source of fluorescence (the $^1S^*$ molecules).

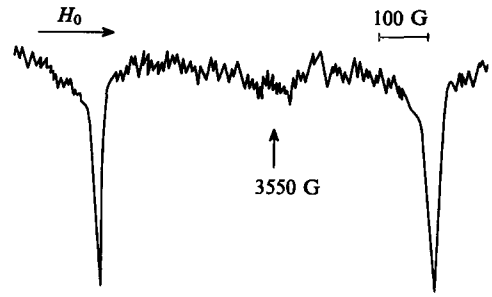


Figure 7. RYDMR spectrum of a pair of triplet excitons in a tetracene single crystal, detected by the prompt fluorescence.[15]

one particular orientation of the crystal with respect to the magnetic field.[15]

RYDMR spectra have been observed in studies of excitons and of charge-transfer complexes in liquids and in solids, F-centres in alkali halide crystals, electron-hole pairs in amorphous semiconductors, the reaction centres in photosynthetic systems, etc.[2,5]

The sensitivity of the RYDMR technique can be estimated. The relative variation $\Delta\gamma$ in the yield of the reaction in pairs produced by resonant mw-induced transitions is determined by the product of the probability P of the transition under the action of mw magnetic field H and of the lifetime τ of the pair:

$$\frac{\Delta\gamma}{\gamma} = \varkappa P\tau\,. \tag{4}$$

For a radical as a particle with a spin of $\frac{1}{2}$

$$P = \frac{1}{2}\left(\frac{g\mu_B}{\hbar}\right)^2 \frac{H_1^2\tau}{1+(g\mu_B/\hbar)(H_0 - H_{res})}\,. \tag{5}$$

The coefficient $\alpha \leqslant 1$ determines the relative variation in the yield γ if the multiplicity of the pair is completely changed. At resonance ($H_0 = H_{res}$)

$$\frac{\Delta\gamma}{\gamma} = \alpha\omega_1^2\tau^2\,, \tag{6}$$

where $\omega_1 = (g\mu_B H_1/\hbar)$. It is easily seen that for pairs with a lifetime $\tau = 5 \times 10^{-9}$ s a value of $\Delta\gamma/\gamma$ of about 1% is achieved for $H_1 = 1$ G at $\alpha = 1$. The very high sensitivity of the RYDMR technique is strikingly illustrated for the aromatic ion-radical pairs in liquids. They are generated at the rate of 2×10^8 s^{-1}, and have a lifetime of 10^{-7} s,[12] and hence the average concentration of the radical pairs available for detection by fluorescence intensity measurements is about 20 per sample, i.e. well below the sensitivity limit of modern ESR spectroscopy ($\sim 10^{11}$ spins per sample).[12]

The RYDMR spectra can be detected also by the optical absorption of triplet molecules produced by the pair-wise coupling of ion-radicals along the triplet channel. These molecules are usually sufficiently long-lived to be accumulated in measurable amounts and monitored by the triplet–triplet absorption of the probing light (in pulse excitation experiments, in particular).

The dissociation of ion-radical or electron-hole pairs produces free charge carriers in concentrations which are susceptible to the mw pumping of the pairs. Therefore RYDMR spectra can be also recorded by monitoring the electric conductivity both in crystals and in liquids.[2] Similarly, the dissociation of pairs of neutral radicals in solutions generates free radicals. This process is spin-independent, but it competes with the spin-selective intrapair coupling, and therefore the yield of free radicals which have escaped recombination should be as

sensitive to the mw pumping as the recombination itself (but, of course, in anti-phase).

RYDMR spectra detected by counting free radicals were first reported by Okazaki et al.,[16] who studied the photoreduction of menadione (MD, 2-methylnaphthoquinone) in sodium dodecyl sulfate (SDS) micelles. The reaction includes the removal of a hydrogen atom from the SDS molecule by the excited MD in triplet state:

$$^3MD + SDSC \longrightarrow (\dot{M}D\dot{H}\ S\dot{D}S) \begin{cases} \longrightarrow \text{coupling products} \\ \longrightarrow M\dot{D}H + S\dot{D}S \end{cases}$$

Only SḊS radicals are trapped by the added water-soluble nitroso spin trap TNO (perdeuterodimethylnitrosobenzene sulfonate) because the chemical reactivity of the spin trap towards the semiquinone radical MḊH is negligibly low. The yield of the stable spin adduct [the nitroxyl radical T(SDS)NȮ] measured by ESR was shown to decrease under mw-pumping (in keeping with the reaction scheme). Indeed, stimulating the triplet-singlet conversion of the RP by resonant mw irradiation induces chemical annihilation of the pair. As a result, the leakage of free radical out of the pair (and consequently the yield of spin adduct) decreases quite noticeably, as shown by Fig. 8. The largest reduction in the yield reaches 8% for the photolysis of protonated SDS micelles and about 14% if the photolysis is carried out in deuterated micelles. The magnetic field dependences of the mw-stimulated chemical response are in fact RYDMR spectra detected by radical escape measurements. The difference in their hyperfine structure confirms the difference in isotopic composition of one of the RP partners: the SDS radical, in which hydrogen nuclei are replaced by deuterons.

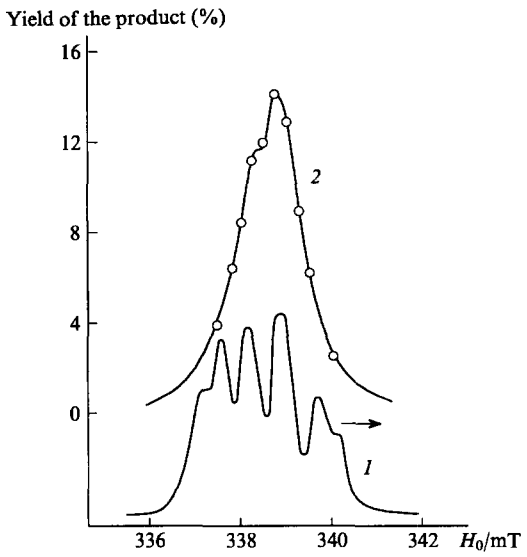


Figure 8. Dependence of the yield of the spin adduct under microwave pumping on the strength of the magnetic field H (or RYDMR spectra) for the photolysis of menadione in SDS (*1*) and deutero-SDS micelles (*2*).[16]

VI. Radio induced magnetic isotope effect

As a means of resonant chemical reception of microwaves RYDMR is nonselective because all the RPs are subjected to the mw perturbation. If the mw pumping is selective with respect to magnetic nuclei it induces a new, Radio Induced Magnetic Isotope Effect (RIMIE). The microwave irradiation of magnetic RPs should accelerate their spin conversion and stimulate their pair-wise reactions (usually recombination), enhancing the nuclear isotope selectivity induced by MIE of the first generation.

The concept of the RIMIE was clearly formulated[17] in 1981 and experimentally embodied[18] in 1991 in the photolysis of dibenzyl ketone (DBK) in SDS micelles. The photolysing laser pulses were synchronised with the mw pulses, and their lengths were chosen so that the RP generated by short laser pulses were exposed to the mw pulse throughout their life time. The frequency of the mw irradiation was chosen to pump selectively only the magnetic RPs [PhĊH$_2$ ^{13}Ċ(O)CH$_2$Ph], while the non-magnetic RPs [PhĊH$_2$ ^{12}Ċ(O)CH$_2$Ph] remained unperturbed by the microwaves (see Scheme 1).

The isotope enrichment S of dibenzyl ketone as a function of chemical conversion is described by the expression

$$\ln S = (1-\alpha)\ln(1-f^*), \qquad (7)$$

where $S = \delta/\delta_0$, δ_0 and δ are respectively the ^{13}C content in the starting ketone and in its residue after the chemical conversion of the 'magnetic' ketone PhCH$_2$^{13}C(O)CH$_2$Ph has reached the value f^*.[4] The coefficient α is the efficiency of the isotope separation (a one-step enrichment coefficient similar to that introduced by Bernstein[19] for the classical, mass-dependent isotope effect).

The experimentally measured isotope enrichment S of DBK as a function of $1-f^*$ in the parameters of Eqn (7) is shown in Fig. 9. As can be seen the one-step enrichment coefficients are different: for the photolysis in the presence of mw $\alpha_{mw} = 1.25 \pm 0.01$, while without mw pumping we have $\alpha_0 = 1.21 \pm 0.01$. Thus the mw irradiation is found to increase the isotope selectivity in the RP and the isotope enrichment of the recovered ketone.

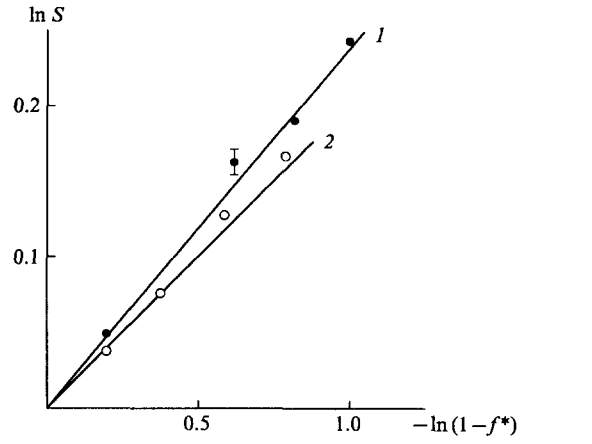


Figure 9. Isotope enrichment S as a function of the chemical conversion f^* of ^{13}C dibenzyl ketone in the coordinates of Eqn. (7):[18] (*1*) with microwave pumping (H_1 = 4.5 G); (*2*) without pumping.

The net contribution of the mw pumping to the recombination probability of the magnetic radical pair is about 6%. This value seems too small at first sight, but allowance should be made for the unfavourable experimental conditions. Firstly, the pumping of only one RP was carried out, which reduces the efficiency of mw irradiation at least two-fold. Secondly, the low amplitude of the mw pumping (H_1 = 0.3 mT) corresponds to the characteristic time of the mw-induced electron spin flip (the time of equilibrating the populations of $T_\pm - T_0$ spin levels) $\tau_{mw} = (\gamma H_1)^{-1}$ = 120 ns. It is much larger than the time interval between radical reencounters in the radical pair (τ_{enc} = 136 ns), so that the pair has not enough time between reencounters to complete the mw-induced spin reorientation, and therefore the $T_\pm - T_0$ transition. This unfavourable relation ($\tau_{mw} > \tau_{enc}$) is probably the main reason for the relatively low efficiency of the mw pumping in the isotope selection. High amplitude microwave pumping would be desirable to bring τ_{mw} closer to τ_{enc} in order to equilibrate the

populations of the $T_{\pm}$ and T_0 states of the radical pair before the moment when the probing contact of the partners takes place.

From this viewpoint the spin locking regime for the nonmagnetic pairs ($PhCH_2$ $^{13}C(O)CH_2Ph$) is thought to be favourable to the separation of isotopes, since it prevents their recombination and thus increases the efficiency of isotope selection. A combination of the two regimes (spin locking for the nonmagnetic pairs and stimulating microwave pumping for the magnetic pairs) would be most efficient.

In these experiments the ideal selectivity of mw pumping is achieved, because the ESR transitions of 'magnetic' and 'nonmagnetic' RP do not overlap and are separately accessible to the pumping action. The radio induced magnetic isotope effect with partially selective pumping was observed by Okazaki et al.[20] even earlier (in 1988) in the photolysis of menadione in SDS micelles consisting of a mixture of protonated and of deuterated sulfonate molecules in a 1:1 ratio. The RYDMR spectra of this system were detected from the yield of SDS radicals (see Section V), taken up by the spin trap and measured as nitroxyl radicals. The spectra are shown in Fig. 8: their overlap prevents the separate pumping of the isotopic forms of the radical pairs, but even with joint, nonselective pumping the yields of protonated and of deuterated SDS are markedly different.[20]

VII. Microwave stimulated nuclear polarisation

Stimulated Nuclear Polarisation (SNP) is the result of mw pumping of ensembles of RPs with selected orientations of the nuclear spins. It is similar to CIDNP, the only difference being that in CIDNP the nuclear spin selection in the RPs via triplet-singlet conversion is accomplished by existing magnetic interactions characteristic of the radicals, whereas in SNP the selection is produced by the resonant microwave field. Again, the radical pair acts as a selective chemical microwave receiver, but now the indicator of the reception is the nuclear polarisation in reaction products.[21]

In chemical reaction subjected to resonant (and therefore nuclear spin selective) mw pumping these two phenomena, CIDNP and SNP, can coexist, so that the experimentally measured NMR spectrum of the product molecules displays both contributions. The experimental technique which can distinguish between them by performing the pumping and the detection separately in time and space was developed by Sagdeev and his coworkers,[26] the pioneers and leaders of SNP studies.[22-25] This technique eliminates the CIDNP contribution and measures the net nuclear polarisation, induced by mw pumping.

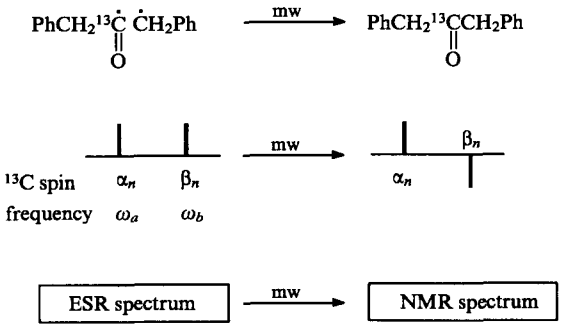


Figure 10. Development of SNP. The selective pumping of the ensemble of radical pairs with α_n and β_n orientations of the spins of ^{13}C nuclei at frequencies ω_a and ω_b accelerates their triplet-singlet conversion and transforms the ESR spectrum of the pair into the NMR spectrum of the molecule produced by its recombination (the molecule inherits the nuclear orientations of its precursor: the radical pair).[2]

The fundamental physics of the SNP phenomenon can again be clearly exemplified by the spin processes in the triplet radical pair [$PhCH_2{}^{13}C(O)CH_2Ph$], generated by the photolysis of DBK (Fig. 10). The ESR spectrum of the pair consists of a central group of lines (not shown in Fig. 10) which belong to the $PhCH_2$ radical, and of a doublet from the $PhCH_2{}^{13}CO$ radical with hyperfine splitting $a(^{13}C)$. Since $a(^{13}C)$ is known to be positive, the low-field line of the doublet is attributed to the ensemble of RPs with ^{13}C nuclei oriented with the field (α_n, spins on the lower Zeeman level), whereas the high-field line belongs to the ensemble with ^{13}C nuclei oriented against the field (β_n, spins on the upper Zeeman level). The fast intersystem T_0-S conversion induced by the HFI equalises the populations of these two spin levels. The mw pumping of the ESR transitions in the first ensemble of pairs at a frequency ω_a stimulates the $T_{\pm}-T_0$ spin conversion and additionally populates the T_0 states of the pairs with nuclear spins α_n causing acceleration of their recombination and the dominant formation of the DBK molecules with α_n spins (the positive SNP). The mw pumping of the second RP ensemble with β_n nuclear spins at frequency ω_b selectively produces DBK molecules with ^{13}C nuclei having β_n spins (the negative SNP). As a result the mw pumping transforms the ESR spectrum of the radical pair into NMR spectrum of a molecule with polarised nuclei, or an SNP spectrum of the absorption-emission, A/E type (Fig. 10, absorption in the high-field component and emission in the low-field component).

As a physical phenomenon SNP offers a powerful method of investigating the chemical reaction mechanisms and of detecting their radical intermediates. This is clearly illustrated by the SNP in the photolysis of deoxybenzoin $PhCOCH_2Ph$ in SDS micelles.[22] The quantum yield of its photolysis is very low: the products are formed in undetectable amounts. In the ^{13}C CIDNP spectra no lines are produced by photolysis with the exception of a single line belonging to the carbonyl ^{13}C nuclei of the starting ketone. It shows strong emission and indicates reversible photochemical processes accompanied by the almost complete regeneration of the starting ketone, so that the reaction scheme is:

$$PhCOCH_2Ph \rightleftharpoons X,$$

where X is the unknown intermediate responsible for the CIDNP of this ketone.

Tarasov and Bagryanskaya[25] have studied the ^{13}C SNP in this system and interpreted the strong SNP spectra (Fig. 11) as a superposition of two doublets. The first (A/E, with a splitting of 120 G) has been attributed to the acyl radical $Ph^{13}CO$, whereas the second, a poorly resolved A/E doublet with a smaller splitting (30 G), was attributed to the radical

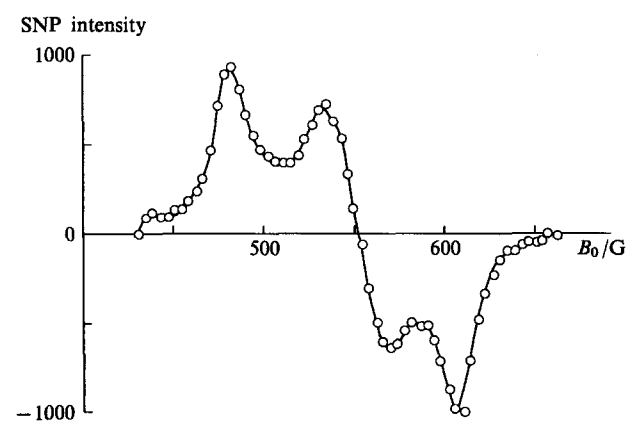


Figure 11. SNP spectrum detected during the photolysis of deoxybenzoin in SDS micelles.[25]

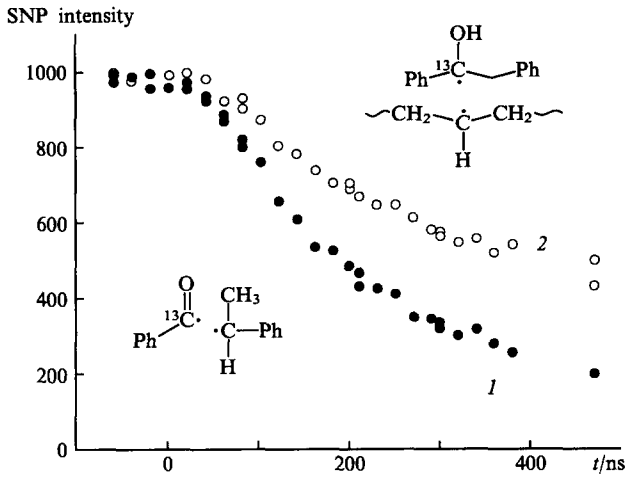


Figure 12. Kinetic behaviour of radical pairs generated by the photodissociation (*1*) and photoreduction (*2*) of deoxybenzoin in SDS micelles.[25]

$Ph^{13}C(OH)CH_2Ph$, the primary product of the photoreduction of the excited triplet ketone by the SDS molecule (RH). These SNP spectra suggest two competing paths for the photochemical transformation of deoxybenzoin: photodissociation and photoreduction via two different intermediates X {the radical pairs $(PhĊOĊH_2Ph)^T$ and $[PhĊ(OH)CH_2Ph\ Ṙ]^T$ respectively}. Both are highly reactive with respect to the ketone regeneration reaction, though their kinetic behaviour (Fig. 12) is different: the recombination is faster in the former than the disproportionation is in the latter.[25]

In stationary SNP detection the radical pairs are exposed to mw pumping throughout their lifetime. In time-resolved (TR) SNP experiments the laser and mw pulses are separated by the time delay τ_d, and therefore TR SNP offers a new possibility of influencing the ensembles of RPs with lifetimes in selected time domains but not shorter than the time resolution (about 30 ns in the best experiments by Sagdeev and coworkers[26–28]).

The study of the photolysis of benzoyl peroxide in CD_3OD [26] is a good illustration of the application of TR SNP. The reaction is known to involve a sequence of singlet RPs, including the pair $(PhĊO_2Ṗh)$ which contains a phenyl radical not accessible by conventional ESR technique under standard conditions. The SNP spectra recorded at $\tau_d = 0$ (Fig. 13) show SNP of opposite signs for the cage (phenyl benzoate) and the escape (benzene) products, in excellent agreement with the reaction scheme and the SNP mechanism. However the TR SNP spectra taken with $\tau_d > 50$ ns are found to be completely inverted for both products. This is because, in the time domain of 50–200 ns, in which the inverted TR SNP spectra have been observed, the SNP is generated in the diffusional RPs such as $(ṖhṖh)$ or $(ṖhĊD_2OD)$. The sign of the SNP in these pairs is the same as in triplet RP. At times $\tau_d < 50$ ns the SNP is completely attributed to the geminal RP $(PhĊO_2Ṗh)$ in the singlet state. The phase inversion as a function of τ_d is shown in Fig. 13*b*: two time domains corresponding to SNP in geminal and in diffusional radical pair ensembles are clearly shown.

A micelle (a microreactor with a boundary surface) confines the RP in a restricted volume. Hence the interradical exchange energy J in micellised RP should be a function of the micelle size, so that the SNP spectra, being sensitive to J, are in fact probes which monitor the exchange energy in RP.

A convincing confirmation of this statement was given by Tarasov et al.,[29] who studied the photolysis of methyldeoxybenzoin (99% ^{13}C abundance in the carbonyl group) in micelles of varying size controlled by the number n of carbon atoms in the detergent molecule $CH_3(CH_2)_{n-1}SO_4Na$. As expected the SNP spectra were strongly dependent on n and therefore on the micelle size (Fig. 14). Both the line broadening and the decrease in doublet splitting are evidence of an increase in J in the

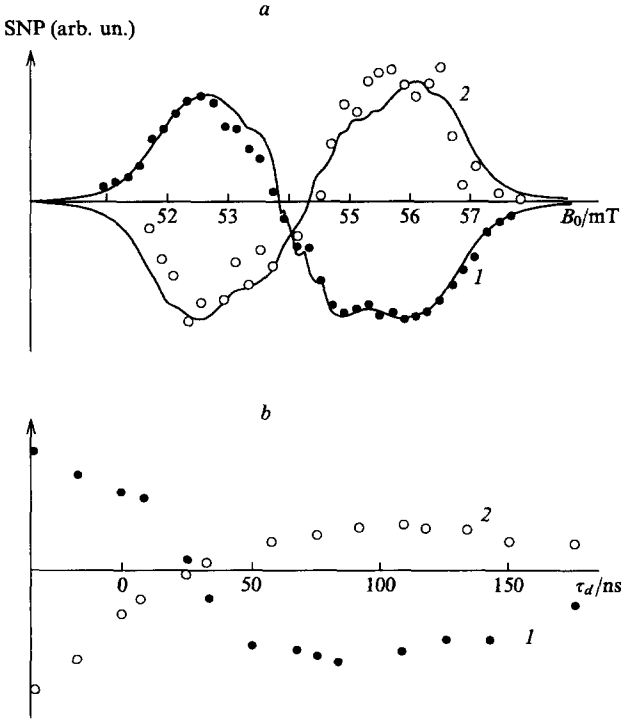


Figure 13. TR SNP spectra of phenyl benzoate (*1*) and benzene (*2*), detected by ^{13}C NMR during the photolysis of benzoyl peroxide (*a*), and their phase inversion as a function of τ_d (*b*).[26]

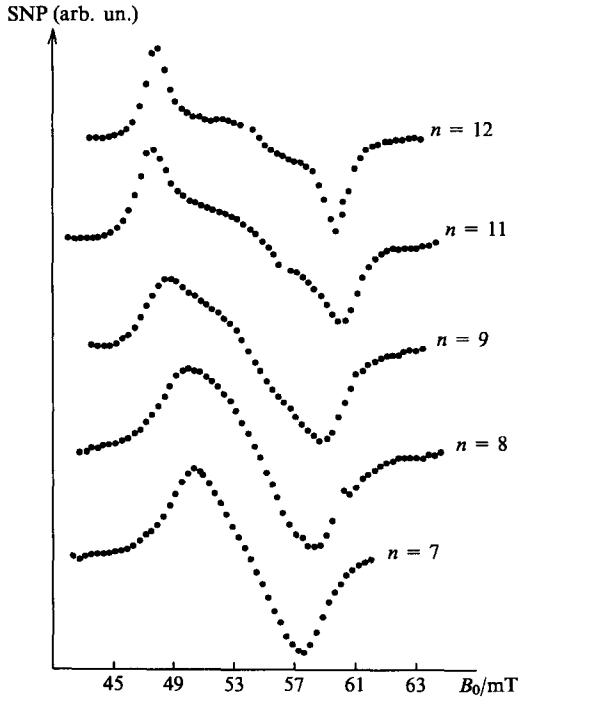


Figure 14. ^{13}C SNP spectra of the radical pair generated by photodissociation of deoxybenzoin in micelles of different size (n is the number of carbon atoms in the detergent molecule).[25]

[Ph^{13}ĊO ĊHMePh] RP as the micelles become smaller. Only in SDS micelles (n = 12) J is negligibly small and the doublet splitting corresponds to the hyperfine coupling constant $a(^{13}C)$ in the PhĊO radical (124 G). The doublet splitting and the J values are given below:[29]

n	$a(^{13}C)$/mT	J/mT
12	12.4	<0.1
11	12.0	0.5
9	10.0	3.4
8	8.4	8.0
7	7.6	14.0

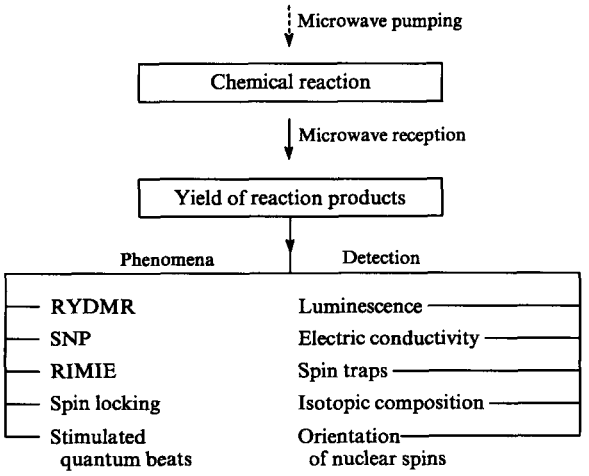
This information is of value for constructing the potential energy surfaces of the interradical reactions and for calculating the spin dynamics and the magnetic effects more exactly.

The strategy of magnetically probing the exchange potential (by SNP spectroscopy, in particular) along the reaction coordinate of chemical bond formation or dissociation is an important supplement to the transition state spectroscopy based on the femtosecond time-resolved optical spectroscopy developed by Zewail.[30] The difference is that femtosecond spectroscopy probes the transition state at short interatomic distances, where $J \gg kT$, whereas magnetic probing deals with the long-distance exchange potential ($J \ll kT$). From this point of view microwave magnetic probing can be treated as the radio spectroscopy of the transition state (the analogue of Zewail's transition state optical spectroscopy).[31]

VIII. Conclusion

Magnetic interactions (as a principal factor in the magnetic scenario of chemical reactions) regulate the spin dynamics and control the spin multiplicity of the radical pairs (as well as the pairs of other spin bearers), and therefore they also control their chemical reactivity. Electromagnetic fields influence the spin dynamics as a new factor which plays new scenes and initiates new phenomena: RYDMR, SNP, RIMIE, spin locking, quantum beats (the latter is beyond the scope of this paper). These remarkable magnetic effects of the second generation are schematically summarised in Scheme 2 as indicators of the chemical reception of radiowaves and microwaves.

Scheme 2



The author is grateful to the readers of this review and hopes that it will inspire them to use the achievements of electromagnetic spin chemistry. Financial support from the Russian Fund for Fundamental Research (grant 93-03-5227) is gratefully acknowledged.

References

1. K M Salikhov, Yu N Molin, R Z Sagdeev, A L Buchachenko *Spin Polarisation and Magnetic Effects in Radical Reactions* (Amsterdam: Elsevier, 1984)
2. A L Buchachenko, E L Frankevich *Chemical Generation and Reception of Electromagnetic Waves* (New York: VCH Publ., 1993)
3. U E Steiner, T Ulrich *Chem. Rev.* **89** 51 (1989)
4. A L Buchachenko *Progress in Reaction Kinetics* **13** 163 (1984)
5. Ya B Zel'dovich, A L Buchachenko, E L Frankevich *Usp. Fiz. Nauk* **155** 3 (1988)
6. A L Buchachenko, V F Tarasov *Acc. Chem. Res.* in press (1993)
7. I R Gould, N J Turro, M B Zimmt *Adv. Phys. Org. Chem.* **20** 1 (1984)
8. *Chemically Induced Magnetic Polarization* (Eds A R Lepley, G L Closs) (London: Wiley, 1978)
9. A L Buchachenko *Khimicheskaya Polyarizatsiya Elektronov i Yader* (Chemical Polarisation of Electrons and Nuclei) (Moscow: Nauka, 1974)
10. E L Frankevich, A I Pristupa, V I Lesin *Chem. Phys. Lett.* (47) 304 (1977)
11. S I Kubarev, S V Sheberstov, A S Shustov *Chem. Phys. Lett.* (73) 370 (1980)
12. O A Anisimov, V M Grigoryants, V K Molchanov, Yu N Molin *Chem. Phys. Lett.* (66) 265 (1979)
13. O A Anisimov, V M Grigoryants, Yu N Molin *Pis'ma Zh. Eksp. Teor. Fiz.* **30** 589 (1979)
14. E L Frankevich, S I Kubarev *Triplet State ODMR Spectroscopy* (Ed. R H Clarke) (New York: Wiley-Interscience, 1982) p. 138
15. E L Frankevich, A I Pristupa, V I Lesin *Chem. Phys. Lett.* (47) 304 (1977)
16. M Okazaki, S Sakata, R Konaka, T Shida *J. Chem. Phys.* **86** 6792 (1987)
17. A L Buchachenko, V F Tarasov *Zh. Fiz. Khim.* **55** 1921 (1981)
18. V F Tarasov, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, A L Buchachenko *Mendeleev Commun.* 85 (1991)
19. R Bernstein *J. Phys. Chem.* **56** 893 (1952)
20. M Okazaki, T Sakata, T Shida, R Konaka, K Toriyama *J. Phys. Chem.* **92** 1402 (1988)
21. R Z Sagdeev, Yu N Molin, K M Salikhov, Yu A Grishin, A V Dushkin, A Z Gogolev *Bull. Magn. Res.* **2** 66 (1980)
22. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, T V Leshina, N I Polyakov *Chem. Phys. Lett.* (117) 220 (1985)
23. E G Bagryanskaya, Yu A Grishin, N A Avdievich, R Z Sagdeev, Yu N Molin *Chem. Phys. Lett.* (128) 162 (1986)
24. R Z Sagdeev, E G Bagryanskaya *Pure Appl. Chem.* **62** 1547 (1990)
25. E G Bagryanskaya, R Z Sagdeev *Progr. React. Kinetics* **18** 63 (1993)
26. N A Avdievich, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *Chem. Phys. Lett.* (155) 141 (1989)
27. I V Koptyug, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *J. Chem. Phys.* **145** 375 (1990)
28. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *Chem. Phys. Lett.* (128) 417 (1986)
29. V Tarasov, N Ghatlia, N Avdievich, I Shkrob, A Buchachenko, N Turro *J. Am. Chem. Soc.* in press (1993)
30. A H Zewail *Science* **242** 1645 (1988)
31. A L Buchachenko, V F Tarasov, N G Ghatlia, N J Turro *Chem. Phys. Lett.* (192) 139 (1992)