Magnetic-spin effects in chemistry and molecular physics

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The influence of an external magnetic field on the chemical and photochemical processes in molecular solids, semiconductors, photosynthetic systems, and liquid solutions, the magnetic (or nuclear-spin) isotope effect, the chemically induced magnetic polarization of electrons and nuclei, the radiofrequency chemical maser, the high-frequency magnetic-resonance modulation of the rates of physical and chemical processes involving paramagnetic particles, and magnetic effects in the molecular physics of gases—all these effects are a consequence of spin selection rules and spin evolution. In this review, we analyze the origin of magnetic spin effects, estimate their quantitative scale, and discuss the time scale of spin dynamics.

CONTENTS

1. INTRODUCTION

The magnetic field was discovered (via the compass needle) in deep antiquity, and presented an enigma for a long time. Without going into historical detail, we recall Mesmer's "healing" magnets of the eighteenth century, Lermontov's "... and magnetism does seem to induce a happy dream," and Einstein's recollections of being startled at the age of four by the effect of a magnet being transmitted through planks of wood.

The great achievement of the nineteenth century was the discovery of the connection between magnetism and electricity (Oersted, Ampère, Faraday, and Maxwell).

The advent of quantum theory and statistical mechanics led to the following classification of magnetic fields capable of influencing particular processes:

1. $\mu H_1 \sim kT$, where μ is the magnetic moment of the electron or atom, k is Boltzmann's constant, and T is the temperature. Fields exceeding H_1 can significantly influence the orientation of the spins of electrons or atoms.

2. $\mu H_2 \sim |E_a|$, where E_a is the level energy of atoms or molecules: $E_a = -m_e c^2 \left(\dfrac{e^2}{\hbar c}\right)^2$. Fields exceeding H_2 have a significant influence on the structure of atoms, their ionization energy, and molecular bonding energy.

3. Finally, the field H_3, defined by

$$\frac{\hbar}{m_e c} H_3 = m_e c^2,$$

can modify the properties of vacuum and, in particular, influence the propagation of electromagnetic waves in vacuum.

When the field H_3 is reached, electrodynamics becomes nonlinear. At the top end, we find typically that $H_3 = 6 \times 10^{13}$ G, and this can only be reached in pulsars. Since photons propagate over distances much greater than the wavelength, strong nonlinear effects, such as $e^+ e^-$ pair production by single photons or rotation of the plane of polarization (Faraday effect) in vacuum, can occur in much weaker fields (10^{11}–10^{12} G). The field H_2 is of the order of

5×10^9 G and is also virtually unattainable under terrestrial laboratory conditions.

The field H_1 is the lowest of the three: its strength at room temperature is $\sim 3 \times 10^3$ Oe or 10^4 Oe at 1 K. Thus, at first sight, it would seem that, under laboratory conditions, appreciable effects can be expected only at low temperatures. Actually, by aligning the spins of electrons in hydrogen atoms, it is possible to prevent the formation of molecular hydrogen (the spins of the two electrons in the hydrogen molecule are antiparallel). It might seem that magnetic fields that can be produced under normal conditions cannot affect molecular or chemical processes for a perfectly indisputable reason: the additional magnetic energy of atomic/molecular particles is negligible in these fields, i.e., it is lower by a factor of 10^6–10^8 than the thermal or chemical energy, and can therefore be neglected.

However, there are many situations in which magnetic effects are significant even in weak magnetic fields. Let us consider some of them.

(1) When a large number N of magnetic moments in some particular region (or particle) of a ferromagnet point in the same direction, the resultant moment of the region is $N\mu$, and the field capable of turning over all the spins is then lower by the factor N. The significant point is that the simultaneous orientation of these N spins is determined not by the magnetic interaction between them but by the exchange interaction. The Pauli principle then ensures that the symmetry of the particle wave function in space and, consequently, the electrostatic energy of the particles, depend on the resultant spin.

In some simple cases (for example, in the H_2 molecule), this ensures that the spins are antiparallel. The molecule H_2 is not magnetic, but there are more complicated systems, e.g., metallic iron, in which the state of minimum energy (ground state) has a large spin, proportional to the number of atoms.

We should not therefore be surprised by the fact that the geomagnetic field (of the order of 1 G) can turn the compass needle or that a field of the order of 10^3 G is sufficient for the magnetic separation of Fe_3O_4 particles with diameters of the order of 1 mm, since the particle contains $\sim 10^{19}$ parallel spins. However, we shall not examine phenomena associated with ferromagnetism.

(2) The fields H_1, H_2, and H_3 were defined above on the basis of an energy criterion. In particular, H_2 was defined by demanding that the field should have an appreciable effect on the energy and the thermodynamic properties of atoms and molecules with zero spins, and that H_3 should affect the properties of systems of atoms (or ions, or free nondegenerate electrons) with spin.

A new situation and new possibilities reveal themselves when we examine nonequilibrium systems. For a small departure from equilibrium, the properties of the system can be characterized by transport coefficients, i.e., coefficients of the first power of the nonequilibrium parameter. These coefficients are the electrical conductivity, Hall constant, thermal conductivity, and diffusion coefficient. If we consider charged particles, their motion in a magnetic field is characterized by the Larmor frequency

$$\omega = \frac{eH}{mc}$$

and the corresponding orbital radius

$$R = (v\omega \cos \theta)^{-1}.$$

These quantities must be compared with the collision frequency and the mean free path. Since collisions are relatively rare, the mean free path is long, and even a weak field can have a considerable effect. This means that weak fields affect the conductivity of metals, and even weaker fields (of the order of 10^{-6} G) will influence very tenuous plasma and cosmic rays under astrophysical conditions. However, this range of phenomena has been discussed in detail in many books and reviews, and will not be reviewed here.

(3) The influence of a magnetic field on the transport coefficients of paramagnetic gases, discovered experimentally in 1913, is highly nontrivial. Section 9 of this review is devoted to it. The magnetic field due to the magnetic moment of the nucleus has a similar effect to that of an external magnetic field. This means that a mixture of magnetic and nonmagnetic isotopes can be separated by diffusion.

(4) A particular place in the hierarchy of magnetic effects belongs to the recently discovered influence of weak magnetic fields (constant or variable, external or internal, and due to the nuclear magnetic moments) on the rate of processes involving the interaction between paramagnetic particles (radicals, electrons, holes, ions, solitons, and triplet molecules) and on the chemical reactions in which they participate. The basis for these effects is the principle of spin selectivity, i.e., the reactions are allowed only from particular spin states. For example, the encounter of two radicals results in the formation of a radical pair in a singlet or triplet state, but the recombination of the radicals into a molecule occurs only from the singlet pair because the reaction in the triplet pair is strictly spin-forbidden. In an encounter of a radical and an oxygen molecule (doublet + triplet), two doublet and one quartet states are produced in the three-spin system, but the attachment of the radical to the oxygen molecule occurs only in one of the doublet states. In the interaction between two triplet molecules, the pair is a singlet, triplet, or quintet, and annihilation is spin-allowed only from the singlet state, and so on.

The magnetic interactions of spins with external and internal nuclear fields have negligible energies but a considerable effect on chemical reactions because they can change the spin of the reacting particles and remove spin selection. These effects are essentially transport phenomena and are the main topic of this review.

However, we must first clearly dissociate ourselves from fantastic assertions concerning the possibility of an effect of laboratory magnetic fields and of the so-called "magnetization" on water. Water and salt solutions in equilibrium have a molecular relaxation time of $\sim 10^{-11}$ s. Water cannot, therefore, retain any "memory" of the effect of magnetic fields upon it, and cannot change its structure or kinetic and thermodynamic properties under the influence of such fields. All that can happen is the agglomeration of iron oxide particles found in commercial water.[1]

All sensational reports of the effect of "magnetized water" on the strength of concrete, crop yields, and so on, are based on irresponsible attitudes to experiments in which a large scatter of experimental data is produced by extraneous factors. We know quite well that, by arbitrarily choosing the "best" results without correct control or statistical analysis, one can be led to practically any desired conclusion.

2. SPIN DYNAMICS

The discovery of the effect of a magnetic field on elementary processes involving the participation of paramagnetic particles, and the interpretation of this phenomenon in terms of the underlying mechanisms, have proceeded more or less at the same time, and practically independently, in different branches of science, i.e., in the physics of molecular crystals, in chemical kinetics, and in semiconductor physics, but the basis of the phenomenon is the same: it relies on the effect of the magnetic field on the spin state of a pair. A particular landmark was the discovery of the effect of the magnetic field on photoconductivity[2,3] and on the intensity of delayed fluorescence[4,5] of the crystals of aromatic hydrocarbons, the discovery of the chemical polarization of nuclei and electrons,[6,7] the discovery of the effect of a magnetic field on the rate of recombination of radical pairs in liquid solutions,[8] and the discovery of the magnetic isotope effect.[9] Among these new methods of modifying the spin state of short-lived pairs of paramagnetic particles, we note the spectroscopy of magnetic resonance, detected by examining the yield of reactions in pairs.[10]

We have already mentioned the spin states of a pair of paramagnetic particles and the chemical selectivity of these pairs. We shall now examine pairs of two spin doublets, such as radical + radical, electron + hole, and so on.

The spin states of a pair of this kind exhibit high chemical selectivity: recombination (annihilation) occurs only in singlet pair; triplet pairs do not react, but survive until triplet-singlet conversion, induced by magnetic interaction, takes place. The dynamic criterion for the appearance of magnetic effects is the ratio of two characteristic times, namely, the pair lifetime τ and its spin evolution time τ_{ev}.

Suppose that the initial state of a pair is a triplet. The transformation of the resultant spin of the pair in the course of spin evolution and the transition between the T_0 and S states is induced by the difference between the Zeeman precession frequencies of electrons [the characteristic spin evolution time is $\tau_{ev} \simeq (\Delta g\beta H)^{-1}$, where Δg is the g-factor difference within the pair] and the hyperfine Fermi interaction between electrons and magnetically active nuclei [the characteristic spin evolution time for a single-nucleus is $\tau_{ev} \simeq (\gamma_e a)^{-1}$]. Transitions between $T_\pm$ and S are induced only by the hyperfine interaction and are accompanied by a change in the orientation of the nuclear spin, i.e., the change in the angular momentum of the electron spin system is compensated by a change in the angular momentum of the nuclear spin system. The characteristic time for the $T_\pm - S$ evolution is $\tau_{ev} \simeq (\gamma_e a)^{-1}$ and decreases with increasing strength of the electron-nuclear magnetic coupling, i.e., with increasing Fermi constant a. The quantities $\Delta g\beta H$ and a lie, on average, in the range 10^7–10^{10} s^{-1}, i.e., τ_{ev} is of the order of 10^{-10}–10^{-7} s.

Diffusive separation of the two partners of a pair and their chemical transformation compete with spin evolution. These processes are described by molecular and chemical dynamics and determine the pair lifetime τ_{chem}.

A radical pair in a liquid is a dynamic system whose partners can separate after initial contact. They can execute diffusive motion, return and meet again, separate once more, and so on. The triplet-singlet evolution of the pair occurs during this motion. The probability of repeated contact between the partners of a radical pair decreases with time approximately as $t^{-3/2}$, but the average lifetime τ_{diff} of a pair is of the order of 10^{-10}–10^{-7} s, depending on the viscosity of the liquid and its molecular organization. The characteristic time τ_{chem} of chemical dynamics, i.e., the dynamics of chemical transformation of at least one of the partners of a pair, lies in the wide range between 10^{-10} s and practically infinity (for chemically stable radicals).

It follows that the characteristic times of spin, molecular, and chemical dynamics are comparable in order of magnitude, and all three processes compete. This leads to a fundamentally important consequence: spin dynamics controls chemical reactions, influences chemical transformations of a pair, and determines its chemical fate, i.e., the pair either reacts if the spin dynamics succeeds in taking the pair to a singlet state during its lifetime, or the two partners leave one another if spin dynamics does not succeed in changing the spin of the pair.

An external magnetic field can influence spin dynamics. Figure 1 shows the Zeeman levels of a radical pair. In zero fields, the triplet states T_0 and $T_\pm$ are degenerate, and the hyperfine and Zeeman interactions mix these three levels with the singlet level. In strong fields, the degeneracy of the $T_0, T_\pm$ levels is lifted, the $T_\pm - S$ spin conversion channels are turned off, and all that remains is the single $T_0 - S$ channel; the result is a change in the rate of triplet-singlet evolution of the spin system.

Spin dynamics can also be controlled by altering the internal magnetic field (for example, by replacing magnetic nuclei with their nonmagnetic isotopes, or by changing the Fermi interaction by changing the electronic structure of radicals). Next, spin dynamics can be influenced by high-frequency fields that induce magnetic-resonance transitions between the Zeeman levels of the radical pair and remove spin selectivity.

The three competing dynamics (spin, molecular, and chemical) are also typical for electron-hole pairs in a liquid or solid. In the latter case, molecular dynamics of the partners migrating in a crystal is, in principle, similar to the dynamics of radicals in a liquid. The only difference is that it occurs in the Coulomb potential that couples the two partners. In doublet + triplet pairs (for example, H + O_2, which precedes the reaction H + $O_2 \rightarrow HO_2$), spin evolution occurs between a doublet and quartet. The chemical reaction is selective with respect to the spin state of the pair: it occurs only in the doublet (forming the spin doublet of the radical HO_2), but is forbidden in the quartet. Annihilation of two triplets is also spin-selective: it occurs only from the singlet state of the T + T pair. Other spin states of this pair (three triplets and five quintets) cannot annihilate. The mixing of some of these states with the singlet state occurs as a result of magnetically sensitive spin evolution.
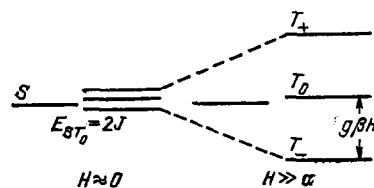

FIG. 1. Zeeman level scheme for a two-spin system in the fields $H \simeq 0$ and $H \gg a$ (Ref. 11).

There is an enormous number of physical and chemical processes in liquids, molecular solids, semiconductors, photosynthetic systems, and so on, that exhibit a high degree of chemical selectivity of spin states. In all these processes, spin dynamics controlled by magnetic interactions removes (partially or completely) the spin selectivity, and influences the final chemical and physical outcome of the process (the course of a reaction, recombination of charges, annihilation, and so on). This is why magnetic interactions, which have negligible energies associated with them, have a very considerable influence on high-energy processes (chemical reactions, luminescence, electrical conductivity, photosynthesis, and so on). This opens the way for new "magnetic" principles for controlling these processes, which rely on spin rather than energy properties. Spin selectivity and magnetic effects have already been discovered for many of these processes while the existence of magnetic effects, their scale, and the conditions for their realization, are confidently predicted for other processes. The theory of spin and magnetic effects has now been developed with sufficient rigor (see, for example, Ref. 11).

We must now note the difference between spin and magnetic effects. Spin effects, i.e., spin selectivities, occur in all states of matter, i.e., in gases, liquids, and solids. However, it is only in liquids and solids that spin effects are accompanied by magnetic effects, because it is only in these systems that the lifetime of pairs of reacting particles is comparable with the spin evolution time, and magnetic forces act on magnetic moments and spins for a sufficient length of time. In gases, the particles are in contact for only 10^{-13}–10^{-14} s, and this time is too short for magnetically induced spin conversion to take place.

There is one other important circumstance: spin and, consequently, magnetic effects occur only when the spin system is isolated from the lattice, i.e., when the spin-lattice electron relaxation time is greater than or at least comparable with the spin evolution time. As a rule, this condition is satisfied in molecular systems. It means that the spin system evolves at an effective temperature $T \approx 0$, so that even weak magnetic interactions with energies lower by 5–6 orders of magnitude than kT are effective in spin evolution. When electron relaxation is fast, its contribution to spin conversion becomes appreciable, and it even occasionally predominates over the Zeeman and Fermi interactions. This is why the chances of discovering magnetic effects in elementary reactions between paramagnetic particles with short electron relaxation times (e.g., Fe^{2+} ions) are smaller than in reactions between organic radicals.

Finally, to conclude this Section, let us consider direct experimental observations of spin evolution. When the lifetime of a radical pair is long enough and spin conversion takes place, it is possible to observe periodic oscillations of the pair between triplet and singlet states (quantum beats). A clear example of such beats was reported in Ref. 12. The recombination of ion-radical pairs, such as (tetramethylethylene)$^+$ + (paraterphenyl)$^-$, produced in the singlet spin state by a pulse of fast electrons, resulted in the formation of a fluorescing molecule of paraterphenyl in a singlet excited state. Since the annihilation of the pair occurs only in the singlet state, the periodic oscillation of the pair between the singlet and triplet states modulates the fluorescence emitted by the paraterphenyl molecule. Figure 2 shows the experi-
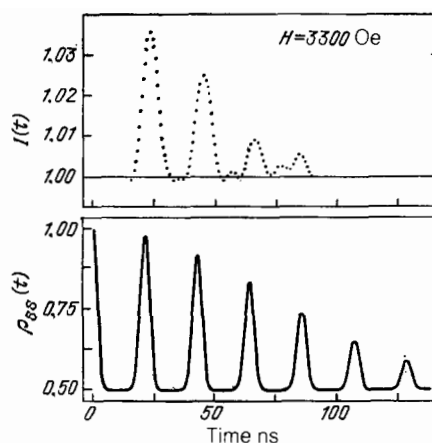

FIG. 2. Quantum beats produced during the recombination of the tetramethylethylene radical cation and the paraterphenyl-D_{14} radical anion.[12] Top—experiment, bottom—theory. $I(t)$—intensity of luminescence from paraterphenyl molecules excited as a result of recombination, $\rho_{SS}(t)$—calculated density of the singlet state of the radical pair as a function of time.

mental and theoretical plots of the fluorescence intensity as a function of time. The period of the quantum beats is in qualitative agreement with the spin evolution period of the pair, induced by the Fermi interaction between the electron and the nuclei in the tetramethylethylene cation.

Qualitatively similar quantum beats have also been observed during the recombination of ion-radical pairs in solutions[13] and in tetracene crystals during triplet-triplet annihilation.[14,15]

3. MAGNETIC EFFECTS IN MOLECULAR SOLIDS AND SEMICONDUCTORS

Traditional optical and electrical methods, and also new methods based on the effects of an external magnetic field on particular stages of nonequilibrium electronic processes and the reactivity of paramagnetic particles, have been used to elucidate the mechanism responsible for the formation of charge carriers and for other processes involving the participation of excited singlet and triplet states in organic solids. The change in the rate of these process stages is detected by examining photoconductivity, fluorescence intensity, optical density, and so on. The effect of the magnetic field is specific enough to enable us to exploit it in studies of the mechanism responsible for these processes, and to detect the presence of magnetically sensitive stages.

Constant or variable external resonance magnetic fields can influence the rate of reactions because these fields influence the spin state of a pair of particles with correlated spins. The magnetic-field dependence of a particular reaction, the range of field strengths in which the course of the reaction is influenced, and the size of the magnetic effect, depend on a large number of factors.

The main factors are as follows. A pair of paramagnetic particles must be formed in the course of the reaction, and participate in it. The reaction in the pair must proceed along at least two competing channels, and the choice of channel depends on the multiplicity of the pair.

The pair lifetime τ must be long enough for the spin state of the pair to evolve in the magnetic field. The lifetime τ

must not be much smaller than ω^{-1}, where ω is the frequency characterizing the evolution of the spin state of the pair.

The pair lifetime must be short enough in comparison with the spin relaxation time ($\tau < T_1$), so that the equilibrium population of all the spin states is not established. One can also imagine a situation in which the pair lifetime is comparable with T_1. The external magnetic field can then influence the spin state of the pair of particles due to the dependence of T_1 on the external magnetic field. The usual situation is that T_1 increases with increasing H_0. This means that spin relaxation is less complete in a strong H_0 than in zero field, so that it is possible to observe the effect of the external field due to the different degree of polarization of pairs produced in the spin-dependent reaction.

Although the conditions enumerated above are relatively stringent, it is found that magnetic effects can be observed in most cases in which mobile particles with spins participate in electronic processes in molecular crystals and polymers. Paramagnetic particles that can participate in different non-equilibrium processes in molecular solids, and determine the sensitivity of the rate of a process to external magnetic fields, include free electrons and electrons captured by traps, positive charges (holes) that determine the electrical conductivity or photoconductivity, triplet excitons with long lifetimes (up to 10^{-2} s in crystals) and high mobility ($D \simeq 10^{-4}$–10^{-3} cm^2/s), which determines their participation in different exciton reactions, free radicals and radical ions, and paramagnetic impurity molecules. The most important impurity, which is also capable of capturing an electron, is the oxygen molecule O_2. Pairs with correlated spins can be produced from any of these particles. The significant point is that at least one of the particles of a pair should be mobile. The effect of the magnetic field has now been detected for many processes in which the above particles participate. We shall examine the influence of magnetic fields on electronic processes typical for molecular solids.

3.1. Processes with participation of doublet-doublet pairs

The excitation of molecular crystals by light in the singlet-singlet absorption band is usually accompanied by the phenomenon of photoconductivity. This is interpreted in terms of a reaction between the singlet excitons $^1D_1$, formed as a result of the absorption of light, and the impurity molecules $^1A_0$. The transfer of an electron from $^1D_1$ to $^1A_0$ leads to the formation of a D^+A^- charge-transfer state, in which the hole D^+ is coupled to the ion A^- by the Coulomb interaction. Even in the absence of impurity molecules, the charge-transfer state can be formed from the $^1D_1$ state as a result of autoionization. The D^+A^- charge-transfer states can either recombine or, having lost some activation energy, dissociate into free charges. Photoconductivity is determined by the rate of production of free holes D^+, which is proportional to the concentration of the D^+A^- pairs. Figure 3 shows a general scheme for these processes, including different spin states of the D^+A^- pair, first proposed in Ref. 3. Here and henceforth, we use the following notation for electronic states: m_{A_n}, here A (or some other letter) is a molecule, m is the multiplicity of the state, and n is the number of the excited state ($n = 0$ for the ground state). Oxidation-reduction reactions can also be described by this scheme. In polar liquid solutions, this type of reaction, with the participation of electronically-excited molecules on the
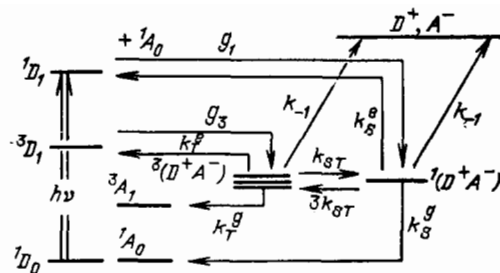

FIG. 3. General scheme of energy conversion processes in an excited molecule $^1D_1$ and charge separation in the presence of acceptor molecule $^1A_0$ (Ref. 22). The following elementary processes and their rates are shown: charge transfer between the excited singlet molecule $^1D_1$ and acceptor $^1A_0$ with the formation of the singlet pair (D^+A^-) (g_1), the analogous process for the excited triplet molecule $^3D_1$ with the formation of the triplet pair $^3(D^+A^-)$(g_3), the corresponding inverse reactions (K_S^c and K_T^c), dissociation of pairs into free charges D^+ and A^- (k_{-1}), recombination of pairs (k_S^g and k_T^g), and intercombination transitions between the spin states of a pair (k_{ST}).

first stage, leads to the formation of exciplexes that subsequently dissociate into ion pairs and free ions. In molecular solids, the formation of pairs such as D^+A^- is usually sensitive to a magnetic field. This suggests that the conditions enumerated above are satisfied. In particular, if we use the condition $T_1 > \tau > \omega^{-1}$ with the typical value $T_1 = 10^{-7}$ s, Onsager radius $R = e^2/\varepsilon k T = 200$ Å, and $\omega = 10^8$ s^{-1}, we find that the magnetic effect can be expected for pairs involving mobile D^+ particles with microscopic mobility μ in the range $2 \times 10^{-4} < \mu < 10$ cm^2/V.s. A relatively high mobility reduces the probability of a repeated encounter between the partners D^+ and A^- of the pair because of the increased probability that D^+ will be trapped by the impurity (it was assumed in these estimates that the impurity concentration was 10^{15} cm^{-3}).

The D^+A^- pairs in Fig. 3 are initially formed in a pure singlet state, since their precursors are singlet particles. In general, the pairs can be formed independently in each state. Transitions between pure spin states S and T are satisfactorily described by the intercombination transition rate $k_{ST}(H_0)$, and the external magnetic field H_0 can alter this constant. The change in the constant $k_{ST}(H_0)$ can be seen in many experimentally measured quantities associated with different channels of the process. For example, the singlet channel usually involves the formation of an electronically excited state during the recombination of D^+ and A^-, which can be studied examining the fluorescence from this state. The triplet channel can lead to the formation of excited triplet molecules, ^3D, recorded by observing either triplet-triplet absorption or delayed fluorescence due to triplet annihilation. A channel in which the reaction rate is usually independent of multiplicity is pair dissociation into free charges, detected by examining the electrical conductivity or other processes involving these charges. The sign of the change in the different process parameters when a magnetic field is applied depends on the ratio of the rate constants, the mechanism responsible for the effect of the magnetic field, and the rate of population of spin states of the pair. It yields additional information on the mechanism responsible for the process.

3.2. Intercombinational transitions in pairs

The possibility of intercombinational transitions in pairs is determined by the interaction of the electron spins with the external magnetic field H_0 and the magnetic field due to the nuclei. The Hamiltonian for this interaction is

$$\hat{H} = g_A\beta\hat{S}_A H_0 + g_B\beta\hat{S}_B H_0 + \hbar \sum_j {}^a A_j I_{aj}\hat{S}_A + \hbar \sum_k {}^b A_h I_{bk}\hat{S}_B$$

$$- \hbar J(r)\left(\frac{1}{2} - 2\hat{S}_A\hat{S}_B\right). \tag{1}$$

where g_A and g_B are the g–factors of the two particles $\dot{A}$ and $\dot{B}$, β is the Bohr magneton, $A_{j,k}$ are the hyperfine interaction constants of the jth nucleus in particle $\dot{A}$ and the k th nucleus in particle $\dot{B}$, $\hat{S}$ is the spin operator, and $J(r)$ represents the exchange interaction. The form of the Hamiltonian shows that the spin of each of the particles $\dot{A}$ and $\dot{B}$ in the external field H_0 precesses around the direction of the field with frequency determined by the Zeeman interaction (first two terms) and the hyperfine interaction. The evolution of the initial spin state gives rise to a difference between the spin precession frequencies of particles $\dot{A}$ and $\dot{B}$. In a weak external field, the evolution process is due to the hyperfine interaction which mixes the state S with all three states T. In a strong field H_0, the levels $T_{\pm 1}$ are split from the level T_0 by the amount $g\beta H_0$. When this splitting is greater than the level width, the S–$T_{\pm 1}$ transitions are forbidden on energy grounds, whereas S–T_0 transitions can occur because of the difference between the Zeeman frequencies (Δg mixing mechanism) and the spin precession frequencies in the local magnetic field of the nuclei (hyperfine mechanism).

The Hamiltonian given by (1) enables us to calculate the spin state of each pair as a function of time, expressed as a superposition of singlet and triplet states, as follows:

$$\psi(t) = C_S(t)|S\rangle + C_T(t)|T_0\rangle. \tag{2}$$

The statistical averaging of a measured physical variable (e.g., lifetime of a pair, rate of recombination of pairs along different channels, and so on) over the entire ensemble of pairs is usually carried out using the density matrix.[16] The transport equation for the density matrix takes into account both the evolution of spins in a pair and the transformation of pairs along channels of different multiplicity.[17,18] Theoretical calculations of magnetic effects with allowance for nuclear spins are possible in an analytic form only when a single nucleus is present.[19] Numerical calculations for more complicated cases are given in Refs. 20 and 21.

The effective mixing of the S and T_0 states by the Δg mechanism occurs over a time of the order of one-half of the period of Larmor precession with frequency

$$\omega = \frac{\Delta g\beta H_0}{2\hbar}.$$

Since $\omega^{-1} < \tau < T_1$, the magnetic effect is expected to saturate in fields

$$H_0^{sat} \gtrsim \frac{2\hbar}{\Delta g\beta T_1},$$

so that, for $\Delta g \simeq 10^3$ and $T_1 = 10^{-7}$ s, we have $H_0^{sat} \gtrsim 3 \times 10^3$ Oe. For the hyperfine mechanism, mixing occurs in zero external field, and the saturation effect is expected for external fields for which the splitting of the triplet sublevels of a pair is such that $g\beta H_0 \gtrsim \Delta E$, where ΔE is the level width determined either by the effective value of the hyperfine interaction constant,

$$E = A_{eff} = \left(\sum_{j,k} A_{j,k}^2\right)^{1/2},$$

or by the short lifetime of the pair: $\Delta E = \hbar/\tau$. Hence $H_0^{sat} \gtrsim A_{eff}/g\beta \simeq 10\text{--}100$ Oe, or

$$H_0^{sat} \approx \frac{\hbar}{g\beta\tau},$$

which, for $\tau = 10^{-9}$ s, gives

$$H_0^{sat} \approx 50 \text{ Oe}.$$

The magnitude of the effect is determined by the change in the effective constant k_{ST} with the external field. For the pure Δg mechanism, the constant k_{ST} increases with increasing field by a substantial factor, but this mechanism is rarely present without a contribution due to the other. The reduction in k_{ST} due to the hyperfine mechanism as the field increases is by a factor of 3. These changes in k_{ST} have different effects on the measured quantities, depending on the functional dependence between them, and also on the magnitude of the constants representing the processes occurring in different channels. For example, when photoconductivity is measured in the process illustrated in Fig. 3, the maximum possible relative change is

$$\frac{\Delta\sigma}{\sigma} = \frac{\sigma(H_0) - \sigma(0)}{\sigma(0)} = 50\%,$$

but this is close to zero when $k_3 \gg k_{ST}$.

3.3. Examples of magnetically sensitive processes

Magnetic effects in solids provide important information on the intermediate stages of processes that are inaccessible to other methods. Although paramagnetic particles are present in the vapor state, their concentration is usually too low for detection by the ESR methods. Even if we use a high rate of production of pairs, e.g., $\sim 10^{18}$ cm^{-3} s^{-1}, with a lifetime $\tau \simeq 10^{-9}$ s, only 10^9 pairs/cm^3 will be present under steady-state conditions, which is equivalent to 10^5–10^6 pairs in the sample, i.e., many orders of magnitude below the sensitivity of the ESR spectrometer.

Magnetic spin effects have now been used to investigate a large number of electronic processes in molecular crystals and polymers, and we shall now consider typical examples.

The mechanism responsible for charge separation of the surface of an anthracene crystal coated with a dye was investigated in Ref. 22. Singlet charge pairs (with the hole located in the anthracene crystal) were produced by exposing the dye film to light. A magnetic field was found to influence the evolution of the spin of the pair. Recombination of charges in triplet pairs gave rise to triplet excitons,[3] which were detected by recording the delayed fluorescence of anthracene, induced by exciton annihilation. Similar studies performed with isotopically substituted materials[23] showed that the hole in anthracene was mobile and the hyperfine interaction occurred only in the dye molecules.

The magnetic effect in dark carrier injection from metal electrodes into a film of tetrathiotetracene was observed in Ref. 24, in which a singlet state with charge transfer was initially formed. In a field of the order of 100 Oe, the effect is due to the hyperfine interaction mechanism. It was found that the accumulation of charges in traps during injection influenced the magnetic effect by modifying the local magnetic field in which the pair spins evolved.[25]

Photogeneration of carriers in rubrene has been used to

show that the accumulation of rubrene peroxide in a film sample gives rise to charge-transfer states in which the acceptor is the peroxide molecule. The magnetic effect also shows the presence of a slow component due to the diffusion of oxygen into the sample.[26] The photoconductivity of crystals of charge-transfer complexes such as anthracene-tetracyanbenzene and anthracene-dimethylpyromellitimide have also been found to exhibit a magnetic effect due to the initial recombination of pairs of charges produced during the photoexcitation of a crystal within the charge-transfer band.[27]

The production of electron-hole pairs by autoionization from the higher-lying singlet excited states has been observed[28] in crystals of para-terphenyl when they were excited up to 10 eV.

Autoionization of these states was also found to result in triplet excitons whose annihilation produced delayed fluorescence, but was sensitive to the magnetic field.

The effect of a magnetic field on the photoconductivity and fluorescence of polyvinylcarbazole[29] has been used to investigate the production of carriers in this important photosensitive conductor. The magnetic effect in the photocurrent was positive, a function of the applied voltage, and showing an increase when acceptor impurities were introduced into the polymer. These observations have led to the conclusion that charge carriers are formed as a result of the dissociation of excited complexes formed by the polyvinylcarbazole molecules and the acceptors. In another photosemiconductor, namely, polyepoxypropylcarbazole containing traces of rhodamine 6G, the magnetic effect on the photocurrent and fluorescence was used to identify the role of oxygen in the production of carriers, namely, the magnetic sensitivity of fluorescence was observed only in the presence of oxygen, and the photoconductivity was higher.[30,31] In polyphenylacetylene containing traces of chloranil, it was found that the photoconductivity was determined by the dissociation of excited charge-transfer complexes formed between the polymer molecule and the additive.[32] The magnetic effect was recorded[32] while the magnetic field was periodically turned on and off, and it was found that the magnetic effect had two components, one fast and the other slow, with different dependence on the magnetic field H_0. This was used to deduce that triplet excitons were moving in the polymer and were interacting with carriers captured by traps, the rate of the process being a function of the magnetic field.

3.4. Magnetic spin effects associated with the motion of charge carriers

The dependence of charge-carrier transport on the spin of colliding particles has been investigated in the literature in terms of a number of models. For example, the scattering of carriers by hydrogen-like impurities was examined in Ref. 33 as a function of the mutual orientation of the spins of the carrier and impurity. Spin polarization in a magnetic field at low temperatures (0.4 K) has been found to produce a change in the photoconductivity of silicon doped with phosphorus.[34] The anomalous magnetoresistance of amorphous germanium and silicon has been interpreted[35] in terms of a model in which hopping conductivity was assumed to be due to transitions via a doubly-charged state of local centers, where the formation of this state depended on the mutual orientation of the spins of the charges. The dependence on

the external magnetic field was assumed to be due to a change in the spin relaxation time when the field was applied.

A new magnetic effect has recently been reported[36,37] in which a weak constant magnetic field of 10–100 Oe was found to influence the mobility of dark carriers; in polyacetylene $(CH)_x$. This effect is anomalous as compared with the usual magnetoresistance effects. It takes the form of a dependence of the change in resistance on the magnetic field that is typical for processes with the participation of pairs of paramagnetic particles. The rate of the process depends on the mutual orientation of the spins of these particles, and is represented by a monotonically increasing curve that tends to saturate in strong fields. The semisaturation field is $H_{1/2} = 30$ Oe, and the maximum size of the effect is $\Delta R / R = 0.6\%$ at 300 K and 3% at 200 K. The effect did not depend on the mutual orientation of the magnetic and electric fields. The effect was interpreted by taking into account the properties of the energy spectrum of polyacetylene, namely, the fact that, at the center of the 1.5-eV band gap, there were levels corresponding to mobile topological defects, i.e., solitons. These occurred at the points at which there was a change of phase in the alternation of single and double bonds in the polyacetylene molecule. Neutral solitons have spin 1/2 and can capture an electron or hole and thus transform into charged diamagnetic solitons. Since the concentration of neutral solitons is up to 2×10^{19} cm^{-3}, it is reasonable to suppose that they can play a dominant role in transport processes. The soliton is an interesting example of a paramagnetic impurity which, in contrast to ordinary impurities, has an intrinsic mobility within the limits of a molecule, although this is not a fundamental feature of the magnetic effect.

The effect was explained as follows in Refs. 36 and 37. Charge carriers (holes) appear in the polyethylene as a result of the capture of an electron by the acceptor impurity (I_2). Magnetically sensitive hopping involves pairs consisting of localized polarons and solitons, in which the polarons are localized near ionized acceptors. The energy levels of such polarons lie at the center of the band gap. The magnetosensitive process can be written in the form of the reaction[1,3]

$$(\dot{h}^+ + \dot{S}) \to {}^1(h^0 + S^+),$$
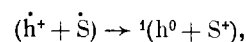
where h^+ is the polaron, $\dot{S}$ and S^+ the neutral and charged solitons, and h^0 the neutral link in the –CH– chain to which the electron from the soliton can hop. There are also charge-transfer processes whose rate is spin-independent. The hyperfine interaction succeeds in mixing all the S and T states during the lifetime of the pair $(h^+ \dots S)$ for $H_0 = 0$, and escapes along the singlet channel deplete all the states of the pair. As the Field H_0 increases, the pair states T_{+1}, T_{-1} cease to mix with the S state, and the number of effective decay channels available to the $(h^+ \dots S)$ pair decreases, which leads to an increase in the pair lifetime in the localized state and, as a consequence, a reduction in the hopping mobility of carriers. Thus, to interpret the anomalous magnetoresistance phenomenon, we must again use the idea of pairs of paramagnetic particles produced under nonequilibrium conditions, whose lifetime is shorter than the spin relaxation time in the medium. A nonequilibrium state occurs in this case as a result of the application of the external electric field. A more detailed theory of this effect is given in Ref. 38.

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Finally, we note the effects of a weak magnetic field on the photoconductivity of illuminated silicon crystals,[39] believed to be due to the spin-dependent recombination of carriers. Magnetic spin effects have also been observed in plastically deformed silicon.[40]

3.5. Annihilation of triplet excitons

Studies of the effect of a magnetic field on photoconductivity were soon followed by observations of a similar effect in luminescence. It was found[41,42] that delayed fluorescence, produced as a result of the formation of singlet molecular excitons in collisions between triplet excitons, was sensitive to the magnetic field, and that the effect of a magnetic field on the intensity of delayed fluorescence in anthracene was due to the magnetic-field dependence of the triplet annihilation rate γ_{TT}.

The annihilation of triplet excitons can be described by the process

$$^3A + {}^3A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^{1,3,5}(^3A \ldots {}^3A) \overset{k_2}{\rightarrow} {}^1A_i + {}^1A_0. \tag{3}$$
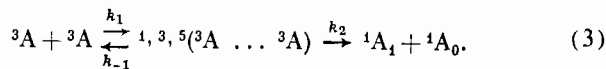
The annihilation rate constant is

$$\gamma_{TT} = \frac{k_1 k_2}{k_2 + k_{-1}},$$

where k_1, k_{-1}, and k_2 are constants representing the collision rate, backscattering, and the formation of singlet products, respectively.

It is assumed that free excitons do not interact with one another before the pair $(^3A \ldots {}^3A)$ is produced. The lifetime of this type of contact pair was assumed to be much shorter than the spin relaxation time, so that the reaction rate depended on the spin state of the pair.

It can be shown that, when the closely spaced levels are nondegenerate, one can use an approximate calculation based on the populations of the stationary states of the spin Hamiltonian of the pair. This is equal to the sum of the spin Hamiltonians of the free triplets:

$$\hat{H} = g\beta H_0 (\hat{S}_1 + \hat{S}_2) + D(\hat{S}_{z_1}^2 + \hat{S}_{z_2}^2) + E(\hat{S}_{x_1}^2 + \hat{S}_{x_2}^2 - \hat{S}_{y_1}^2 - \hat{S}_{y_2}^2). \tag{4}$$

The contact pair of two triplets has nine spin substates, forming a singlet, a triplet, and a quintuplet. The rate of production of each substate is $k_1 n_T/9$, where n_T is the concentration of free triplet excitons. The scattering process is spin-independent and, in contrast to it, the spin conservation rule is significant for annihilation. The rate of annihilation of each $i$the spin state can be written in the form $k_2|S_i|^2$, where S_i is the amplitude of the singlet component in this state. Annihilation from the ith substate then has the probability

$$\frac{k_2 |S_i|^2}{k_{-1} + k_2 |S_i|^2}.$$

The total rate of annihilation is obtained by summing the probabilities over all substates:

$$\gamma_{TT} = \frac{1}{9} k_1 \sum_{i=1}^{9} \frac{k_2 |S_i|^2}{k_{-1} + k_2 |S_i|^2}, \tag{5}$$

from which it follows that γ_{TT} increases with increasing number of states containing a fraction of the singlet component. As in the case of doublet-doublet pairs, the reason for the magnetic effect is that the magnetic field modifies the distribution of the singlet component over the states. The spin Hamiltonian (4) consists of two parts that describe the Zeeman splitting and the splitting in zero fields, respectively. When $H_0 = 0$, the eigenstates of the Hamiltonian correspond to the principal values of the dipole tensor of the zero field H_0^T, and, in an anthracene single crystal, only three spin states are then found to have the singlet component. The application of a magnetic field $H_0 < H_0^T$ leads to the additional mixing of states corresponding to H_0^T, and to the distribution of the single component over a larger number of states, i.e., an increase in γ_{TT}. In the strong-field region $(H_0 \gg H_0^T)$, the Zeeman splitting is much greater than the zero-field splitting, and the latter can be regarded as a perturbation. Spin states are then quantized along the external field, and only two singlet states remain, i.e., there are fewer of them than in zero fields. The value of γ_{TT} is thus reduced in strong fields and, consequently, there is a reduction in the fluorescence intensity. The rate constant $\gamma_{TT}(H_0)$ calculated in this way is found to be in good agreement with experiment. The most complete theory of magnetic-field modulation of the rate of triplet-triplet annihilation is given in Ref. 43, where both the spin and space wave functions of the triplet exciton are used in explicit form.

In the process that is the opposite of (3), and in which the singlet excitation splits into a pair of triplet excitations, the change in the spin state of the pair under the influence of the external magnetic field appears as a change in the intensity of fast fluorescence. Such studies have been reported not only for tetracene[44] and rubrene,[45] in which the energy of the two triplet excitons is close to the energy of the singlet excitation, but also for anthracene, in which the vibrationally-excited singlet excitons were found to split.[46]

In molecular crystals containing impurity molecules, e.g., anthracene with a tetracene impurity, different triplets can annihilate and produce magnetically sensitive delayed fluorescence by both the crystal itself and the impurity.[47]

3.6. Reactions between triplet excitons and radicals

It was found in Ref. 48 that the rate of quenching of triplet molecular excitons in anthracene by paramagnetic centers was reduced when a magnetic field was applied, and an interpretation of this phenomenon was put forward. When the triplet exciton ^3A collides with the radical ^2R or some other spin 1/2 paramagnetic particle, the result can be a scattering of the triplet, which is spin-independent, or quenching. Quenching involves a transition from the initial spin state, that is a mixture of a doublet and a quartet, to a pure doublet final state

$$^3A + {}^2R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^{2,4}(^3A \ldots {}^2R) \overset{k}{\rightarrow} {}^1A + {}^2R. \tag{6}$$
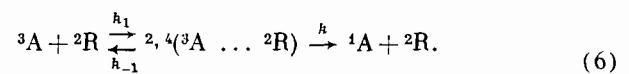
The rate k_l of a transition from each of the six lth initial substates to the final state depends on the amplitude of the doublet component that it contains:

$$k_l = k(|D_l^+|^2 + |D_l^-|^2),$$

where $D^\pm$ is the amplitude of the doublet component $m_s = \pm 1/2$ in the initial state. The total rate of quenching of the exciton by the paramagnetic impurity is

$$Q = \frac{1}{6} q \sum_{l=1}^{6} \frac{k_l}{k_{-1} + k_l}, \tag{7}$$

where q is the rate of collisions between excitons and radicals and k_{-1} is the rate of scattering. Quenching will be a maximum for a uniform distribution of the doublet component over all the six substates, i.e., for

$$|D_l^+|^2 + |D_l^-|^2 = \frac{1}{3}$$

for all l. Minimum quenching occurs for a complete separation of the doublet and quartet. Calculations show that the quenching rate is a maximum in zero field. Application of the external magnetic field ensures that the doublet component becomes localized on four substates, and quenching is reduced.

The photocurrent is often found to be sensitive to a change in the rate constant for the interaction between the triplet excitons and charges captured by traps. This interaction produces quenching of the triplet excitons and the appearance of free carriers.[49,50]

3.7. Reactions involving oxygen

In reactions between triplet excitons and oxygen molecules, the intermediate pair involves the stable particle[3] (O_2). The discovery of the effect of the magnetic field on the rate of photoexcitation of tetracene[51] was soon followed by a theoretical model of this phenomenon.[52] It is based on the magnetic sensitivity of the rate constant γ for the process that is one of the initial stages of excitation:

$$^3A + {}^3(O_2) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [{}^3(O_2) \ \dots \ {}^3A] \overset{k_2}{\rightarrow} {}^1A_1 + {}^1(O_2). \qquad (8)$$
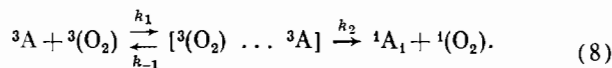
The calculation was performed for anthracene molecules and the results do not depend on the state in which the singlet oxygen is formed. The spin Hamiltonian for the pair $[{}^3A + {}^3(O_2)]$ is

$$\hat{H} = g_1\beta H_0\hat{S}_1 + \hat{S}_1 D_1 \hat{S}_1 + g_2\beta H_0 \hat{S}_2 + D_2\left(\hat{S}_{2z}^2 - \frac{2}{3}\right), \qquad (9)$$

where D_1 and D_2 are the zero-field splitting tensors, the indices 1 and 2 refer to anthracene and oxygen, respectively, and the direction of the z axis is taken along the axis of the molecule O_2. The calculation takes account of the very sharp difference between the zero-field splitting of anthracene and oxygen (300 Oe and 30 kOe) and the twofold degeneracy of the oxygen levels in zero fields due to the axial symmetry of O_2. The form of the function $\gamma(H_0)$ is reproduced in Ref. 52 and is in good agreement with experimental data.[51] The change produced by the magnetic field in the rate of photooxidation leads to a change in the stationary concentration of oxygen, which is a slow process due to the diffusion of oxygen in the sample. Hence, the effect of the magnetic field on the oxygen concentration during photooxidation is also found to have a slow component.[26]

4. MAGNETIC EFFECTS IN PRIMARY PHOTOSYNTHETIC PROCESSES

The separation of charges produced during photoexcitation is a key problem for the understanding of primary photosynthetic processes, and is common to organic semiconductors and biological systems. It is particularly important in relation to the conversion of solar energy into electric power, using electronic processes in solids. Studies at the interface between molecular semiconductor electronics and biology are particularly interesting because, on the one hand, they enable us to simulate individual elementary pro-

cesses that are important for biology, using relatively simple molecular systems, and, on the other hand, they enable us to exploit the principles underlying the organization of processes that lead to maximum efficiency.

4.1. Spin effects in processes involving chlorophyll molecules

Studies of photoprocesses in model systems have shown that the behavior of chlorophyll is typical for organic molecules with a conjugated system. The application of a magnetic field to a solid layer of chlorophyll-a produces two changes in the photoconductivity of outgassed chlorophyll films with different time constants, namely, a fast increase in photoconductivity ($\tau \ll 1s$), followed by a slow reduction with a time constant $\tau \cong 10$–100 s (Ref. 53). Each component has its own dependence on H_0. The former has a dependence typical for the hyperfine interaction mechanism in donor-acceptor pairs, and the second has a dependence typical for a pair consisting of a triplet exciton and a trapped carrier. The formation of separated charges in processes involving excited chlorophyll molecules in the liquid phase has been investigated by studying the influence of the magnetic field on the photoconductivity of solutions of chlorophyll-a in isopropyl alcohol containing different donors (pyrene, diethylaniline) and acceptors (nitrobenzene, benzoquinone).[54] The semisaturating field for the magnetic effect is relatively low (about 30 Oe) and this suggests that the mechanism responsible for the mixing of singlet and triplet states of radical ion pairs is the hyperfine interaction. The deactivation of the chlorophyll molecule excited by light and the generation of free carriers are very similar, on the whole, to the scheme reproduced in Fig. 3, but there are also differences. Thus, for a pair consisting of radical ions of chlorophyll and nitrobenzene, the pair energy level (1.69 eV) lies above the triplet level of chlorophyll (1.33 eV), whereas for the chlorophyll-benzoquinone pair, it lies below this level (1.14 eV). In the second case, the triplet radical pairs cannot be combined into an excited triplet chlorophyll molecule, while return to the ground state is forbidden by spin selection rules. This means that recombination of the singlet pair should be faster than that of the triplet pair. Accordingly, the positive sign of the observed magnetic effect suggests the preferential formation of radical ion pairs via the triplet state of chlorophyll. The energy level of the chlorophyll-nitrobenzene pair lies above the chlorophyll triplet level, so that the pair is populated via the chlorophyll singlet (1.85 eV). Studies of model reactions in chlorophyll solutions[54] have shown that the transfer of the electron to the acceptor in the excited singlet chlorophyll molecule occurs when the energy of its triplet state is insufficient to produce an ion pair. On the other hand, if the transfer of the electron is possible both from the singlest and the triplet states, electron transfer at moderate acceptor concentrations occurs preferentially along the triplet channel. The same studies have shown that pheophytin can act as an acceptor relative to excited chlorophyll.

4.2. Spin effects in reaction centers

In contrast to films and solutions that are relatively homogeneous systems, chlorophyll is distributed nonuniformly in the cells of photosynthesizing organisms, and is concentrated mostly in functional photosynthetic units which, in

turn, aggregate into large formations, i.e., chloroplasts. Each cell consists of 20 to 100 chloroplasts. Within each photosynthetic unit, a large number of light-collecting molecules operates on the photochemically active chlorophyll molecule, forming a "reactive center" with the primary donor and acceptor, and certain other molecules. It is generally accepted that the primary photochemical photosynthetic reaction is a reversible oxidation-reduction transformation of chlorophyll in a reactive center.[55] This reaction produces a separation of charges whereby an electron is transferred over the system of acceptors to the nicotinamide adenine dinucleotide phosphate (NADP) and, by reducing it, stores energy for dark synthesis reactions.

We have already seen that methods involving the effect of a magnetic field on the spin state of radical ions can be applied to charge separation processes. The early work on the effect of a magnetic field on spin processes during photosynthesis was carried out on reactive centers of certain photosynthesizing bacteria. Nanosecond optical spectroscopy was used in Ref. 56 to show that the yield of triplet states in isolated reactive centers of photosynthesizing bacteria was reduced when the magnetic field was applied. The dependence of the effect on H_0 is a negative "step" that reaches 50% at room temperature, with a semisaturation field of about 500 Oe. These results are explained in Ref. 56 in terms of the formation of the singlet radical ion pair $^1(P^+I^-)$ in the reactive center in which the singlet-triplet conversion takes place at an H_0-dependent rate. In the work reported in Ref. 56, and in the great majority of subsequent publications, electronic transport in reactive centers was blocked by chemical reduction of the secondary acceptor FeQ to the state FeQ$^-$, or by the removal of this acceptor. The lifetime of the radical ion pair (P^+I^-) is then much greater than under natural conditions and amounts to 10 ns. The magnetic effect was also investigated in Ref. 57 in chromatophores of photosynthesizing bacteria *Rhodopseudomonas sphaeroides* with a view to isolating reactive centers and carotenoid-free mutant R-26 of these bacteria. Measurements were made of the triplet-triplet absorption and its dependence on the magnetic field. The lifetime of the bacteriochlorophyll triplets at room temperature was found to be 5 μs in the absence of carotinoids to which the triplet excitation was transferred. Figure 4 shows a scheme of primary processes that explains the effect of the magnetic field on the yield of bacteriochlorophyll triplets ^3T.

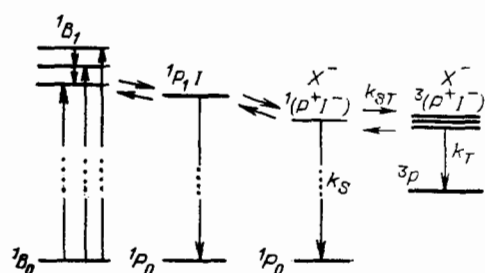The assumption that the radical pair can play a part in the S-T transition in reactive centers was put forward even

FIG. 4. Schematic of primary processes in reactive centers of photosynthesizing bacteria: ^{54}P—bacteriochlorophyll in a reactive center, $^1B_1$—bacteriochlorophyll of an antenna, $^1(P^+I^-)$ and $^3(P^+I^-)$—radical ion pairs in singlet and triplet states; I—primary acceptor (chlorophyll-a, pheophytin-a or bacteriopheophytin-a, X$^-$—reduced secondary acceptor preventing pair dissociation.

before the experimental confirmation of this fact on the basis of the magnetic effect in Ref. 58. In Ref. 59, the mixing of singlet and triplet states of the pair was explained in terms of the hyperfine interaction and, hence, an explanation was offered for the polarization ($m = 0$) of the chlorophyll triplets in an external magnetic field (all the triplet sublevels are equally populated in zero fields).

Theoretical calculations of the magnetic effect in reactive centers were carried out in Ref. 60. The magnetic field was found to be very dependent on the presence of the exchange interaction between P$^+$ and I$^-$ and between I$^-$ and FeQ$^-$ (X$^-$). The exchange interaction $J(P^+I^-)$ produces an increase in the effect in fields corresponding approximately to $2J$ because of the mixing of the S and T$_{+1}$ states. This increase has not been observed experimentally, which means that J is small (less than 10 Oe). The exchange interaction $J(I^-X^-)$ violates the spin correlation in the pair (P^+I^-), which leads to a reduction in the magnetic effect. Calculations show that $J(I^-X^-)$ is of the order of 2 Oe.

The transformation of singlet into triplet pairs competes with the recombination process that leads to fluorescence. Consequently, one would expect that the magnetic field should affect the fluorescence of photosynthesizing bacteria. It was found in Refs. 61 and 62 that the application of a magnetic field increased by 1–3% the fluorescence intensity from chemically reduced bacteria. Studies of the effect of a magnetic field on the yield of radical pairs and triplet states in reactive centers freed from the secondary acceptor FeQ, using nanosecond resolution, have shown[63] that the triplet yield was increased and the semisaturation field decreased with time. The experimental data were used to determine the rate constants for the recombination of singlet and triplet pair states ($k_S = 3.9 \times 10^7$ s^{-1} and $k_T = 7.4 \times 10^8$ s^{-1}) and the magnitude of the exchange interaction [$J(P^+I^-) = 3.3$ Oe].

In Refs. 64 and 65, magnetic effects were compared for normal and completely deuterated bacteria. When all the protons are replaced with deuterons, the hyperfine interaction constant should, according to the calculations reported in Ref. 60, produce a reduction by 25% in the triplet yield. However, this did not occur. The magnetic effect and the semisaturation field did not change as a result of deuteration.[65] There is no explanation, as yet, of this fact.

Magnetic effects in photosynthesizing systems under natural conditions are much smaller than those observed in chemically prepared samples. Synchronous detection of the magnetic effect produced by an amplitude-modulated magnetic field has been successfully used[66] to measure the very small (up to a few thousandths of a percent) changes in the fluorescence intensity over a time interval of the order of a second. When leaves of plants held in the dark were illuminated, the fluorescence produced mostly by photosystem II was found to vary with time, following the so-called induction curve: at first ($\sim 10^{-9}$ s), the antenna pigments that received energy in energy-transfer processes from electronically excited chlorophyll molecules were found to fluoresce, and, thereafter, they received further excitation energy due to the recombination of the radical ions. The shape of the induction curve between 0.1 and 100 s is determined by the change in the conditions under which recombination and separation of charges and pairs take place. By recording changes in the corresponding magnetic effect, it is possible to

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obtain information on the evolution of the spins of the radical ions during the pair lifetime, and to estimate the lifetime. The two basic experimental results that have been obtained for leaves of the higher plants are that the magnetic effect has been recorded and investigated near the fluorescence maximum on the induction curve, i.e., when the reactive centers of the photosystem II were essentially blocked by electrons filling the pool of acceptors and, in the steady state, for times in excess of 60 s on the induction curve.[66] By that time, the adaptation of the leaf to light and the activity of photosystem I ensured that the pool of acceptors was exhausted and the escape of charges along the electron transport circuit was the principal pair decay channel. The dependence of the relative change in the fluorescence intensity on H_0 in these two cases is shown in Fig. 2. It is clear that the semisaturation field of reactive centers closed to dissociation is about 16 Oe, whereas the corresponding figure for open centers is about 200 Oe. This leads to an estimated lifetimes of radical ion pairs in reactive centers of 10 ns and 250 ns for open and closed centers, respectively.

We may therefore conclude that magnetic effects in photosynthesis are a source of information on the general properties of the pair separation process in organic semiconductors and reactive centers. It is interesting to note that the magnetic sensitivity of leaves persists as the temperature is reduced to 77 K. This shows that the motion of charges in pairs is essentially electronic rather than ionic in character, which enables us to consider that solid-state models are closer to reality than liquid solutions.

Comparison of primary processes produced by light in biological photosystems and photosystems based on organic semiconductors shows that both cases demonstrate the absorption of light, energy migration, autoionization of excited molecules, and charge separation and migration. The basic differences are due to the high efficiency of charge separation in photobiosystems as compared with homogeneous semiconductors. Determinations of the lifetime of pairs in open and closed reactive centers show that the initial, geminate recombination of charges (at the rate of 10^8 s^{-1}) in closed centers becomes much less probable in open centers because of the high rate of irreversible transitions of electrons from the primary acceptor to the electron-transport circuit. Such fast transitions can be due to the fact that two processes take place in reactive centers, namely, (1) rapid dissipation of electron energy and (2) localization of the electron on acceptor molecules with successively increasing electron affinity. During photosynthesis, charge separation
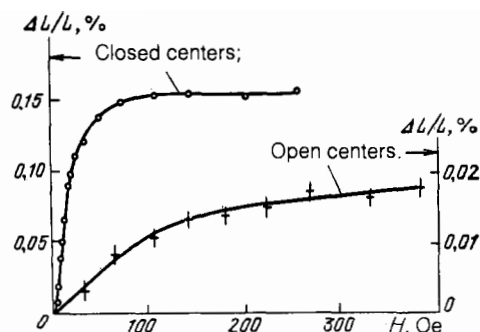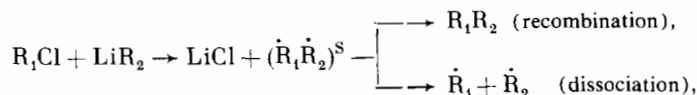

FIG. 5. Relative change in the intensity of fluorescence of green leaves of plants as a function of the magnetic field for closed and open reactive centers of photosystem II.[66] The higher semisaturation field of open centers compared to closed ones is a consequence of the reduction in the pair lifetime from 10 ns to 250 ps.

occurs because of the deeper localization of the electron as it travels away from the positive charge, with the loss of a fraction of its energy. The reverse process, i.e., recombination, becomes energetically unfavorable. Simulation of this principle may turn out to be useful for the development of efficient charge-separation systems. The part played by triplet excited states of chlorophyll, formed in closed reactive centers and in the antenna, has not been adequately investigated.

5. EFFECT OF A MAGNETIC FIELD ON CHEMICAL REACTIONS

The empirical search for the effects of a magnetic field on purely chemical processes has a long history. Such searches are usually initiated by people who do not appreciate (or simply ignore) the important physical fact that magnetic energy is negligible in comparison with chemical energy. The desired effects were often "discovered," but subsequent, more rigorous, experimental investigations, usually performed by serious scientists, negated such results. This peculiar duel has continued for almost a century, but it was only after the discovery of spin phenomena that the problem of the magnetic field in chemical reactions was placed on a firm scientific basis.

Reliable and metrologically well-founded field effects in chemical reactions in the liquid phase were discovered in 1972 (Ref 8). Reactions of photosubstituted benzyl chlorides with butyllithium, investigated in Ref. 8, are described by the scheme

$$R_1Cl + LiR_2 \rightarrow LiCl + (\dot{R}_1\dot{R}_2)^S \begin{cases} \longrightarrow R_1R_2 \quad \text{(recombination)}, \\ \\ \longrightarrow \dot{R}_1 + \dot{R}_2 \quad \text{(dissociation)}, \end{cases}$$

where R_1 are the radicals $C_6F_5\dot{C}H_2$, n-$FC_6H_4\dot{C}H_2$, and $(C_6F_5)_2\dot{C}H$, and R_2 is the radical $\dot{C}_4H_9$ (the dot represents an unpaired electron in a radical).

The precursor of the products of cross recombination R_1R_2 and symmetric recombination R_1R_1 and R_2R_2 is the radical pair $(\dot{R}_1,\dot{R}_2)$ in the singlet state, formed during the chemical interaction between the two molecules R_1Cl and

R_2Li. The ratio of the product yields $(R_1R_2)/(R_1R_1)$ is a function of the magnetic field (Fig. 6). It is readily seen that this effect is in excellent agreement with the predictions of the spin theory: the S-$T_{\pm}$ conversion channels close as the field increases (Fig. 1), and there is a reduction in the loss of pairs to the triplet state. The result is a reduction in the rate of dissociation of pairs and an increase in the rate of the
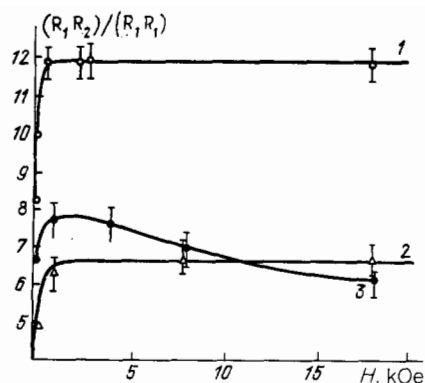
FIG. 6. Product yield ratio $(R_1R_2)/(R_1R_1)$ as a function of magnetic field in the reaction of C_4H_9Li with pentafluorobenzyl chloride (1), fluorobenzyl chloride (2), and decafluorodiphenylchloromethane (3).[67]

competing recombination reaction. For the first two reactions with $R_1 = n\text{-}FC_6H_4\dot{C}H_2$ and $C_6F_5\dot{C}H_2$ in the radical pair $(\dot{R}_1\dot{R}_2)^S$ we have $\Delta g \simeq 0$, and the singlet-triplet conversion is induced only by the Fermi interaction, so that the field effect is saturated even in weak fields $H \simeq a$; the effect is much greater for the second reaction because the Fermi interaction in the radical $C_6F_5\dot{C}H_2$ (five fluorine atoms) is greater than in the radical $n\text{-}FC_6H_4\dot{C}H_2$ (one fluorine atom).

In the third reaction with $R_1 = (C_6F_5)_2\dot{C}H$, the $S\text{-}T_{\pm}$ conversion channels at first close as the field increases, and this is accompanied by an increase in the pair recombination probability. The result is that the ratio $(R_1R_2)/(R_1R_1)$ initially increases. However, in this case, $\Delta g \neq 0$ in the radical pair $(\dot{R}_1\dot{R}_2)$, and the increase in the field is accompanied by an increase in the rate of $S\text{-}T_0$ conversion, so that there is a greater loss of pairs to the triplet (dissociative) state, and, hence, a reduction in the probability of recombination. All this means that the ratio $(R_1R_2)/(R_1R_1)$ passes through a maximum.

The particular feature of the above reactions is that they involve radicals in the form of complexes with butyllithium associates (hexamers and tetramers). These radical complexes have low molecular mobility, which facilitates more complete S-T conversion and amplifies magnetic effects. The viscosity of the solvent should have an analogous effect. These theoretical predictions were confirmed experimentally: in low-viscosity solvents, the magnetic field had no detectable effect on the reacti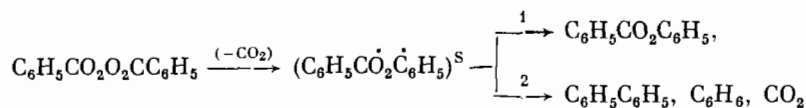on, but, as the viscosity was increased, the magnetic effect was found to increase (up to about 50%). However, in very viscous systems, the effect was again absent because the pair lifetime was long and S-T conversion became periodic and reversible (quantum beats; see above).

The significance of the researchers cited above is that these were first published reports of the discovery of stable and reproducible effects of magnetic fields on chemical reactions in the liquid phase, indicating the scale of the effects and confirming the basic predictions of the theory, i.e., the fact that the field effects are significant only in reactions involving radical pairs with high values of Δg (or high Fermi energies) and slow molecular dynamics ("large" radicals and viscous solutions).

The papers that we have just cited have stimulated extensive research into the effects of the magnetic field in different reactions. The results are discussed in reviews and books.[11,67,68] This research activity continues to grow, and is now attracting dozens of papers each year. It is not our task here to analyze these papers; we confine our attention to some examples illustrating these effects in different types of reaction.

Radical ions pairs $(\dot{M}^+M^-)$ are produced in the singlet state in the pulsed radiolysis of aromatic hydrocarbons in cyclohexane or squalane. Their annihilation (recombination) results in singlet excited fluorescing molecules M*. The Fermi interaction induces S-T conversion and reduces the fluorescence intensity, increasing the fraction of triplet pairs whose annihilation results in triplet–excited nonfluorescing molecules M. The singlet yield increases, whereas the triplet yield decrease with increasing magnetic field. The reason for this effect is the same as in the experiments of Molin et al.: as the field increases, the $S\text{-}T_{\pm}$ conversion is turned off, the fraction of pairs retaining the initial spin multiplicity increases, and there is an increase in the fluorescence intensity. In agreement with theoretical perdictions, the size of the effect reaches its limit in weak fields $H \simeq a$ ($\Delta g = 0$) and is higher in viscous solvents. The effect depends on the Fermi energy: it increases along the series of hydrocarbons, in which the electron-nuclear hyperfine interaction constants increase in the corresponding conjugated radicals, and decreases on deuteration, in which the hyperfine interaction falls by almost an order of magnitude.[69] Similar effects have been found in numerous reactions induced by flash (including laser) photolysis.

In the thermal decomposition and the photolysis of benzoyl peroxide according to the scheme
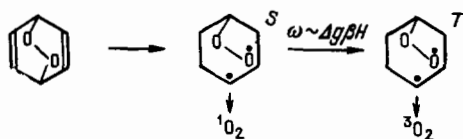
$$C_6H_5CO_2O_2CC_6H_5 \xrightarrow{(-CO_2)} (C_6H_5C\dot{O}_2\dot{C}_6H_5)^S \xrightarrow[\quad 2 \quad]{\overset{1}{}} \begin{array}{l} C_6H_5CO_2C_6H_5, \\[4pt] C_6H_5C_6H_5, \ C_6H_6, \ CO_2 \end{array}$$

the yield of the recombination products, i.e., phenylbenzoate, $C_6H_5CO_2H_5$, decreases monotonically with increasing field, and there is also a monotonic increase in the yield of other products. The intermediate singlet radical pair $(C_6H_5C\dot{O}_2\dot{C}_6H_5)^S$ recombines (path 1) or dissociates into isolated radicals (path 2), which are then tr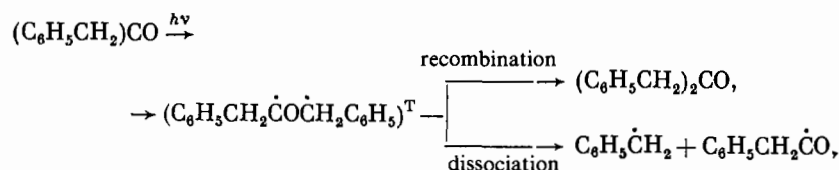ansformed into other products (diphenyl, benzene, and so on). The quantity Δg is large in this pair, and the Zeeman energy difference is much greater than the hyperfine interaction energy, so that the magnetic field accelerates only the $S\text{-}T_0$ conversion and increases the cross section for the dissociative conversion of the pair. The yield of phenyl benzoate is therefore found to

decrease monotonically with increasing field.[70]

In the thermolysis of the endoperoxides of aromatic compounds, the magnetic field has an effect on the yield of the singlet oxygen:[71]

$$\text{(endoperoxide)} \longrightarrow \overset{S}{\text{(diradical)}} \xrightarrow{\omega \sim \Delta g \beta H} \overset{T}{\text{(diradical)}}$$

$$\downarrow \,^1O_2 \qquad\qquad \downarrow \,^3O_2$$

Fragmentation of the primary singlet diradical produces singlet oxygen, and fragmentation of the triplet diradical generates oxygen in the ground triplet state. An increase in the field is accompanied by an increase in the rate of S-T_0 conversion (the main contribution is due to $\Delta g \beta H$), the yield of $^3O_2$ increases monotonically, and the yield of $^1O_2$ decreases.

The intervention of the magnetic field in spin conversion is particularly well represented in chain reactions in which the initiation and breaking of kinetic chains occurs in radical pairs. For example, in the photolysis of dibenzyl ketone, the triplet-excited ketone molecule decays, forming a triplet pair:
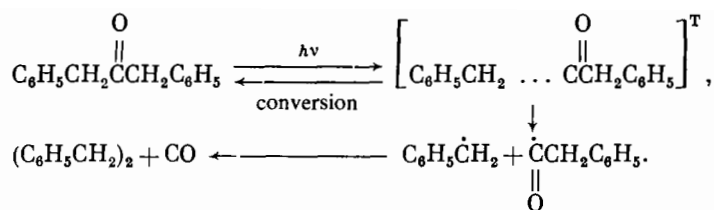
$$(C_6H_5CH_2)CO \xrightarrow{h\nu}$$

$$\rightarrow (C_6H_5CH_2\dot{C}O\dot{C}H_2C_6H_5)^T - \begin{cases} \xrightarrow{\text{recombination}} (C_6H_5CH_2)_2CO, \\ \xrightarrow{\text{dissociation}} C_6H_5\dot{C}H_2 + C_6H_5CH_2\dot{C}O, \end{cases}$$

which then either recombines (after T-S conversion) or dissociates into isolated radicals. The quantum yield of radicals in this photolysis depends on the magnetic field: it increases by 20% even in weak fields ($H \simeq 100$ Oe) because the $T_\pm$-S conversion channels are turned off.

In the radical chain polymerization of styrene in aqueous emulsion in which dibenzyl ketone acts as the photoinitiator, the rate of initiation of polymerization in fields $H \gg a$ is higher because of the increase in the quantum yield of the radicals from the photoinitiator. Since the growth of the kinetic polymerization chain (and the growth of the macromolecule) occurs within a single microreactor, i.e., the emulsion "droplet" of the monomer, the initial radical pair, whose partners lead the polymerization, retains its spin correlation and remains in the triplet state throughout the polymerization process. The recombination of the growing macroradicals is therefore reduced by the magnetic field, and there is an associated reduction in the rate at which the kinetic chains break off, and a growth in the length of the resulting macromolecule. Both effects, i.e., the higher initiation rate and the lower rate at which kinetic chains break off, lead to a fivefold increase in the rate of polymerization and a comparable increase in the molecular mass of the resulting polymer even in fields[72] $H \approx 500$ Oe. This is a clear example of how even weak magnetic-field effects can be "multiplied up" in chain reactions, and can reach quite large-scale effects.

The influence of a magnetic field has also been found in reactions of heteroorganic compounds, photo- and radiation-induced decay reactions, isomerization and ionization of molecules, and thermal reactions of various kinds. The size of the effect in terms of the product yield of luminescence or conductivity is a few tens of percent, whereas, in terms of the rate of interaction of radicals with one another, it amounts to a few hundred percent. Magnetic field effects are also being used by chemists as a diagnostic tool for chemical reaction mechanisms, since they signal the participation of radicals in chemical transformations, whereas the dependence of the effect on the magnetic field indicates which particular radicals predominate in the reaction. When

$\Delta g = 0$ in radical pairs, the field effect saturates for $H \simeq a$. If, on the other hand, the main contribution to S-T conversion of pairs is the Zeeman energy difference, the effect grows monotonically in proportion to $H^{1/2}$, and this suggests that the reaction proceeds through radical pairs with $\Delta g = 0$. When the two contributions (a and $\Delta g \beta H$) superimpose, the field dependence of the magnetic effect exhibits a maximum (for example, curve 3 in Fig. 6).

The sign of the effect is also important for diagnostic purposes: theory shows that it depends on the spin multiplicity of the radical pairs and changes when there is a change in the sign of the $S \rightarrow T$ or $T \rightarrow S$ spin conversion. All these predictions have been frequently seen experimentally. However, the field effects are often small (a few percent) and the experiments have to be metrologically sound if they are to be detected.

6. MAGNETIC ISOTOPE EFFECT

Chemical interaction between radicals is selective in the electron spin of the radical pair and is therefore selective in nuclear spins, as well, since the two spin systems (electronic and nuclear) are coupled by the hyperfine (Fermi) magnetic interaction. The selectivity of reactions with respect to spins and magnetic moments of nuclei, i.e., the dependence of the reaction rate on the nuclear magnetic moments of the reacting radicals, produces a difference between the reaction rate of radicals containing magnetic and nonmagnetic nuclei. This is the magnetic (or nuclear spin) isotope effect. It was discovered experimentally in a number of reactions (thermal and photochemical fragmentation of benzoyl peroxide, photolysis of ketones in solution and in micelles, and chain oxidation of hydrocarbons and polymers). The magnetic isotope effect in these reactions leads to the separation of isotope pairs such as ^{12}C, ^{13}C and ^{16}O, ^{17}O. Let us illustrate this process by a number of examples.

The photolysis of dibenzyl ketone occurs via the fragmentation of the excited molecule in the triplet state with the formation of a triplet radical pair:
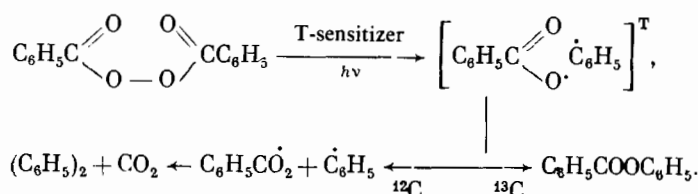
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$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \underset{\text{conversion}}{\overset{h\nu}{\rightleftarrows}} \left[C_6H_5CH_2 \ldots \overset{O}{\overset{\|}{C}}CH_2C_6H_5 \right]^T ,$$

$$(C_6H_5CH_2)_2 + CO \longleftarrow \quad C_6H_5\dot{C}H_2 + \underset{O}{\overset{\|}{\dot{C}}}CH_2C_6H_5.$$

The main products of the photolysis reaction are dibenzyl $(C_6H_5CH_2)_2$ from the recombination of the benzyl radical $C_6H_5\dot{C}H_2$ and carbon monoxide CO from the fragmentation of the benzoyl radical:

$$C_6H_5CH_2\dot{C}O \rightarrow C_6H_5\dot{C}H_2 + CO.$$
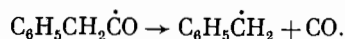
The primary triplet pair

$$[C_6H_5\dot{C}H_2 \ldots \overset{O}{\overset{\|}{C}}CH_2C_6H_5]$$
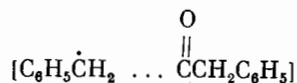
has two possible fates: it either undergoes conversion of the singlet state and recombines during its lifetime, regenerating the original dibenzyl ketone molecule, or the radicals leave the pair by diffusion and transform in solution into dibenzyl and carbon monoxide. The competition between these two transformations of the radical pair depends on the T-S conversion rate and, consequently, on whether the carbon nuclei in the radicals are magnetic or nonmagnetic. When the radicals $C_6H_5\dot{C}H_2$ and $C_6H_5CH_2\dot{C}O$ contain the nuclei of the magnetic isotope ^{13}C, the radical pairs experience more rapid T-S conversion, and tend to recombine. The regenerated dibenzyl ketone is then enriched with the ^{13}C nuclei. The triplet-singlet conversion of pairs whose radicals do not contain ^{13}C is retarded, and the radicals tend to leave such pairs. The products formed by them (dibenzyl and CO) are then enriched by the nonmagnetic isotope ^{12}C.

Actually, it turns out that, during the photolysis of dibenzyl ketone with the natural concentration of ^{13}C, the initial ketone is enriched by a factor of 2–3 with the ^{13}C isotope, whereas dibenzyl and CO are depleted. The separation of isotopes depends on the degree of transformation of the original ketone: the amount of remaining ketone decreases as its concentration of ^{13}C increases.

It follows that the radicals in radical pairs are sorted according to their nuclei: radicals with magnetic nuclei are directed by the reaction into one set of chemical products, while radicals with nonmagnetic nuclei are directed to another. The efficiency of the sorting process increases with increasing energy of electron-nuclear hyperfine interaction, i.e., with increasing difference between the rates of triplet-singlet conversion of radical pairs with magnetic and nonmagnetic nuclei. Thus, in the photolysis of dibenzyl ketones, the most highly ^{13}C-enriched is the central carbon of the CO group, since the hyperfine interaction is a maximum (125 Oe) on the carbon of the CO group in the radical $C_6H_5CH_2\dot{C}O$. On other carbon nuclei of this radical, and of its partner $C_6H_5\dot{C}H_2$, the hyperfine interaction is much smaller and its contribution to isotope sorting is slight. Another example of an isotope selective reaction is the photo fragmentation of benzoyl peroxide:

$$C_6H_5C\overset{O}{\underset{O-O}{\diagdown}}CC_6H_5 \xrightarrow[h\nu]{\text{T-sensitizer}} \left[C_6H_5C\overset{O}{\underset{O\cdot}{\diagdown}} \dot{C}_6H_5 \right]^T ,$$

$$(C_6H_5)_2 + CO_2 \leftarrow C_6H_5\dot{C}O_2 + \dot{C}_6H_5 \underset{^{12}C}{\longleftarrow} \underset{^{13}C}{\longrightarrow} C_6H_5COOC_6H_5.$$

When the T-sensitizer is present, photolysis is accompanied by the formation of the triplet radical pair consisting of the benzoyl radical $C_6H_5\dot{C}O_2$ and the phenyl radical $\dot{C}_6H_5$. When any of the pair radicals contains ^{13}C nuclei, such pairs with magnetic nuclei transform more rapidly into singlet pairs and recombine into phenyl benzoate $C_6H_5CO_2C_6H_5$, which carries off the ^{13}C nuclei. Pairs containing nonmagnetic isotopes tend to fragment into the radicals $\dot{C}_6H_5$ and $C_6H_5\dot{C}O_2$, where the latter fragments into CO_2 and $\dot{C}_6H_5$, and the final products, namely, diphenyl $(C_6H_5)_2$ and CO_2, are depleted in the isotope ^{13}C. The highest isotope separation efficiency is found in the case of the phenyl radical, in which the hyperfine interaction is considerable on one of the carbon atoms and amounts to about 150 Oe.
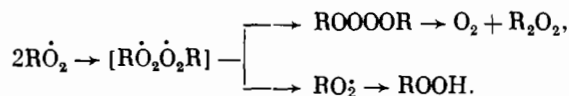
These two reactions were, in fact, the first in which the magnetic isotope effect[9] was discovered, and its properties and the conditions for its maximum manifestation were established.

Oxygen isotope separation has also been found in chain reactions of polymer oxidation by molecular oxygen.[73] The magnetic isotope effect that is responsible for isotope separation appears in this reaction at the stage at which the two peroxide radicals interact:

$$2R\dot{O}_2 \rightarrow [R\dot{O}_2\dot{O}_2R] \begin{cases} \rightarrow ROOOOR \rightarrow O_2 + R_2O_2, \\ \rightarrow RO_2^: \rightarrow ROOH. \end{cases}$$

Here again, when one of the radicals in a pair, say $R\dot{O}_2$ (R represents a macromolecular chain), contains ^{17}O as an end atom (magnetic nucleus), the radical recombines more rapidly into the tetroxide ROOOOR, which is very unstable and regenerates molecular oxygen from the two central atoms, which removes the ^{17}O nuclei. Radicals containing the nonmagnetic isotopes ^{16}O and ^{18}O leave the pairs and transform into molecules of the hydroperoxide ROOH. The regenerat-

ed oxygen is thus ^{17}O-enriched, whereas the hydroperoxide is depleted in this isotope. Figure 7 shows that, as the molecular oxygen is used up in the reaction, its degree of enrichment with the ^{17}O isotope increases and substantially exceeds the enrichment with the ^{18}O isotope, showing that the magnetic isotope effect is much greater than the classical (mass) isotope effect.

The magnetic isotope effect and the isotope separation induced by it have been seen in many reactions, and a theory has been developed that can predict the magnitude and sign of the effect. Searches are in progress for the effect in other heavy nuclei.

In contrast to the classical isotope effect that depends on the mass of the isotopic nuclei, the new effect depends on the magnetic properties of nuclei. Moreover, it has a number of other striking properties, e.g., it is sensitive to the molecular dynamics of the radicals and radical pairs, it depends on the external magnetic field and the lifetime of the radicals (chemical dynamics), its magnitude exceeds by one or two orders of magnitude the magnitude of the classical effect, and the magnitude and sign of the effect depends, in addition, on the spin multiplicity of the radical pair, i.e., the reversal of multiplicity is accompanied by the reversal of the direction of spin conversion and, correspondingly, a change in the sign of the magnetic isotope effect.

The discovery of the magnetic isotope effect is equivalent to the discovery of a new principle of fractionation of isotopes, based on the magnetic moments of the nuclei in natural processes. By analyzing isotope anomalies in the composition of geological or cosmic objects, and by comparing them with the predicted magnetic isotope effect, it is possible to deduce the orign and pathways of chemical evolution of matter on geological and cosmogonic scales. The magnetic isotope effect has also been used as a basis for new methods of investigating chemical and biochemical processes.

7. CHEMICAL RADIOFREQUENCY MASER

One of the remarkable magneto-spin effects discovered soon after the discovery of the magnetic field effect in photochemical and photophysical processes in molecular solids (1965) was the chemically induced polarization of nuclei (1968). The rate of triplet-singlet conversion of radical pairs depends on the magnetic moment of the nuclei and the hyperfine interaction constant, but its magnitude is determined
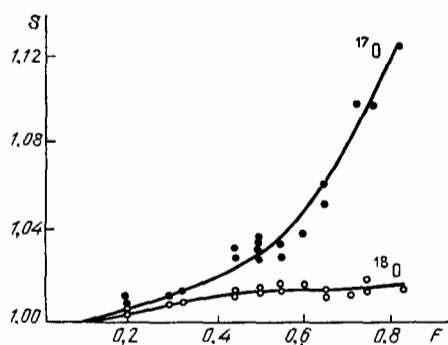

FIG. 7. Isotope concentration S of ^{17}O and ^{18}O in molecular oxygen as a function of its conversion F in the chain reaction of oxidation of polypropylene.[73]

by the total energy of the electron-nuclear interaction, which depends on the nuclear spin component. Radical pairs that differ by nuclear orientation must therefore have different rates of triplet-singlet conversion. It follows that the chemical interaction between the radicals in a pair can be used to sort not only magnetic and nonmagnetic nuclei in different molecules (as in the case of the magnetic isotope effect), but it can also be used to perform the sorting of magnetic nuclei according to their orientation: nuclei with a particular orientation are directed by the reaction to one sort of product, whereas those with opposite orientation to another. The result is that molecules of one type have nuclear polarization of a given sign, whereas molecules of the other type have nuclear polarization of a different sign.[6,7] This is the net effect of chemically induced polarization of nuclei in strong magnetic fields (of the order of a few kOe).

The remarkable property of the chemically induced polarization of nuclei is the large magnitude of the polarization P, which is usually 10^3–10^4 and is much greater than the Overhauser limit. However, there are reactions in which $|P|$ assumes record values and approaches the limit

$$|P_{\lim}| = \frac{2kT}{\hbar\gamma_n H_0}.$$

Thus, the photolysis of cyclododecanone in the liquid phase at 20 °C in a field of 125 Oe produces negative polarization of the protons in this molecule with $|P| \gtrsim 3.6 \times 10^6$, and the probability that the proton is "thrown" into the upper Zeeman state when a chemically active photon is absorbed is in excess of 0.3, i.e., the nuclear polarization quantum yield is 0.3 (Ref. 74). There are also other reactions that are known to have an enormous nuclear polarization.

When the nuclear polarization is negative, the inverted population of nuclear Zeeman states corresponds to a nuclear Zeeman reservoir of molecules (the products of the chemical reaction) with a considerable amount of energy. When this energy exceeds the generation threshold, the negatively polarized nuclear spins exhibit coherent precession that has a transverse nuclear magnetization component. Spontaneous radiofrequency generation of the chemical reaction products then takes place, i.e., the generation of an alternating current of frequency equal to the nuclear spin precession frequency $\gamma_n H$. The chemical reaction then behaves as if it were a molecular radiofrequency quantum-mechanical generator, i.e., a chemical maser.[75,76]

For a monomolecular reaction with rate constant k and nuclear polarization P of reaction products, the condition for the self-excitation of the maser (the condition for the generation threshold) is

$$\frac{(1 - PkT_1)^{1/(1-kT_1)}}{(1-P)^{kT_1/(1-kT_1)}} > 1 + \frac{\Delta f}{\gamma_n \eta q M_0},$$

where P, k, and M_0 are the "chemical parameters," whereas Δf, η, T_1, and q are the radiophysical parameters, M_0 is the equilibrium nuclear magnetization of the radiating molecules, Δf is the half-width of the NMR line, η and q are, respectively, the duty factor and quality factor of the circuit in which the chemical pumping takes place, and T_1 is the spin-lattice nuclear relaxation time. The ability of chemical reactions to generate a high-frequency current provides a bridge between such apparently disparate sciences as chemistry and radiophysics. The property was discovered experimentally in 1978 in the photochemical reaction between por-

phyrin and quinone.[77] The emitters were the quinone molecules, in which a very high proton polarization was established by the reverse chemical transfer of an electron between the reaction partners, i.e., the porphyrin and quinone molecules. Figure 8 shows a typical tracing of the chemically stimulated high-frequency radiation produced in this reaction. The introduction of light (photochemical pump) is followed by a "dead time" during which the inverted population of Zeeman levels and the nuclear polarization are produced. When the generation threshold is reached, the chemical generator signal appears and, after a transition period, the system continues to oscillate for a long time (more than an hour). Generation ceases when the light is turned off (the pump is removed). Different generation states have been achieved in this system, including continuous, aperiodic, and "chemical pulsar" states.

Another example of a chemically pumped radiofrequency maser is that relying on the thermal decomposition of benzoyl peroxide $C_6H_5CO_2CO_2C_6H_5$ at 120° in cyclohexanone. The emitter was one of the main reaction products, i.e., benzene, whose protons had negative polarization exceeding the generation threshold.[78]

Radiofrequency generation is a property of chemical reactions that can be exploited to develop new methods of investigating chemical reactions and new radiofrequency devices, such as magnetometers and chemical masers, in which the working medium consists of the chemical reaction products with inverted nuclear magnetization. A prototype magnetometer, based on the photodisintegration of cyclododecanone, has been developed at the Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences. In a certain definite sense, we are seeing the emergence of a new subject, namely, chemical radiophysics, that is concerned with the generation and reception of radiofrequency radiation at the chemical, molecular level.

8. RESONANCE MAGNETIC MODULATION OF THE RATES OF PROCESSES INVOLVING PAIRS OF PARAMAGNETIC PARTICLES

8.1. Principle of the method for radical pairs

Magnetic effects are seen only when an intermediate pair of paramagnetic particles has a nonequilibrium population of its spin states. One can then expect that resonance transitions between the levels with nonequilibrium populations and a given multiplicity may alter the rate of interaction between the paramagnetic particles in the pair. Although this idea was formulated as far back as 1966 (Ref. 4), theoretical estimates of the conditions under which microwave magnetic fields could have an appreciable effect on the process involving pairs of this kind were found to be not too favorable: when the pair lifetime is less than 10^{-7} s, the necessary microwave magnetic field is $H_1 > 10$ Oe. This unavoidably produces heating of the sample when the field acts continuously. It has been found that, if the pairs are detected by recording their fluorescence, it is sufficient for the microwaves to produce a change of only 10^{-2}–10^{-3}% in the rate of the process, and this is attainable for $H_1 = 0.1$–1 Oe.

The first experiment demonstrating the possibility of a resonance magnetic effect in a short-lived pair of paramagnetic particles was carried out using charge-transfer states produced in the interaction between singlet excitons and impurity molecules of rubrene peroxide in rubrene. A study was made of the fluorescence of thin (3–5 μm) polycrystalline films of rubrene (tetraphenyltetracene) with an area of 0.3 cm^2. The films were deposited by vacuum sublimination onto a quartz substrate, and were placed in the resonator used for the optical detection of magnetic resonance.[79] It was found that the fluorescence intensity from samples at room temperature was reduced as a result of the resonance transitions. The spectrum consisted of poorly resolved lines and was interpreted as a doublet, typical for the magnetic resonance spectrum of radical ion pairs. Similar spectra were subsequently recorded and found to change with increasing degree of photooxidation of rubrene.[80] The spectra reproduced in Fig. 9 show the appearance of the two central lines during photooxidation. They are due to transitions in the doublet-doublet pairs ($D^+ \ldots A^-$) against the background due to pairs of triplet excitons, whose nature will be discussed later. An increase in the concentration of the peroxide molecules A suppresses the formation of triplet exciton pairs and the electron transfer from the rubrene molecule D to the peroxide molecule A. The splitting observed in the spectrum, $\delta H_0 = 250$ Oe, was due to the interaction between the radical ions in the pair. Figure 10 shows the transition scheme for this system that explains the observed effect, where G is the exciting intensity, L is the recorded fluorescence intensity, and $k_{ST}(H_0)$ is the intercombinational tran-
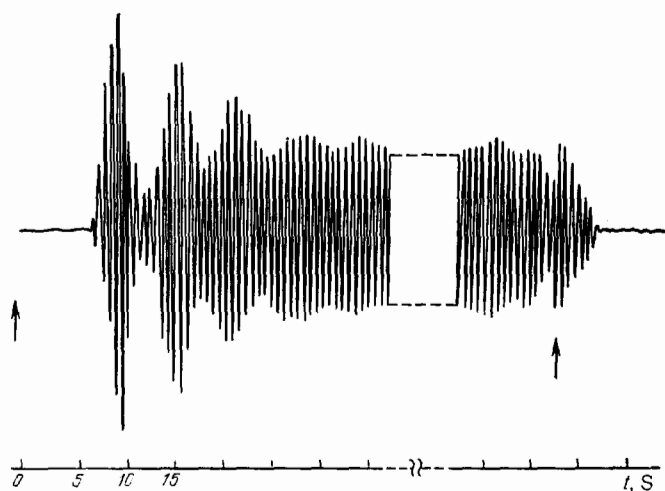
FIG. 8. Chemically induced high-frequency emission from a chemical laser using the photochemical reaction between porphyrin and quinone.[76] Arrows indicate the instants at which light is turned on (beginning of the chemical pump) and turned off. The generation frequency is 60 MHz and the signal is recorded after detection at low frequency.
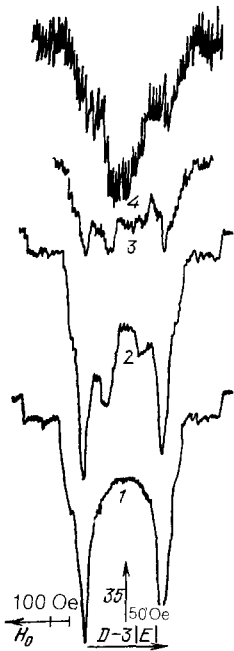
FIG. 9. Magnetic resonance spectra recorded by RYDMR in reactions of short-lived pairs produced during the photoexcitation of rubrene:[80] 1–4 spectra recorded by detecting the fluorescence of solid films of rubrene as the photooxidation of rubrene with oxygen is increased; 2–4 show the appearance of central lines due to transitions in the doublet-doublet pairs $(D^+ \ldots DO_2^-)$ formed in the reaction $^1D_1 + DO_2 \rightarrow (D^+ \ldots DO_2^-)$, where D is the rubrene molecule and DO_2 is rubrene peroxide. Spectrum 1 is due to transitions in the two-triplet pair $(^3D \ldots {}^3D)$ formed during the dissociation of the excited singlet rubrene molecule: $^1D_1 + {}^1D_0 \rightarrow ({}^1D_0 \ldots {}^3D)$.

sition rate constant, which is a function of the external magnetic field. Recombination of the radical ion pairs $^3(D^+ \ldots A^-)$ leads to the formation of triplet excitons in rubrene. The observed resonance quenching of fluorescence is determined by the transitions $\hbar\omega$ in external magnetic fields H_{01}, H_{02}, and H_{03}.

It is important to note that exceptionally high sensitivity is achieved when magnetic resonance is detected by observing fluorescence. In the first experiments, 10^7 pairs of particles with lifetimes of 5×10^{-9} s were recorded in the sample. The sensitivity was subsequently substantially increased. At present, by recording the spectrum for 30 min, it
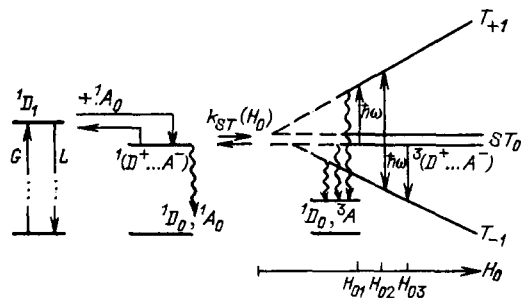

FIG. 10. Formation of doublet-doublet pairs illustrating the relation between the resonance transitions $\hbar\omega$ in the triplet pair of radical ions $^3(D^+ \ldots A^-)$ and the fluorescence intensity.[80]

is possible to obtain a detectable signal from 100 pairs of spins in the sample.

This has been used as a basis for the experimental investigation of short-lived pairs of paramagnetic particles in the condensed phase. In contrast to the usual optically detected magnetic resonance (ODMR), in which transitions between magnetic levels of a molecule produce a change in the probability of optical transitions in the molecule, in the new method, the transitions between Zeeman levels of paramagnetic particles alter the mutual reactivity of these particles. This change in reactivity produces a change in the rate at which the reaction products are produced, which can be detected by any, not necessarily optical, method. This feature of the method is the basis for its name: reaction yield detected magnetic resonance (RYDMR). The changes in the yield of reaction products from pairs can be detected not only by means of luminescence, but also by means of electrical conductivity, specific optical absorption, or other properties that are kinetically related to processes in pairs.

8.2. Size of magnetic resonance effect

The relative change in the yield y of a pair process, due to resonance transitions, is given by the product of the transition probability, the microwave field H_1 causing the transition, and the pair lifetime τ:

$$\frac{\Delta y}{y} = \alpha P \tau.$$

For a radical

$$P = \frac{1}{2} \left(\frac{g\beta}{\hbar} \right)^2 \frac{H_1^2(\tau)}{1 + (g\beta/\hbar)^2 (H_0 - H_0^{\mathrm{res}})^2}. \tag{10}$$

The coefficient $\alpha < 1$ gives the relative change in the yield for a complete change in pair multiplicity. At resonance, $H_0 = H_0^{\mathrm{res}}$ and

$$\frac{\Delta y}{y} = \alpha \omega_1^2 \tau^2,$$

where $\omega_1 = g\beta H_1/\hbar$. It can be shown that, for pairs with a lifetime of 5×10^{-9} s, the fraction $\Delta y/y$ is of the order of 1% for $H_1 \simeq 1$ Oe (with $\alpha = 1$). The minimum detectable value of $\Delta y/y$ depends on the parameter being measured. If this parameter is the luminescence intensity, the minimum value of $\Delta y/y$ is given by the number N of photons reaching the detector during the signal acquisition time:

$$\left(\frac{\Delta y}{y} \right)_{\min} \sim N^{-1/2}.$$

8.3. Detection of RYDMR spectra using electrical conductivity

A change in the photoconductivity under the influence of a constant magnetic field is a reflection of the change in the total concentration of singlet and triplet states with charge transfer, since carriers are released from these states. This follows from the scheme shown in Fig. 5. It may be expected that resonance transitions between Zeeman levels of states $T_{\pm 1}$ and the mixed state $S - T_0$ (Fig. 10) give rise to a change in the photoconductivity if the lifetimes of these states are different. Such changes have, in fact, been observed. Two types of sample were used in the early experiments, namely, a bulk sample (layer of tetracene between two deposited electrodes) and a surface sample. The samples were placed in the resonator of an ESR spectrometer in which they were exposed to a microwave magnetic field

$H_1 \perp H_0$ and were illuminated by a hot-filament lamp producing 10^{15} photons/cm^2. The photocurrent generated in the bulk specimen for a potential difference of 20 V between the electrodes at $T = 300$ K was 10^{-7} A; a comparable current was generated in the surface sample for a potential difference of 150 V. The RYDMR spectrum consisted of a single line with a full width at half height of 17 Oe. The polarity of the spectrum was negative: the photoconductivity was reduced by the microwave field.[81]

In bulk specimens, the source of carriers at room temperature is the interaction between singlet excitons and an electrode, and also the dissociation of states with charge transfer. The concentration of singlet excitons $^1D_1$ is a function of the rate of the reaction between singlet excitons and impurity molecules $^1A_0$ (the most probable impurities are the molecules of tetracene peroxide). This rate, in turn, depends on the population of singlet states with charge transfer. In a magnetic field $H_0 = 500$ Oe, singlet states with charge transfer are mixed with $m = 0$ triplets. Triplet states with $m = \pm 1$ remain unpopulated. The vertical arrows in Fig. 10 show resonance transitions in a pair that deplete the mixed S-T$_0$ state and reduce the concentration of singlet excitons $^1D_1$ detected by recording the reduction in photoconductivity.

In surface samples, dissociation of states with charge transfer is the dominant source of carriers. Its rate is independent of multiplicity. The reduction in the total concentration of pairs $(D^+ \ldots A^-)$ due to transitions between Zeeman levels of the triplet state shows that the lifetime of the mixed state S $-$ T$_0$ is greater than the lifetimes of states with $m = \pm 1$.

The RYDMR method based on photoconductivity can also be used to investigate charge-transfer in crystals of weak charge-transfer complexes, such as anthracene-tetracyanobenzene (A-TCNB); Ref. 82. Polycrystalline samples were employed and absorption of light was found to produce excited pairs $(D^+ \ldots A^-)$ that subsequently dissociated into free carriers. The recorded RYDMR signal was negative, indicating that the lifetime of the triplet state of the pair was shorter than that of the mixed state containing the singlet. The photoconductivity of A-TCNB crystals was found to exhibit a positive static photoconductive magnetic effect. Comparison of these data leads to the conclusion that the mixing of singlet and triplet states of these pairs is due to the hyperfine interaction.

Thus, by using the change in photoconductivity as a means of detecting magnetic resonance, we obtain new information on the mechanism responsible for the transformation of electronic excitation energy. The method is useful for systems in which intermediate states are not seen in fluorescence.

The increase in the dark electrical conductivity of polyacetylene films[83] when conditions for electron spin resonance are satisfied is an interesting example of the magnetic resonance effect in the case of a nonequilibrium particle pair. This result is the first direct demonstration of the production of nonequilibrium pairs of paramagnetic particles, whose polarization is due to the flow of current through the sample. The magnetic resonance spectrum consists of a line of positive polarity of width 10 Oe. It was recorded by measuring the change in the current flowing through the specimen. It not only confirms the spin origin of the magnetic effect in the electrical conductivity of polyacetylene, but also indicates that pairs of doublet particles participate in the current flow. According to the interpretation given in Ref. 83, these particles are a polaron and a paramagnetic defect in a conjugated chain, i.e., a soliton. The change in the pair lifetime due to a resonance transition in the triplet state of a pair produces a change in the hopping mobility of carriers.

8.4. Pulse methods

There are definite advantages in using pulse methods to produce reactions, induce resonance transitions in pairs, and achieve time-resolved detection of luminescence or absorption of light by reaction products. Actually, since the relative change in the reaction rate is

$$\frac{\Delta y}{y} \sim \tau^2,$$

the ability of favor pairs with short lifetimes by artificially induced delay between pair production and the detection of recombinational luminescence can substantially enhance the effect. Moreover, high pump intensities can be used without causing sample heating when short pulses (of the order of 10 ns) are employed. High values of H_1 can be used with pulsed microwave radiation.

Pulsed excitation has been used to investigate the separation of pairs of radical ions in nonpolar liquid solutions containing dissolved donor and acceptor molecules. This is an important reaction in radiation chemistry. Ionization of the solution produces solvent ions and electrons, but the charge of the ion is rapidly transferred to the donor impurity, and the electron is trapped by the acceptor. The particular feature of the nonpolar medium is the initial geminate recombination of the impurity ion. Charge transfer processes, electron capture, and recombination of pairs of charged donors and acceptors occur in a time of 10^{-9}–10^{-8} s, during which spin-lattice relaxation does not succeed in altering the spin state of the pair. These reactions have been found to exhibit a magnetic effect[84] due to the suppression of the mixing of the S and T$_{\pm 1}$ states of the pair by the external magnetic field, which in turn is due to the hyperfine interaction in the radical ions.

The magnetic resonance spectrum of radical ion pairs $(C_{10}H_8^+ \ldots C_{10}H_8^-)$, produced by ionizing radiation in a 10^{-2} M solution of naphthalene in squalane, was recorded in Ref. 85. The ionizing radiation was in the form of fast positrons from a ^{22}Na source. Since the emission of a positron by this isotope is accompanied by the emission of a γ-ray, it was possible to synchronize the measurement of recombinational fluorescence with the ionization pulse. By introducing a delay, it was possible to measure the fluorescence from sufficiently long-lived radical ion pairs with lifetimes in excess of 10^{-9} s. The application of the microwave field of a given frequency to the sample in the resonator of the spectrometer produced a reduction in the rate of photon counting when the resonance conditions for the absorption of microwave power were satisfied. Magnetic resonance spectra of biphenyl ions with resolved hyperfine structure were obtained by adding biphenyl molecules to the squalane.

Periodic pulses of fast electrons (5–55 ns) were used in Ref. 86 to produce ionization in solutions of pyrene in decalene. 100-ns pulses of microwave power were used, and the position of these pulses relative to the ionization pulses could be varied. An adjustable delay between the microwave pulse

and the time at which recombinational fluorescence was recorded could also be introduced.

More detailed studies by the same method[87] were carried out on 10^{-3} M diphenyl oxazole in cyclohexane. They showed that the RYDMR spectra of pairs of radical ions with lifetimes between 30 ns and 4 μs could be recorded by measuring the reduction in the fluorescence yield of the geminate recombination products.

Pulsed RYDMR has also been found to be effective in connection with photosynthesis problems. It has been used to record the magnetic resonance spectra of radical ion pairs during bacterial photosynthesis. The RYDMR signal was in the form of a single peak of width 30 G in the case of quinone-free sample and 135 G in the case of the reduced sample. The samples were pumped by laser pulses. The RYDMR signal was observed by recording optical absorption due to the formation of triplet molecules of bacteriochlorophyll during the recombination of radical ion pairs. The positive sign of the signal was a direct indication that the precursors of the radical ion pairs were singlet excited states of bacteriochlorophyll. The interaction energy of the pairs was estimated.

It was shown in Ref. 89 that the duration of the charge-separation process in a reactive center could be altered under the influence of resonance transitions in the range 22–25 ns. A version of RYDMR was therefore implemented, in which detection was based on the change in the pair lifetime. The pair lifetime can be reduced by the application of a modest microwave power per pulse (< 1 kW). If, on the other hand, the microwave power is increased so that H_1 becomes greater than the hyperfine splitting, the observed lifetime is increased, in accordance with the expected motion of spins in strong fields H_1.

8.5. RYDMR spectra of pairs containing triplet particles

There are considerable opportunities for the application of the RYDMR method to the study of pairs of triplet particles in molecular solids and in liquid solutions. In this case, the method is based on the measurement of changes in the rate of annihilation of pairs of triplet excited particles produced by resonance transitions between Zeeman levels of a pair.

Annihilation is described by (3). Figure 11 shows the level scheme of a pair of identical triplet excitons in a magnetic field. The energy levels are obtained by summing the energies of the corresponding levels of two triplet excitons on the assumption that there is no interaction between the triplets. In a strong external magnetic field $H_0 \ll D, E$ (D and E are the fine splitting parameters of triplet excitons), two of the nine spin states of a pair of equivalent triplet particles contain a singlet component with amplitudes respectively equal to 1/3 and 2/3. These are the states SQ_1 and SQ_2 in Fig. 11. The singlet components of these states are mixed with the components of a quintuplet. Other states of the two-triplet pair (Q_{+1}, Q_{+2}) are pure triplets and quintuplets. When a resonance microwave field is applied, the possible transitions are those with $\Delta m = \pm 1$ at constant total spin angular momentum, where m is the magnetic quantum number. Consequently, only the transitions that involve levels containing a singlet component can produce a change in the rate of a reaction proceeding along the singlet channel. Triplet states of a pair of equivalent triplet particles do not contain a singlet admixture, and transitions between them will not in-
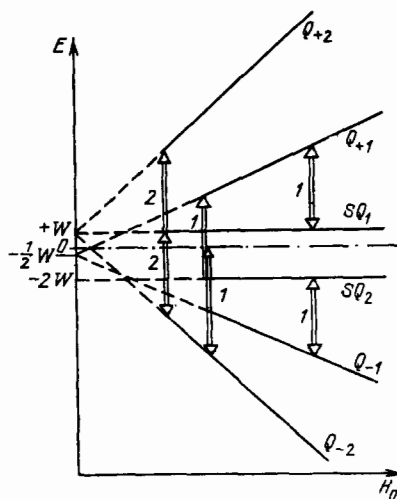

FIG. 11. Energy-level diagram of a pair of equivalent triplet particles in a strong magnetic field.[95] The energy is determined by the Zeeman interaction and fine splitting in triplet particles, and depends on their orientation relative to the constant external magnetic field H_0. SQ_1 and SQ_2 are the energy levels of mixed singlet-quintuplet states, and Q are the levels of the pure quintuplet states. The triplet levels of the pair are not shown. Transitions marked with the figure 1 correspond to $\Delta m = \pm 1$ and those marked with the figure 2 correspond to $\Delta m = \pm 2$. These transitions produce a change in reaction yield in the singlet channel.

fluence the total population of levels containing a singlet. In the case of formation of a pair of nonequivalent triplets, or of configurational interaction between them, the singlet component is mixed with states of all multipolarities. It is important to emphasize that the population of the quintuplet levels Q_{+1} and Q_{-1} that do not contain a singlet component is much higher than the populations of mixed levels SQ_1 and SQ_2. This is a consequence of the fact that each level is populated at the same rate ($k_1 n_T/9$, where n_T is the triplet concentration and k_1 is the triplet collision rate constant), whereas the lifetime of states containing the singlet component is shorter than that of the pure quintuplet state. Hence, the microwave field gives rise preferentially to transitions from quintuplet to singlet states, thus increasing their population. This is why the RYDMR spectrum of a two-triplet pair has a positive sign and corresponds to the ESR spectrum of triplet particles.

Such spectra have been observed in studies of delayed fluorescence at room temperature in polycrystalline powders of the charge-transfer complex anthracene-dimethylpyromellitimide[90] and in single crystals of the complex anthracene-tetracyanobenzene.[91] The spectra of pairs of triplet excitons have also been produced in studies of the fast fluorescence of tetracene[90] and rubrene[92] when excited singlet molecules, responsible for the fluorescence, led to the formation of a pair of triplet excitons in the reaction that was the inverse of triplet annihilation.

Interesting features of the RYDMR spectrum were observed when polarized triplet excitons took part in the formation of two-triplet pairs. When the exciton spins were polarized, the rate of population of the pair levels (Fig. 11) was not the same, and this could give rise to a change in the sign of the RYDMR signal if polarization ensured that central levels (containing the singlet) were more highly populated than the pure quintuplets. This inversion of the RYDMR

lines for a particular orientation of the anthracene-tetra-cyanobenzene crystal has been observed experimentally,[93,94] which means that the populations of levels with $m = \pm 1$ and 0 are not equal in triplet excitons.

When the lifetime of triplet pairs is long, there is a probability that double resonance transitions can be produced for sufficient microwave power levels. In Fig. 11, these are transitions from Q_{+2} (in a weaker H_0) and Q_{-2} (in a stronger H_0) to the level SQ_1 that contains the singlet component. Double transitions are observed in the RYDMR spectrum as narrow lines of anomalous polarity, whose intensity is proportional to the square of the microwave power.[95]

Important photochemical reactions involving triplet excitons with doublet particles are an example of the quenching of the triplet excitation by free radicals, or energy transfer to a trapped electron or hole. The RYDMR spectrum of the pairs ($^3D \ldots \, ^2R$) was established experimentally in Ref. 96 by recording the change in the intensity of delayed fluorescence due to the annihilation of triplet excitons in polycrystalline anthracene-dimethylpyromellitimide in which the lifetime of the triplet excitons was determined by their interaction with free radicals produced by exposure to γ-rays. The RYDMR spectrum contained three lines of positive polarity: one due to radicals and two due to triplet excitons. The transition scheme for the pair ($^3D \ldots \, ^2R$) is shown in Fig. 12, which illustrates resonance transitions in triplets and doublets that are seen as changes in the yield of the reaction (6) into the doublet channel. We note that, when quenching of triplet excitons by radicals is employed, and the corresponding RYDMR spectrum is recorded, the minimum number of radicals necessary for the signal to be detectable is much smaller than that necessary to produce a signal in the most sensitive ESR spectrometer ($< 10^{11}$ particles).

8.6. Magnetic resonance effects in spin-dependent processes in other physical systems
8.6.1. Positronium atoms

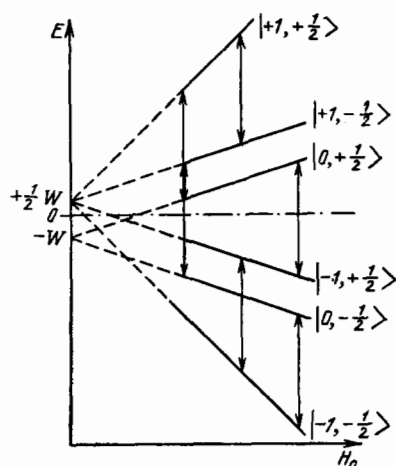The positronium atom is a short-lived electron-positron pair held together by the Coulomb interaction. Its transfor-

FIG. 12. Energy-level diagram of a pair consisting of a triplet particle and a radical in a strong magnetic field.[96] The wave functions are shown for each level together with the resonance transitions in triplets (T) and radicals (R) that produce a change in the rate of quenching of the excited triplet states by radicals, i.e., a change in the yield of the reaction $^3D + \, ^2R$ into the doublet channel.

mations are very dependent on the relative orientation of the spins of the two component particles. The positronium atom was the first analog of a pair of paramagnetic particles in molecular crystals.[3] The positronium atom has singlet and triplet states, referred to as para- and ortho-states. They are separated by 8.41×10^{-4} eV due to the exchange and dipole-dipole interactions, and have different lifetimes and decay modes. The para-states live for 1.25×10^{-10} s and decay by electron-positron annihilation with the emission of two photons. The ortho-state lives for 1.4×10^{-7} s and produces three photons in the annihilation process.

Transitions between ortho- and para-states can be produced by the Zeeman interaction. An external magnetic field mixes the para- and ortho-states ($m = 0$) by the Δg-mechanism. It is important to remember that, in contrast to the electron, the magnetic moment of the positron is antiparallel to the spin, so that positronium has $\Delta g = 2g$. The external magnetic field does not, therefore, have any effect on the energy of triplet levels with $m = \pm 1$, but it does alter the energy of the singlet level and of the triplet level with $m = 0$. In an external magnetic field, the triplet state acquires partially the properties of a singlet state, and the lifetime of positronium prior to annihilation is reduced.

Transitions between levels with $m = \pm 1$ and $m = 0$ were investigated in Ref. 97 for ortho-positronium. They were stimulated by microwave radiation in electron spin resonance, and were found to lead to a change in the lifetime of the positronium atom and its decay modes.

8.6.2. Ionic crystals

A change in the intensity of F-center fluorescence was produced in alkali-halide crystals[98,99] as a result of the resonance absorption of microwave power used to stimulate transitions between triplet levels of an F-center pair in a constant external magnetic field. Here again, there are pure spin effects due to the dependence of the reaction yield on the pair multiplicity. The F-center is an anion vacancy occupied by an electron and constituting a spin 1/2 paramagnetic particle. When the F-center is excited by light (F*), it can "react" with a neighboring center in the ground state (F_0), separated from it by 10–80 Å. This is an electron-tunneling process of the form ($F^* + F_0) \rightarrow \alpha + F'$. Since the reaction products α and F' exist only in the singlet state, electron transfer occurs in singlet pairs of F-centers. The $F^* \rightarrow F_0 + h\nu$ transition occurs in the F* center in the triplet pair $^3(F^* + F_0)$, and can be seen by recording the resulting fluorescence. The illuminated crystal initially has the equilibrium ratio of triplet to singlet F-center pairs. The pair polarization necessary for the detection of the influence of an external field was produced by exciting the F-centers with light, which resulted in the preferential removal of singlet pairs in a faster process.

Ionic crystals illuminated at low temperatures produce an afterglow due to the tunneling recombination of trapped electrons and holes that remain for a long time after illumination. This process involves pure spin effects due to the fact that only singlet pairs of charges will recombine. Polarization of the spins at low temperatures by an external magnetic field produces a reduction in the emission intensity. This has been used to produce a magnetic resonance effect in the rate of tunneling recombination, leading to an increase in the afterglow intensity from NaCl-Ag and KCl-Ag crystals ex-

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posed to x-rays[100] at 77 K. The afterglow can be amplified not only by heating the sample, but also by exposing it to light. Optically-detected ESR, using the photostimulated luminescence of alkali-halide and fluorite crystals was reported in Ref. 101.

8.6.3. Amorphous semiconductors

Spin effects in amorphous semiconductors are largely due to the dependence of the rate of recombination of photoexcited carriers on the direction of their magnetic moments. In the first paper reporting the observation of a change in the photoconductivity of silicon[102] under ESR conditions, the effect was ascribed to a reduction in the equilibrium polarization of electron and hole spins produced by an external microwave magnetic field. The polarization is defined by

$$P = \frac{n_2 - n_1}{n_2 + n_1},$$

where n_2 and n_1 are, respectively, the numbers of spins of a particular type of particle that are parallel and antiparallel to a chosen direction (for example, the direction of the external magnetic field). The equilibrium polarization in an external magnetic field H_0 is given by

$$P = \frac{1}{2} \frac{g\beta H_0}{kT},$$

i.e., $P \approx 10^{-3}$ at room temperature for $H_0 = 3000$ Oe. The change in the rate of recombination of electrons and holes along the singlet channel, due to the establishment of equilibrium polarization in the magnetic field, is given by

$$\frac{\Delta w}{w} = P_e P_h = 10^{-6}.$$

Resonance transitions in triplet pairs reduce the degree of polarization, so that effects due to the microwave field are expected to amount to $\lesssim 10^{-6}$. The discovery of resonance changes in photoconductivity[103] that were higher than this by two or three orders of magnitude has led to the proposal[104] of the same mechanism of nonequilibrium polarization in pairs due to the spin dependence of the rate of recombination, which is usually employed to interpret magnetic effects and magnetic resonance detected by the reaction yield in molecular crystals and solutions. In amorphous silicon, the pairs are formed from charged donor and acceptor centers with energies close to the Fermi level (the so-called "soft" centers). Their recombination results in the emission of luminescence, and changes in this emission can be used to record magnetic resonance spectra. Methods based on the spin dependence of the rate of a process are now widely used to investigate the properties of semiconductors.[105]

9. MAGNETIC EFFECTS IN THE MOLECULAR PHYSICS OF GASES

In 1930, Sentfleben discovered that a constant magnetic field produced a relative change of a few thousandths in the thermal conductivity of oxygen. Two years later, a similar effect was discovered in the shear viscosity of oxygen.[106] The transport properties of the paramagnetic gas NO behave similarly. The magnetic effect saturates at relatively high fields and the level of saturation is a function of H/p, where p is the gas pressure, and does not exceed 1%.

The physics of the phenomenon is clear from the following simple considerations. When a temperature gradient is present, the molecular velocity distribution is distorted so that the hotter molecules move preferentially into cold regions and colder molecules into hot regions. In colliding beams of nonspherical molecules, collisions between these molecules tend to align their angular momenta in the direction of the beams, which produces an increase in the diffusion coefficient. Kagan and Maksimov[107] have shown that this alignment anisotropy lies at the basis of the Sentfleben effect. A paramagnetic molecule has a magnetic moment that is associated with the angular momentum of the molecule as a whole. The external magnetic field induces a precession of the magnetic moment around the direction of the field, partially destroying the anisotropy of the molecular alignment. This produces a change in the diffusion coefficient and thermal conductivity in a magnetic field.

The size of the effect depends on the degree to which the alignment anisotropy is destroyed during a free collisionless flight of a molecule. In other words, it depends on the ratio of the precession frequency ω_L and the mean free time τ. Since ω_L is proportional to H and τ is inversely proportional to p, the product $\omega_L \tau$, which characterizes the degree to which the anisotropy of angular moment is destroyed, depends on H/p. Complete destruction of anisotropy is achieved for $\omega_L \tau \gg 1$, and the magnetic effect saturates for the corresponding values of H/p.

An analogous effect has been observed for diamagnetic polyatomic molecules.[108] In these molecules, rotation produces the magnetic moment

$$\mu_{\text{rot}} = g_{\text{rot}} \mu_N J,$$

where μ_N is the nuclear magneton and g_{rot} is the rotational Landé factor. Thus, for example, in N_2 at room temperature, $J \simeq 8$ and $\mu_{\text{rot}} \simeq 3\mu_N$, which is lower by a factor of 10^3 than the magnetic moment of paramagnetic molecules. This means that the magnetic effect is much smaller than for paramagnetic gases (for example, in H_2, it amounts to about 10^{-5}) and saturation of the effect as a function of H/p is reached in much stronger fields because the saturation condition $\omega_L \tau \gg 1$ is satisfied only in very strong fields for low ω_L.

An unusual magnetic effect in the molecular physics of gases was proposed by Zel'dovich and Maksimov,[109] namely, the effect of nuclear spin on the gas diffusion coefficient. The idea is that, in molecules with nonmagnetic nuclei, the angular momentum is conserved during the free flight of the molecules, and the diffusion coefficient is determined by the manner in which the flight path is averaged over the collision cross section. In molecules with magnetic nuclei, the interaction between the nuclear spin and the angular momentum (the spin-rotation coupling) means that the latter is not conserved during the free flight, and the molecule "somersaults." This means that, initially, the collision cross section is averaged over all the orientations, and this average is then used to determine the mean free path. These situations give rise to different results, so that the diffusion coefficients for identical molecules differing by only the nuclear spin (but not the mass) will be different.

In principle, this effect can be used to separate molecules with isomeric nuclei. The necessary condition is $\tau^{-1} \ll \Delta E$, where τ is the time between collisions and ΔE is the separation between the hyperfine (spin-rotation) levels.

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The condition is valid at low pressures at which the total angular momentum $F = K + 1$ is a good quantum number and the molecule precesses around F between collisions. It is precisely under these conditions that magnetic nuclei affect the transport properties of molecules. At high pressures, the collision frequency is much greater than the level splitting, the coupling between the nuclear spin and the rotational angular momentum has little effect, and the nuclear spin does not influence diffusion. Other conditions under which the effect can be observed (high rotational quantum states in which spin-rotation coupling is enhanced, asymmetric molecules, etc.) are discussed in Ref. 109.

Spin effects include the optical excitation of isotopes, which is selective in nuclear spin and was proposed by Zel'dovich and Sobel'man.[110] It is well known that the radiative transition

$$ns^2\,{}^1S_0 - nsnp\,{}^3P_0$$
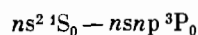
is forbidden in the atoms of alkali-earth elements, zinc, cadmium, mercury, and other atoms with nuclear spin equal to zero. For isotopes with nonzero spin, this rule is partially relaxed by the Fermi interaction which produces a mixing of the ${}^1P_1$ and ${}^3P_0$ states. The admixtures χ of the ${}^1P_1$ state to ${}^3P_0$ is given by

$$\chi = |\langle {}^3P_0 I|V|{}^1P_1 I\rangle\,\Delta E^{-1}| = a\,\frac{[I\,(I+1)]^{1/2}}{2\sqrt{3}\,|\Delta E|},$$

where V is the hyperfine interaction Hamiltonian that produces the mixing, a is the hyperfine interaction constant, and ΔE is the gap between the ${}^3P_0$ and ${}^1P_1$ states. Quantitative estimates of the effect have been made for the ${}^{199}Hg$ and ${}^{201}Hg$ atoms, and criteria were formulated for its experimental detection and use in the separation of magnetic and nonmagnetic isotopes.[110] In contrast to the magnetic isotope effect considered earlier in Section 6, here the hyperfine interaction removes the spin-orbit selection rule (simultaneously for spin and orbital angular momentum).

Magnetic effects in the molecular physics of gases include the quenching of luminescence by a magnetic field. This effect was first observed as far back as 1913 in iodine vapor. The lifetime of the phosphorescent state $B({}^3\Pi_{0u}^+)$ of the iodine molecule was found to fall by a factor of almost two when a magnetic field of 15 kOe was applied. The lifetime was found to be given by

$$\tau\,(H) \sim (a + bH^2)^{-1}$$

for fields up to 50 kOe. The maximum effect was observed when phosphorescence was excited in the 545-nm band, but the effect was sharply reduced when excitation was produced in other bands. The effect is due to the fact that the magnetic field mixes a level of the bound state $B({}^3\Pi_{0u}^+)$ with an energy-degenerate level in the dissociative continuum of states 0_u^-. In other words, the magnetic field induces a predissociation of the phosphorescing state of I_2, reducing its lifetime and its luminescence intensity.[111] There are three parts of the Hamiltonian of the excited molecule that are responsible for predissociation. Natural predissociation (in the absence of the magnetic field) is induced by the rotational Hamiltonian

$$\mathscr{H}_R = -\,2BJ\,(L + S),$$

"magnetic" predissociation is due to the Zeeman Hamiltonian

$$\mathscr{H}_z = \mu H\,(L + 2S),$$

and the third contribution is due to interference between the first two. Luminescence quenching is linear or quadratic in the field, depending on the relative magnitude of these contributions.

It is clear that the magnitude of the effect must fall with increasing vapor pressure of the luminescing molecules or extraneous gases, since collisional dissociation reduces the lifetime of the predissociative state and the effectiveness of magnetic predissociation. This prediction has been confirmed experimentally, and it has been shown that both spontaneous and collisional predissociation depend on the magnetic field.[112]

Analogous effects have been found in the luminescence of other molecules, namely, NO_2, SO_2, CS_2, $C_2O_2H_2$, and CH_2O. As in the case of iodine vapor, these effects are due to radiationless transitions from the excited states of molecules, stimulated by the magnetic field.[113] The physical effects give rise to chemical effects. For example, the magnetic field expands the dissociation channel of excited iodine molecules and increases the concentration of iodine atoms. The latter act as catalysts for the chemical cis-trans-isomerization process in cis-butane, so that the application of a magnetic field of 85 kOe produces an observable increase in the yield of trans-butane from cis-butane by 30% when this reaction is photosensitized by iodine vapor. This magnetic effect has been seen in photolysis in the 5460 Å band, i.e., in the same band in which there is a maximum magnetic effect in the predissociation of iodine molecules.[114] Conversely, the magnetic field slows down the photolysis of CS_2 (Ref. 115), and this is correlated with magnetically induced quenching of CS_2 luminescence. The reason for this correlation is that the initial excited state ${}^1A_2$ of this molecule is chemically active, and the magnetic field quenches this state and reduces its population, thus suppressing the chemical reaction.

10. CONCLUSION

A chemical reaction is a physical process involving the regrouping of atoms and the rearrangement of the electronic shells of reacting particles, which result in the formation of new particles, i.e., the reaction products. The aim of chemistry as a science of the transformation of matter is to develop effective methods for controlling this process with a view to producing different materials in the most economical and effective way (called, nowadays, *progressive technologies*). The traditional method of controlling chemical reactions is to pump energy into the reacting particles or into the external degrees of freedom (simple heating) or internal degree of freedom (photolysis, radiolysis, plasma, infrared laser chemistry, and so on).

The new methods of controlling molecular processes and chemical reactions are based on the selectivity of these processes with respect to the angular momenta of molecules (in molecular processes) and the spin angular momentum of electrons and nuclei of the reacting particles (in chemical reactions).

The change in the angular momentum is induced by magnetic interactions whose energy is negligible under normal conditions, i.e., the new principles of controlling chemi-

cal reactions are determined by spin rather than by energy.

This is why the rates of spin-selective processes depend on the magnetic interactions that alter the spins of the reacting particles and remove (partially or completely) the spin selectivity. They include processes with the participation of paramagnetic particles (free radicals, carbenes, triplet molecules, and paramagnetic ions), i.e., triplet-triplet annihilation, the quenching of triplets by paramagnetic particles, recombination of radicals, electron-hole annihilation, and so on. The rates of these processes depend on the external magnetic field (constant or high-frequency) and on the internal magnetic field produced by magnetic nuclei. This is why magnetic effects can be detected by recording the luminescence of solutions and crystals, the photoconductivity of molecular solids and semiconductors, photosynthesis and quenching of luminescence by paramagnets, radical chemical reactions, and processes involving the participation of molecular oxygen.

Methods based on the effect of external magnetic fields can be used to investigate the intermediate stages of processes in which a reactive pair of paramagnetic particles is formed. The resonance method yields information about these particles that can be obtained by the ESR method but only at high particle concentrations (higher by 6–8 orders of magnitude). Moreover, RYDMR spectra provide information about the nature of the interaction in pairs and on the motion of active particles, their lifetimes and relaxation, and the kinetic relationship between the measured parameter and the yield of the process in a pair. Reaction products excited by electrons have been investigated experimentally, mostly by optical methods. Measurements of resonance effects in photoconductivity and dark conductivity show, even in the absence of other evidence, that the detection of resonances can be based on the more remote consequences of changes in the pair reaction rate. In principle, magnetic and magnetic resonance effects can be expected to show up in all the parameters of complex physicochemical and biological systems that are kinetically related to elementary processes in paramagnetic particle pairs. This approach can be used to detect spin-sensitive stages and to determine the parameters of intermediate particles and complex systems. The only problems are those relating to the choice of the most sensitive and conveniently measured parameters, and of experiments that can be carried out over a reasonable length of time.

The discovery of magnetic effects and of the spin selectivity of chemical reactions has revealed the fundamental role that magnetic interactions play in chemistry. It has led to the creation of a new and actively developing subject. Its principal achievements are the development of new "magnetic" principles for controlling chemical reactions, the discovery of a new principle of separation of isotopes, and the development of new magnetic resonance methods and new "magnetic" methods of diagnosing the mechanisms controlling molecular, chemical, and biochemical processes.

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