Russian Chemical Reviews

January 1983

Translated from *Uspekhi Khimii*, 52 3-19 (1983)

U.D.C. 538.541.51

Chemically Induced Radio-frequency Emission and Chemical Radiophysics

A.L.Buchachenko and V.L.Berdinskii

Chemical reactions involving free radicals can yield molecules with inverted populations of the nuclear Zeeman levels and able to store energy in the nuclear Zeeman reservoir. These molecules produce a radio-frequency electromagnetic field which induces radiative transitions between the Zeeman levels resulting in the conversion of the stored energy into radio-frequency emission from the molecules. The dependence of the recombination probability of the radicals on their spin state allows the elementary acts of radical reactions to be controlled by the application of radio-frequency electromagnetic fields ("chemical" radio receiver). The generation and reception of r.f. radiation in chemical reactions are the object of a new field of science: chemical radiophysics. 29 references.

CONTENTS

I.	Introduction	1
II.	Chemical pumping	2
III.	Self-excitation of chemically induced radio-frequency fields	4
IV.	Experimental observations of radio-frequency generation	5
V.	Theory of the chemical raser	8
VI.	Chemical "radio receiver"	9
VII.	Chemical radiophysics	11

I. INTRODUCTION

Chemical reactions are used to produce either new substances and materials or energy. The chemical energy released during a reaction "heats up" the translational, vibrational, and rotational motion of the molecules, and excites their electron shells. The emission of heat and light by the reacting system is a result of this "pumping" of energy into the molecules. More "organised" methods of converting chemical energy into radiation (chemical lasers) have been studied in recent years, and the mechanisms of the chemical action of laser radiation have been determined[1]. In the whole of that work the energy of the chemical reactions was emitted in the visible or infrared region of the spectrum.

We have recently observed emission at radio frequencies[2] from chemical reactions, resulting from the energy pumping of the Zeeman nuclear levels which act as an energy reservoir for the molecule. This new phenomenon (chemically induced radio-frequency emission) offers a bridge between the previously unrelated sciences of chemistry and radiophysics.

The aim of this review is to examine the physicochemical foundations and the theory of this new phenomenon, to establish the present state of knowledge on the effect of radio-frequency fields on the elementary acts of chemical reactions in solids, liquids, and gases, and to discuss the chemical consequences and the prospects of new developments in physical chemistry arising from this phenomenon. Problems of fundamental importance in chemical radiophysics

include: firstly, the role of the spin degrees of freedom of the molecules and radicals in chemical reactions, and the mechanism of the chemical pumping of the nuclear Zeeman levels; secondly, the way and the conditions under which the energy stored in the Zeeman reservoir is converted into the energy of radio-frequency emission; thirdly, the conditions and the mechanism which enable a radio-frequency field, acting on the spins of electrons and nuclei, to influence the chemical behaviour of atoms, molecules, and radicals.

II. CHEMICAL PUMPING

Transitions between nuclear Zeeman levels are accompanied by reorientation of the nuclear spins and magnetic moments which interact with the external magnetic field. Hence the pumping of the Zeeman reservoir (i.e. the creation of an excess or even an inverted population of the upper Zeeman levels) is equivalent to creating a negative polarisation of the nuclei. The mechanisms of chemically induced nuclear polarisation are well known[3-5], and the phenomenon of chemical polarisation of the nuclei (CPN) was discovered[6,7] in 1967. It was found that in chemical reactions involving paramagnetic particles (free radicals) a non-equilibrium population of the nuclear Zeeman levels is developed in the product molecules, resulting in nuclear polarisation (positive if the excess population resides in the lower Zeeman level, and negative if the population excess, or even inversion, affects the upper level). The non-equilibrium occupancy of the levels manifests itself in the nuclear magnetic resonance spectra of the product molecules as an anomalously strong absorption (for positive CPN) or induced emission (for negative CPN). Some examples of CPN are shown in Fig.1.

Chemical polarisation of the nuclei is created during the elementary acts of the interaction between radicals: their recombination, or their disproportionation. It arises from spin-forbidden processes in chemical reactions. The simplest physical interpretation of this phenomenon is the following. Spin (i.e. the momentum of rotation of the electrons and nuclei) is conserved in chemical reactions, and therefore reactions involving a change of spin are rigidly forbidden. Thus when two radicals collide their electronic spins can either be added (total spin of the pair $S = 1$, triplet state) or subtracted ($S = 0$, singlet state). The products of the recombination of radicals are usually diamagnetic, i.e. they have zero spin, and therefore they must have been formed from singlet radical pairs. Triplet pairs do not recombine. However, triplet–singlet conversion of the pair can take place during the lifetime of the triplet pair under the influence of the external magnetic field and of the internal (hyperfine, or Fermi) interaction between electrons and nuclei. The rate of conversion depends on the orientation of the spins and of the magnetic moments of the nuclei: for some orientations the rate is high, and radical pairs having these orientations are rapidly converted into the singlet state and recombine, giving reaction products.

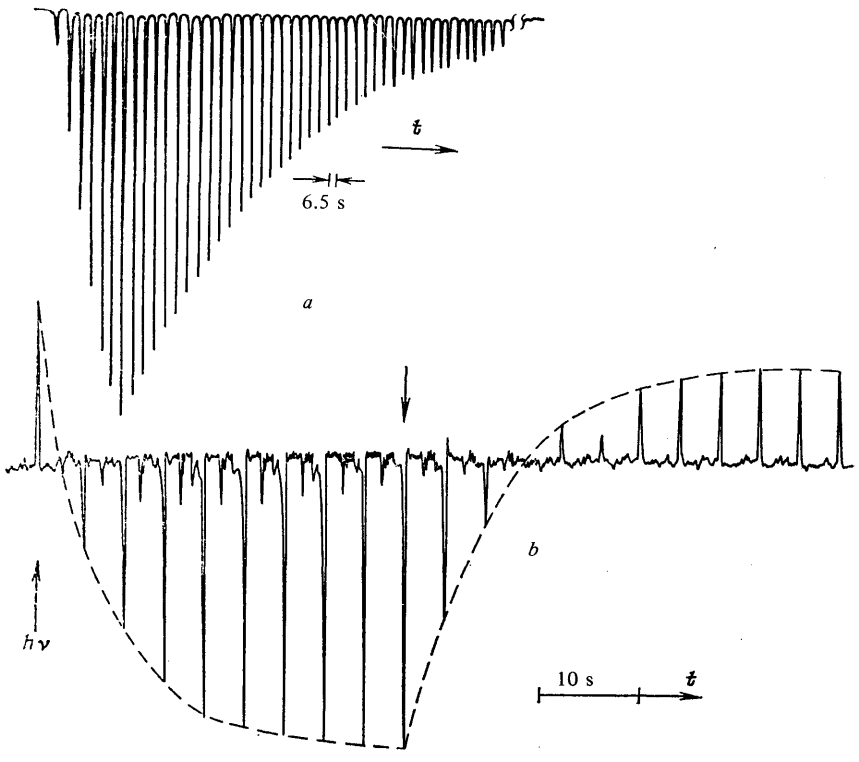


Figure 1. Chemical polarisation of ^{31}P nuclei in trimethylphosphate during the reaction with cyclohexylperoxydicarbonate (*a*), and of the protons in the CH_2 groups of dibenzylketone during photolysis (*b*). The arrows denote the switching on and off of the light.

In the radical pairs with the opposite nuclear orientation the triplet–singlet evolution is hindered, and the radicals in these pairs give different products. In this way the chemical reaction can "sort" the radicals for nuclear spin orientation and direct the radicals with a given type of nuclear orientation towards certain products and those with the opposite type towards other products. In this way some reaction products acquire a positive nuclear polarisation while others acquire a negative polarisation. As a rule, because of differences in chemical shift, the nuclei in the various products are characterised by different NMR frequencies, and therefore CPN is easily detected by NMR.

The sign of the CPN depends on the initial spin state of the radical pair, on the difference between the g-factors of the radicals, and on the sign of the hyperfine electron–nucleus interaction, but the CPN is invariably of opposite signs in the products of radical recombination and in the products of other radical conversions (without recombination). Obviously, the sign of the CPN is determined by the chemical nature of the radicals and by the type of chemical reaction involving the radical pair.

The sorting of nuclei with respect to orientation as a CPN mechanism is characteristic of reactions taking place in strong magnetic fields (about 10^3 Oe).[3] In weak magnetic fields (including the Earth's field) the reaction orients the nuclei as well as sorting the nuclei according to orientation. The electron–nucleus magnetic interaction couples the electrons and the nuclei into a single system in which the total angular momentum (spin) is conserved, so that the change in spin of one particle (electron) can be compensated by the change in spin of another (nucleus). Therefore the triplet–singlet conversion of the radical pair is accompanied by nuclear polarisation: the nuclei are transferred from the lower to the upper Zeeman level and are oriented against the field, producing an excess population of the upper level and a negative polarisation. In this mechanism of CPN the sign of the nuclear polarisation is again dependent on the initial spin state of the radical pair.

Thus the chemical interaction of radicals, being selective with respect to the electron spin of the radical pair, is also selective with respect to nuclear spin, since the two spin systems (electrons and nuclei) are coupled through the magnetic hyperfine interaction.

In principle, any nucleus having a non-zero magnetic moment can be polarised during the reaction, but CPN is most often observed in the widely distributed isotopes with a nuclear spin of $I = 1/2$, such as ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{119}Sn, etc.

Since radical recombination takes place in all radical reactions, CPN may be found in practically all reactions involving a free-radical step, and it may be treated as unambiguous proof of the existence of such a step. Therefore CPN has become an important method of establishing the mechanism of chemical reactions, and is now widely used for this purpose.

The magnitude of the CPN is measured by the polarisation coefficient P. Under Boltzmann equilibrium conditions the populations of the upper and the lower Zeeman level are n_-^0 and n_+^0 respectively, and under non-equilibrium conditions (i.e. in the presence of polarisation) the quantity P is defined by the expression

$$P = \frac{n_+ - n_-}{n_+^0 - n_-^0} , \qquad (1)$$

where n_+ and n_- are the non-equilibrium occupancies of the lower and the upper level. The polarisation coefficient is a measure of the factor by which the non-equilibrium occupancy difference created in the molecules at the instant of their generation from the radical pair exceeds the equilibrium value. With positive polarisation $n_+ > n_-$ and $P > 0$, whereas with negative polarisation we have a population inversion of the Zeeman levels and $P < 0$.

The quantity P depends on the spin and magnetic moment of the nucleus, on the electron–nucleus interaction energy, on the difference between the g-factors of the radicals in the pair, and on the strength of the magnetic field, i.e. on all the magnetic parameters which determine the rate of the triplet–singlet transitions of the radical pairs (spin dynamics). Furthermore P also depends on the diffusional mobility of the radicals (the molecular dynamics of the pair) and on the lifetime of the radicals (chemical dynamics), which jointly determine the time during which the pair must exist in order to undergo triplet–singlet conversion. Knowing the parameters of the spin, the molecular, and the chemical dynamics of the radical pair we can calculate the parameter P (see Refs.3 and 4 for a more detailed discussion).

The energy stored in the Zeeman reservoir as a result of nuclear polarisation is easily calculated. The ratio of the equilibrium occupancies is

$$n_+^0/n_-^0 = \exp(\hbar\gamma_n H_0/2kT) \approx 1 + \hbar\gamma_n H_0/2kT , \qquad (2)$$

where $\hbar\gamma_n H_0$ is the energy of the radio-frequency quantum, i.e. the excess energy of the nucleus in the upper Zeeman level (γ_n is the gyromagnetic ratio of the nucleus, and H_0 is the magnetic field intensity), and kT is the thermal energy. From this expression we obtain the Zeeman energy of N polarised nuclei in a magnetic field H_0:

$$E_z = -\frac{1}{2} PN(\hbar\gamma_n H_0)(\hbar\gamma_n H_0/2kT) , \qquad (3)$$

For example, in a field of 15000 Oe the Zeeman energy of 1 mole of protons with a polarisation coefficient $P = -10^3$ is $\sim 10^{-4}$ J at 30 °C. The energy of the Zeeman reservoir is proportional to the nuclear polarisation coefficient, and therefore the chemically induced emission of radio frequencies is most likely to be found in reactions with strong nuclear polarisation.

The large absolute value of the polarisation coefficient $|P|$ is a striking feature of CPN: values of 10^2–10^4 are common. However, in some reactions the coefficient $|P|$ can be even larger and approach the limiting value $P_{\lim}$:

$$|P_{\lim}| = (2kT/\hbar\gamma_n H_0) . \qquad (4)$$

Thus in the photolysis of cyclododecanone in the liquid phase at 20 °C in a field of 125 Oe a coefficient $|P| > 3.6 \times 10^6$ was observed for the protons of this molecule, and the probability of transferring the proton to the upper Zeeman level by the absorption of one quantum of photochemically active light[8] was greater than 0.3, i.e. the quantum "yield" of the nuclear polarisation was ≥ 0.3.

In the photosensitised decomposition of cyclohexanone diperoxide in solution at 20 °C in a field of ~200 Oe, a coefficient $|P| > 4 \times 10^5$ was observed[9] in the resulting cyclohexane, with a quantum "yield" of ~0.036 for the nuclear polarisation. Though this value is an order of magnitude lower than in the previous case, it is surprisingly large, and well beyond the range accessible by using existing methods of orienting nuclei in the condensed phase (for example, the Oberhauser effect).

Thus chemical reactions can generate large amounts of nuclear polarisation and store large amounts of energy in the Zeeman reservoir of the reaction products.

III. SELF-EXCITATION OF CHEMICALLY INDUCED RADIO-FREQUENCY FIELDS

A population inversion of the Zeeman levels is a necessary but by no means sufficient condition for the emission of the Zeeman energy stored in the reaction products in the form of radiation. The frequencies of the transitions between the nuclear Zeeman levels depend on the strength of the external magnetic field and correspond broadly to the radio-frequency range (from super-long to ultra-short waves). In this range the probability of spontaneous radiative transitions between levels is very small. For example, for a proton in a magnetic field of 7500 Oe this probability is 10^{-25} s^{-1}, corresponding to an emission time of 10^{17} years[10]. This is enormously greater than the spin–lattice nuclear relaxation time (1–100 s), after which the occupancy of the Zeeman levels reverts to the equilibrium thermal (Boltzmann) distribution and the energy of the Zeeman reservoir is irreversibly converted into thermal energy of the lattice. Therefore it is important to establish the conditions under which the Zeeman energy of the reaction products is emitted as r.f. radiation instead of being converted into heat by the spin–lattice relaxation processes.

The magnetic moments of the negatively polarised nuclei (μ_n) can be combined into an overall magnetisation vector **M** oriented in opposition to the outer magnetic field. The reaction products will generate r.f. radiation, i.e. they will create the necessary electromagnetic field, only when self-excitation of the Larmor precession of the nuclear magnetisation vector **M** round the direction of the external field $\mathbf{H}_0$ can take place (Fig. 2). The antiparallel orientation of the vector **M** with respect to the field $\mathbf{H}_0$ is unstable, and as a result of random fluctuations the vector **M** can deviate from this orientation and begin to rotate round the direction of the field $\mathbf{H}_0$ (i.e. to precess). Once the precession has started the vector **M** begins to induce an electromagnetic field which forces it to deviate still further from the external field $\mathbf{H}_0$ (Fig. 2).

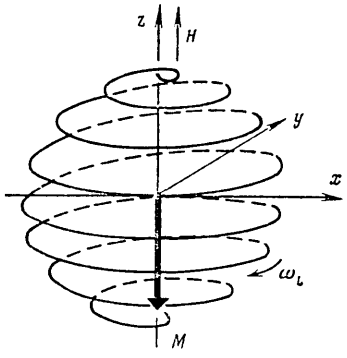


Figure 2. Precession of the magnetisation vector of negatively polarised nuclei. The tranverse components M_x and M_y are oscillating in the xy plane at the precession frequency ω_L.

The self-excitation of the precession of the vector **M** ensures the presence in the ensemble of molecules (reaction products) of transverse variable components of the total magnetisation $M_x(t)$ and $M_y(t)$, oscillating at the Larmor frequency $\omega_L = \gamma_n H_0$ in a plane perpendicular to the direction of $\mathbf{H}_0$. The longitudinal component M_z varies slowly in chemical reactions. Therefore the radio-frequency electromagnetic field in the region surrounding the sample is generated only by the transverse component of the magnetisation, $M_\perp = (M_x^2 + M_y^2)^{1/2}$. If the sample containing chemically polarised reaction products is placed inside an induction coil the precessing vector **M** induces a high-frequency e.m.f. in the coil. This process is the exact analogue of the generation of an e.m.f. in the winding of any electrical generator, the only difference being that in this case the magnet is rotation (and not the rotor): the role of the rotating magnet is played by the transverse component of the nuclear magnetic moment. This is the simplest, classical account of the generation of a chemically induced radio-frequency field.

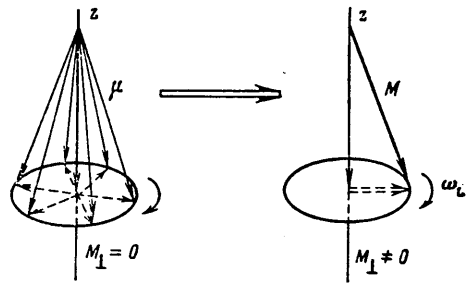


Figure 3. Transition from non-coherent motion to coherent precession of negatively polarised nuclear magnetic moments (frequency ω_L).

Self-excitation of the precession of the overall vector **M** denotes the appearance of spontaneous synchronisation (coherence) in the motion of the nuclear magnetic moments of the product molecules (Fig. 3). In the absence of coherence the magnetic moments of the individual nuclei orientated against the field H_0 precess independently of each other, their precession phases are random, and the transverse components of the magnetisation are randomly "strewn" in the precession plane. As a result there is no net transverse magnetisation ($M_\perp = 0$). The r.f. electromagnetic field generated by the reaction acts on the magnetic moments of the nuclei and compels them to precess consistently, synchronously, and coherently, so that all the precessions are in phase, and the transverse components become aggregated in an overall vector $M_\perp \neq 0$. In other words the resulting coherent electromagnetic field induces a further avalanche-like increase in the synchronisation of the precession of the nuclear magnetic moments. The amplified electromagnetic field takes control of the precession of **M**, and as a result the (initially) negatively oriented magnetisation vector tends to become oriented along the field direction (Fig. 2). This intrinsic coherent electromagnetic field induces forced radiative transitions between the Zeeman levels. The probability of forced transitions is very much greater than the probability of spontaneous emission, and therefore the energy of the Zeeman reservoir can be radiated instead of being dissipated as heat.

Thus the situation is similar, in principle, to that in a laser, where the emission of radiation is a forced (stimulated) process. It is therefore legitimate to treat the chemical reaction as a chemical quantum generator of radio frequencies: a raser (by analogy with the laser).

The coherence is perturbed by transverse magnetic relaxation processes through the random local fields H_{loc} which cause a scatter in the frequencies and phases of the precessing magnetic moments of the individual nuclei: the transverse components of the magnetisation vector become "dispersed", opposing the development of coherence (Fig.3). To ensure coherence, the field H^* created by the chemical reaction products, which "collects" the transverse components of the magnetisation, must be greater than H_{loc}: $H^* > H_{loc}$. In other words the coherence time T_2^* must be less than the nuclear transverse relaxation time T_2, i.e. the rate of development of coherence must be greater than the rate at which coherence is perturbed.

Thus two conditions must be fulfilled for the self-excitation of electromagnetic radiation in chemical reactions: negative polarisation of the nuclei, to allow energy to be stored in the Zeeman reservoir, and coherence of the nuclear spin system, to "rescue" the Zeeman energy from thermal relaxation and to stimulate its emission in the form of radiation. These two conditions are closely bound together: if the Zeeman energy is small, i.e. if the magnetisation vector M is small, the electromagnetic field induced by the precession of M and its coherence will both be weak, and they will be unable to compete with the transverse nuclear relaxation processes which perturb the coherence. Therefore in order to excite raser generation we need to achieve a well defined critical level of chemical nuclear polarisation (the vector M_z) corresponding to an amount of stored Zeeman energy called the generation threshold. A theoretical analysis of the self-excitation conditions and of the generation threshold is given in Section V.

IV. EXPERIMENTAL OBSERVATIONS OF RADIO-FREQUENCY GENERATION

Chemically induced radio-frequency emission was first observed in the photochemical reaction between porphyrin and quinone[2,11], and somewhat later in the thermal decomposition of benzoyl peroxide[12].

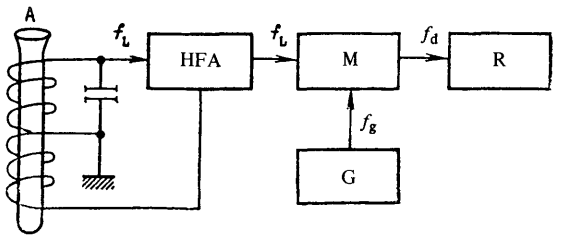


Figure 4. Block diagram of the radio circuit used to detect the chemically induced radio-frequency field: A is a tube containing the polarised reaction products, HFA is a high-frequency amplifier, M is a mixer, G is a standard generator, R is a recorder. The magnetic field H_0 is perpendicular to the coil axis[2].

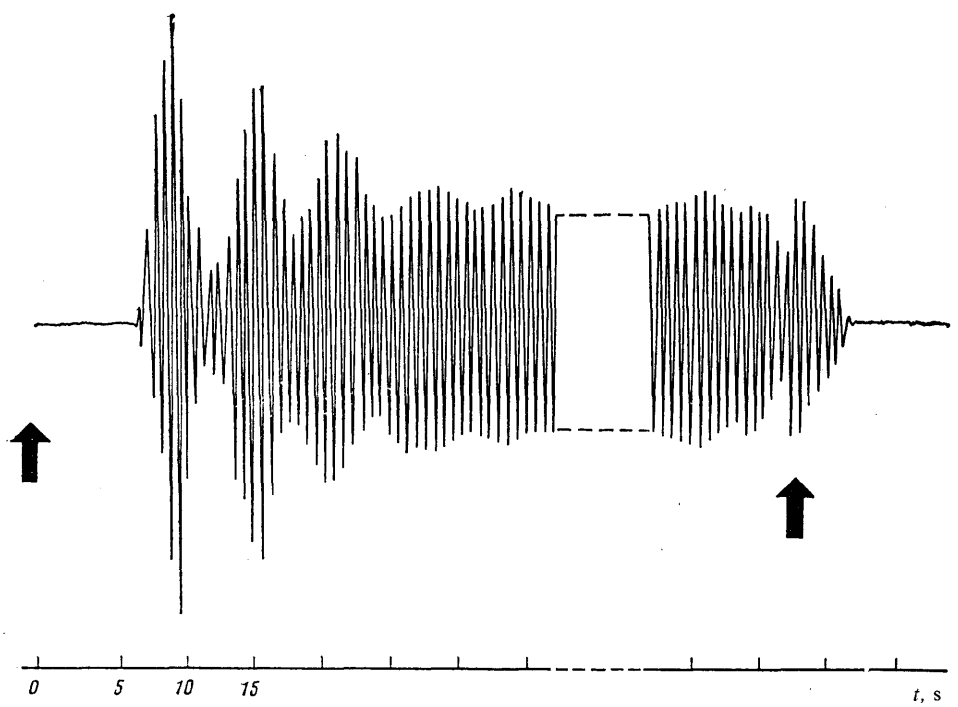


Figure 5. Chemically induced radio-frequency emission from polarised quinone molecules (signal recorded at the low frequency f_d; H_0 = const); the arrows denote the switching on and off of the light[2].

The reaction between porphyrin and *p*-benzoquinone is

$$\Pi \xrightarrow{h\nu} \Pi^*$$
$$\Pi^* + Q \xrightarrow{H^+} \Pi^{\ddagger} + \dot{Q}H$$
$$\Pi^{\ddagger} + \dot{Q}H \rightarrow \Pi + Q + H^+ ,$$

where Π is a porphyrin molecule (octamethyltetraphenylporphyrin), Q is the quinone, $\dot{Q}H$ is the semiquinone radical, and $\Pi^{\ddagger}$ is the porphyrin cation radical. The ion radicals produced by the electron transfer reaction undergo disproportionation to give quinone molecules with negatively polarised protons. The result is a continuous pumping of

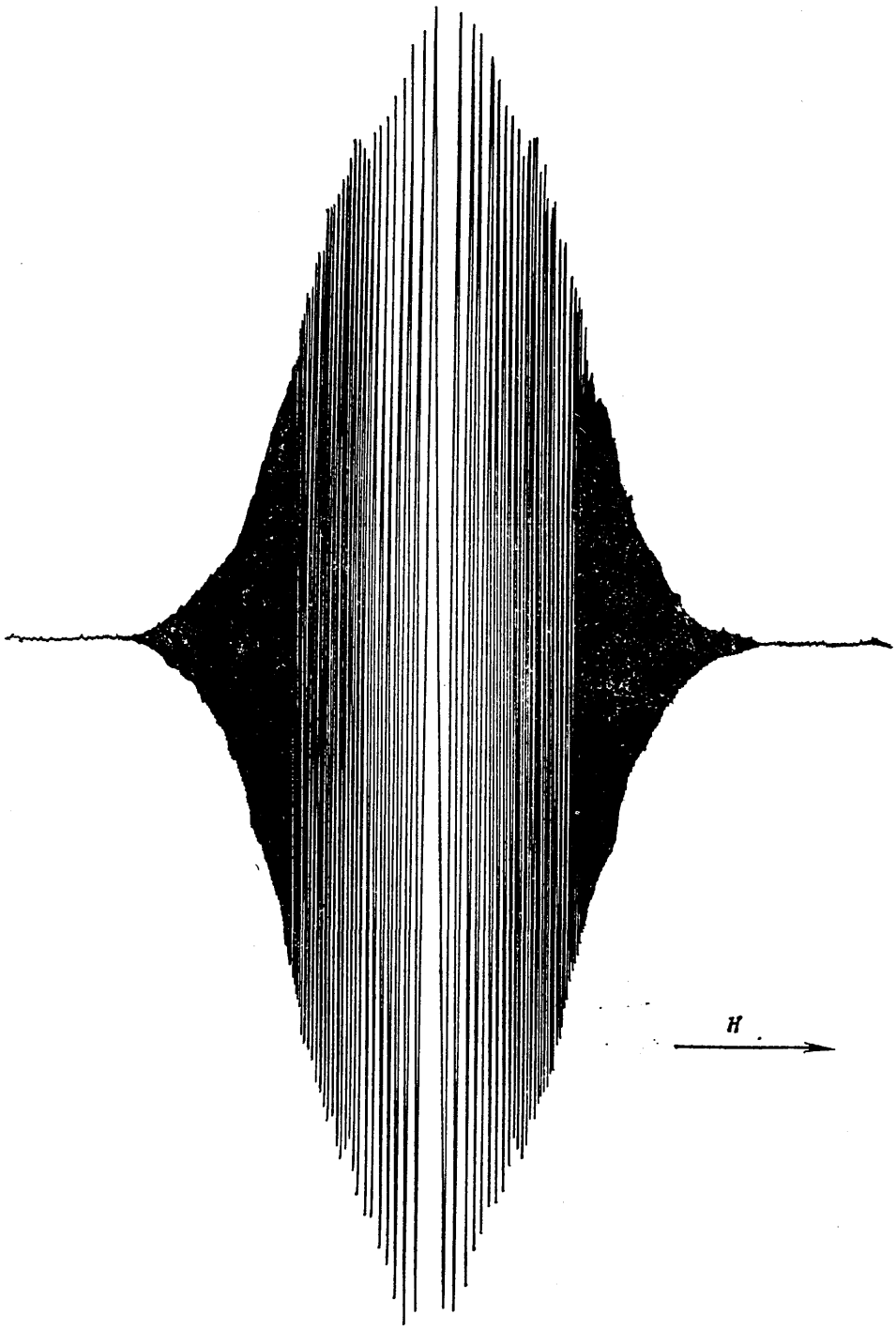


Figure 6. Chemically induced radio-frequency emission from polarised quinone molecules. Signal recorded with periodic variations in the field H_0.

the Zeeman energy reservoir of the protons in the quinone molecule, with a magnetisation vector oriented against the field H_0.

The reaction was carried out in a tube surrounded by the coil of an oscillator circuit, and initiated by light in the absorption band of the porphyrin (λ = 546 nm). The circuit was tuned to the frequency of the Larmor precession of the nuclear magnetisation vector of the quinone molecule (f_L = 100 MHz) in a field $H_0 \cong$ 24000 Oe, corresponding to an emission wavelength of 3 m. A block diagram of the radiation detection circuit is shown in Fig.4. In order to lower the generation threshold the Q-factor of the oscillator circuit was increased by additional feedback from the high-frequency amplifier. After amplification of the signal from the chemically induced radio-frequency field a low-frequency signal is obtained at the difference frequency $f_d = f_L - f_g$ (where f_g is the frequency of the reference generator), and this is amplified by a low-frequency amplifier and displayed on a recorder and an oscilloscope. The self-excitation of the precession was additionally monitored at the high frequency f_L by an h.f. oscilloscope connected to the output of the high-frequency amplifier. A record of the chemically induced signal is shown in Fig.5. Generation begins 5–10 s after the admission of light and the onset of the reaction, i.e. when the system reaches the generation threshold. After this short initial transient a steady-state regime is established: this regime can be maintained for a long time, because the reaction is almost ideally reversible. The radio-frequency generation stops when the light is switched off and the reaction comes to an end. The generation process can be repeated several times with the same sample by switching the photochemical pumping system on and off.

Fig.6 shows a record of the radio-frequency generation obtained by slowly varying the field H_0 (by 10^{-3} Oe) with the recorder carriage connected to the field scan. Changes in field strength produce a change in the generation frequency f_L, and hence in the detected difference frequency f_d. Thus $f_d = 0$ at the centre of each bundle of signals, where the Larmor precession frequency coincides with that of the reference generator f_g, and f_d increases towards the edges of the bundle. This behaviour of f_d shows unequivocally that the signal is due to chemically induced radiation.

In another series of experiments[11] the radio-frequency field was detected in a crossed coil system (Fig.7). The auxiliary coils are connected to the output of the high-frequency amplifier, and the generation signal is connected to the input of the same amplifier. As in the previous experiment, $H_0 \cong$ 24000 Oe, and the precession frequency is 100 MHz.

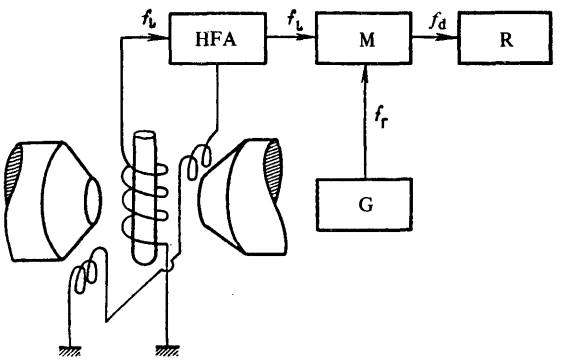


Figure 7. Block diagram of the apparatus used to detect the chemically induced radio-frequency field with crossed coils: HFA is a high-frequency amplifier, M is a mixer, G is a standard generator, R is a recorder[12].

The generation signals detected in this way from the photochemical reaction between porphyrin and quinone are shown in Fig.8. The signals were recorded by amplitude detection with a constant field H_0. In this case steady-state generation is not established after the initial transient, and the emission consists of regularly spaced short bursts of radiation. In this regime the reaction system behaves like a radio-frequency "chemical pulsar".

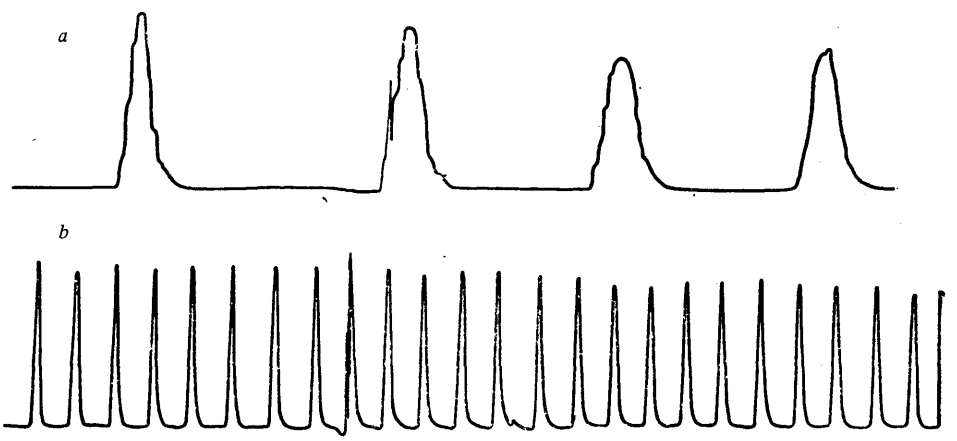


Figure 8. Chemically induced radio-frequency emission from quinone molecules in a constant field H_0 ("chemical pulsar" regime): *a*) duration of record 50 s, *b*) duration of record 250 s.[12]

The strength of the r.f. fields generated by the reaction products has been measured in experiments on the self-excitation of the precession of the total nuclear magnetisation vector **M** in a rotating system of coordinates[12], involving a non-resonant magnetic field H_1 rotating in a plane perpendicular to the constant field H_0. The r.f. field was generated in the negatively polarised protons of the benzene molecules produced by the thermal decomposition of benzoyl peroxide in cyclohexanone (120 °C, peroxide concentration 0.5 M). The reaction involves free-radical steps, and is accompanied by strong negative polarisation of the benzene protons. From the CPN kinetics the effective rate constant of the reaction

$$(PhCO_2)_2 \xrightarrow{k} C_6H_6 \ ,$$

was determined ($k = 2 \times 10^{-2}$ s^{-1}), for which the polarisation coefficient is $P = -400$. Under these conditions the negative polarisation of the protons is retained for 3–4 min after the onset of the reaction. In these experiments the e.m.f. produced in the coil was measured: it was found to be ~2 μV, corresponding to a magnetic component of the electromagnetic field generated by the reaction of ~1.6×10^{-7} Oe. From this we can estimate the emission temperature as $T_{em} \cong 10^{28}$–10^{29} K, so that the energy of the non-equilibrium emission from the reaction is 25–27 orders higher than the energy of the equilibrium (Boltzmann) radio-frequency emission. In comparison we note that the energy of the radio-frequency radiation from one of the best known cosmic emitters (the OH radical maser) is only ~10^{13} K, i.e. the chemical radio-frequency generators are "brighter" than their cosmic analogues. However, the absolute efficiency of the chemical generator is negligibly small, because the heat capacity of the spin systems is low and only a very small fraction of the energy of the chemical reaction can be accomodated in the Zeeman reservoir.

V. THEORY OF THE CHEMICAL RASER

We have based a theoretical analysis[13] of the chemical radio-frequency generator on the standard Bloch equations which describe the behaviour of the nuclear magnetisation vector[14]:

$$\frac{dM_x}{dt} = \omega M_y - \gamma_n M_z H_y - 2\pi\Delta f M_x$$

$$\frac{dM_y}{dt} = -\omega M_x + \gamma_n M_z H_x - 2\pi\Delta f M_y$$

$$\frac{dM_z}{dt} = \gamma_n (M_x H_y - M_y H_x) - \frac{M_z - M_0}{T_1} + P\frac{dM_0}{dt} \ , \qquad (5)$$

where M_x, M_y, and M_z are the components of the magnetisation vector, M_0 is the equilibrium magnetisation, H_x and H_y are the components of the variable magnetic field generated in the coil by the chemical reaction products, T_1 is the spin–lattice relaxation time of the nuclei, Δf is the half-width of the NMR line at half height, and γ_n is the gyromagnetic ratio for the nuclei of interest. Eqns.(5) differ from the conventional Bloch equations only in the term $P(dM_0/dt)$, which characterises the rate of generation of nuclear magnetisation by the reaction, i.e. the rate of chemical pumping.

The self-excitation threshold for the precession of the chemically induced nuclear magnetisation vector is defined by the condition

$$|M_z| > \Delta f/\gamma_n \eta q, \qquad (6)$$

where η is the filling coefficient of the coil and q is the Q-factor of the circuit. Of course, the parameter M_z should be negative. If the condition (6) is obeyed we expect self-excitation of the precession of the vector **M** (Fig.3). Under these conditions we observe a transverse component of the magnetisation, $M_\perp = (M_x^2 + M_y^2)^{1/2}$, whose value increases exponentially, and a high-frequency e.m.f. is induced in the coil. Its amplitude is given by

$$u = (4\pi/c)\, q w s \eta \omega_L M_\perp \ ,$$

where w is the number of turns in the coil, s is its cross-sectional area, and c is the velocity of light.

For unimolecular reactions of the type of A → B, with a rate constant k and polarisation coefficient P, the self-excitation condition becomes

$$\frac{(1 - PkT_1)^{1/(1-kT_1)}}{(1-P)^{kT_1/(1-kT_1)}} > 1 + \frac{\Delta f}{\gamma_n \eta q M_0} \ , \qquad (7)$$

where some of the quantities (P, k, M_0) are "chemical" parameters, others (Δf, η, T_1, q) are radiophysical.

The generation dynamics are illustrated in Fig.9: they were obtained by solving the system (5) on an analog computer. In the case of pulsed chemical pumping the generation consists of a single signal (Fig.9*a*): the parameter M_z quickly reaches the generation threshold, and then the transverse component $M_\perp$ appears. The relationship between M_z and $M_\perp$ (the phase diagram of the nuclear magnetisation) consists of a single loop (see insert in Fig.9*a*). In this case the chemical pumping pulse is accompanied by a single generation pulse.

With strong and sustained chemical pumping the radio-frequency emission takes the form of a regular series of pulses (Fig.9*b*). During the intervals between the pulses the chemical reaction in the system continues to create magnetisation, which reaches the generation threshold after some time. The phase diagram consists of many superimposed loops. This generation regime was demonstrated in Fig.8 (the chemical "pulsar"). If the rate of chemical pumping is lowered the pulse regime may change into continuous steady-state generation (see experiment in Fig.5).

In decaying reactions, i.e. with damped chemical pumping, we observe a smooth transition from one generation regime to the other (Fig.9*c*): the pulsed generation regime changes to continuous generation, which in turn decays as the chemical reaction comes to an end. Depending on the kinetics of the chemical reaction, i.e. on the kinetics of the chemical pumping of the Zeeman reservoir, different generation regimes can be established. Several of these have been demonstrated experimentally (see Section IV).

We have so far discussed only the radiation generated in a reacting system located in the coil of a tuned oscillator circuit. However, excitation of a chemically induced radio-frequency field is possible, in principle, even in the absence of special resonance circuits, i.e. in "free" space. The conditions for excitation of this type have been studied[15], and the generation threshold was found to be determined by the condition

$$|M_z| v = \frac{3c^3}{2\gamma_n T_2 \omega_L^3} \ , \qquad (8)$$

where ν is the volume of the sample containing the polarised reaction products, and T_2 is the characteristic time for the "disruption" of the coherence. From formula (8) we can obtain the minimum volume ν_{min} of reaction products with the maximum nuclear polarisation coefficient consistent with self-excitation of the precession in free space. For a concentration of polarised protons $N = 10^{-2}$ mole litre^{-1}, $T_2 = 10$ s, and $f_L = \omega/2\pi = 100$ MHz, we find that $\nu_{min} \cong 10$ litre. If we increase the frequency, ν_{min} decreases as ω_L^{-3}.

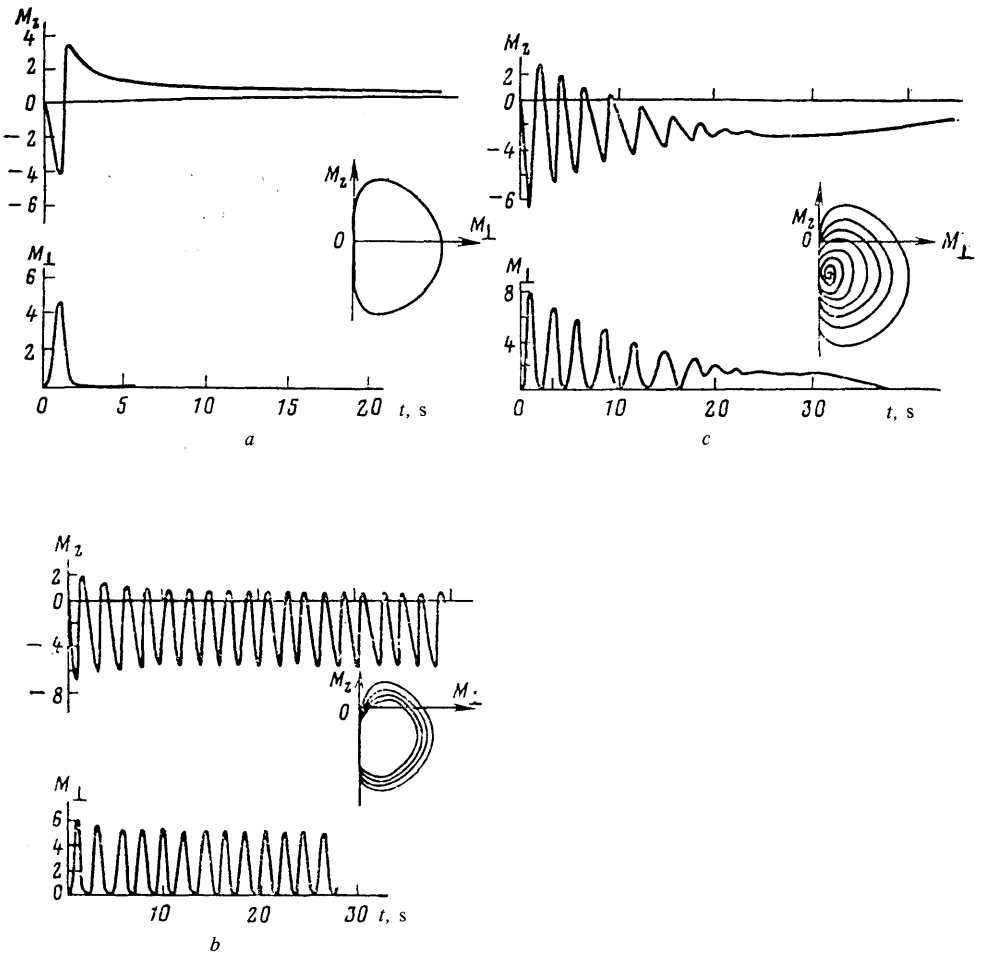


Figure 9. Radio-frequency generation dynamics of the chemical raser: *a*) for a fast reaction, *b*) for a reversible photochemical reaction, *c*) for a slow unimolecular reaction. In each case the "phase diagram" of the nuclear magnetisation in $M_\perp$, M_z coordinates is shown as an insert. The intensity of radio emission is proportional to $M_\perp^2$.[13]

Throughout this review we have dealt with the radio-frequency emission generated by the precessing total magnetic dipole of chemically polarised nuclei. The electromagnetic field of this type of dipole can be arbitrarily divided into three components[16]: the short-range field, decreasing as R^{-3} (where R is the distance from the source); the intermediate range field, decreasing as R^{-2}; the long-range field, decreasing as R^{-1}. In all the experiments discussed above the short-range region was detected. The electromagnetic field in the long-range region (which is often assumed to be the relevant region in discussion of radio emission) has not so far been experimentally explored because its strength is very low. However, in principle this field can be observed by using extremely sensitive instruments (similar to those employed in radio astronomy).

VI. CHEMICAL "RADIO RECEIVER"

We have shown that a chemical reaction can generate r.f. radiation. It is therefore legitimate to ask whether, conversely, r.f. radiation can affect chemical reactions, or in other words whether a chemical reaction can act as a receiver and detector of radio emission. An answer in the affirmative is suggested by the known effect of a radio-frequency field on the spin systems of reacting species, which can alter the rate of a chemical reaction or the yield of products by allowing previously spin-forbidden transitions. Several experimental realisations of this type of "chemical" radio receiver have been described.

A clear example is the effect of an electromagnetic field on reactions involving paramagnetic species (radicals and triplet excitons) in solids[17-20]. Using this phenomenon

(i.e. the sensitivity of the elementary acts of chemical reactions to an external electromagnetic field) the authors[17–20] have developed a new radio-spectroscopic method of detecting paramagnetic intermediates in reactions, which they have called RYDMR (Reaction Yield Detected Magnetic Resonance).

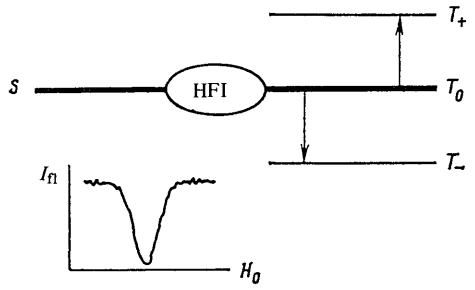


Figure 10. Principle of detection by the RYDMR spectrum, recorded for the fluorescence of the molecules formed in ion-radical recombination reactions. The hyperfine interaction (HFI) induces singlet–triplet transitions, and the external electromagnetic field at the ESR frequency induces a "loss" of radical pairs to the T_+ and T_- states. The result is an increased yield of triplet molecules, a decreased yield of singlet (fluorescing) molecules, and a decrease in the fluorescence intensity. The vertical arrows denote the transitions between T_0 and $T_\pm$ levels at the ESR frequency.

The basic idea of the method is shown in Fig.10. Assume that the interaction between two radicals (the cation M^+ and the anion M^-) takes place by electron transfer:

$$M^{\cdot+} + M^{\cdot-} \rightarrow (M^{\cdot+}M^{\cdot-}) \rightarrow M^* + M \ ,$$

so that one of the molecules (M*) is formed in an excited state. If the electron transfer occurs in a singlet ion-radical pair the excited M* molecule will be in a singlet (S) state, and it will fluoresce. In the ion-radical pair ($M^{\cdot+}M^{\cdot-}$) the hyperfine electron–nucleus interaction (HFI) induces singlet–triplet conversion of the pair into the T_0 state (see Fig.10), from which a triplet (non-fluorescing) M* molecule is obtained. The S–T_0 transitions are reversible, with characteristic times of 10^{-8}–10^{-10} s. If the ion-radical pair experiences a variable field which induces resonant transitions from the T_0 to the T_+ and T_- states, the decrease in the number of pairs in the T_0 state produces an increased "loss" of singlet pairs. The yield of singlet M* molecules falls, and the yield of triplets increases. The frequency of the field which produces a change in the relative yield of singlet and triplet product molecules corresponds to ESR transitions in the radical pair, and therefore the dependence of the intensity of fluorescence on the magnetic field H_0 can be used to detect the ESR spectrum of the ion-radical pair (optical detection of ESR). The decrease in fluorescence associated with the decreased number of singlet pairs occurs at resonance values of the steady magnetic field, for which the splitting of the levels (T_0–$T_\pm$) corresponds to the frequency of the oscillating field.

The RYDMR spectra of excited charge transfer complexes in molecular crystals were first obtained in this way[17]. In this case the external electromagnetic field affects the probability of transitions between spin states in a pair consisting of two triplets, and it alters the rate of annihilation of the triplets with formation of an excited singlet fluorescing molecule. The RYDMR spectra of the radical + triplet exciton pair have also been observed[21].

A method of obtaining the RYDMR spectra of ion-radical pairs in liquids has recently been developed[22,23], and the ESR spectra of various ion-radicals have been obtained. The RYDMR technique has been used also to investigate the nature of the ion-radical pairs formed in the primary act of photosynthesis[25].

Another application of the RYDMR technique is in the detection of the magnetic resonance spectra of short-lived pairs of paramagnetic species, and in the measurements of their lifetimes (10^{-6}–10^{-10} s). The method offers a high sensitivity, often several orders better than the sensitivity of traditional magnetic resonance methods. Thus in the RYDMR detection of ion-radical pairs in liquids by fluorescence measurements a sensitivity of 20–100 pairs in the sample has been claimed[22]. Some estimates of sensitivity are given in Ref.20: in particular, for the annihilation of a triplet pair in molecular crystals a variable field in which the amplitude of the magnetic component is $H_1 = 1$ Oe produces a change of 10^{-5} in the rate of the process. In general, in order to allow an electromagnetic field of amplitude H_1 to influence the spin state of a pair of paramagnetic particles during the lifetime τ of the pair, we must satisfy the condition

$$\gamma_e H_1 \tau \approx \pi \ , \qquad (9)$$

where γ_e is the gyromagnetic ratio of the electron. Thus for pairs with $\tau \simeq 10^{-8}$ s we need $H_1 \simeq 20$ Oe. The RYDMR effect is a consequence of the influence of an external electromagnetic field on the course of chemical reactions in a condensed phase, and it can be detected not only from changes in the yield of singlet and triplet molecules under the influence of a variable field, but also from the relative yields of recombination and dissociation products of the pairs, from photocurrents, etc.

Zhitnikov and coworkers[26–28] have shown that a resonant radio-frequency field can affect the elementary acts of chemical reactions in the gas phase (for example, the ionisation by collision of helium and alkali metal atoms). As in the previous examples this effect of the r.f. field can be explained by the presence of spin-forbidden physicochemical processes which can be controlled by varying the spin state of the interacting particles.

Consider, for example, the ionisation of helium atoms. In the ground state (1^1S_0) the helium atom is diamagnetic, since the spins of the two electrons are compensated and their orbital moment is zero. When excited (for example, by a high-frequency gas discharge) the helium atoms pass into a metastable triplet state (2^3S_1) characterised by a total electron spin $S = 1$ and a lifetime of several microseconds. The energy of the metastable state is 19.77 eV, and its ionisation potential is 4.7 eV. Under normal conditions one of the two helium atoms with triplet excitation passes into the ground state (as a result of inelastic collisions), and the other atom is ionised. This produces an electron–ion plasma, easily detected by changes in the luminescence and in the electrical conductivity of the medium. Irradiation of the sample with circularly polarised light in a magnetic field H_0 causes optical orientation of the metastable helium atoms, i.e. it favours the occupancy of one of the three Zeeman sublevels of the triplet state. Very high degrees of

polarisation can be achieved in this way, and a very large fraction of the excited helium atoms have their magnetic moments in the same orientation with respect to the field H_0.

Optical orientation is found to have a large effect on the ionisation of the atoms by the collision reaction

$$\mathrm{He}\,(2^3S_1) + \mathrm{He}\,(2^3S_1) \rightarrow \mathrm{He}\,(1^1S_0) + \mathrm{He}^+\,(1^2S_{1/2}) + e^- \ ,$$

where e^- denotes a free electron. The total spin of the particles formed by this reaction is 1. Therefore this reaction is forbidden by the law of spin conservation (i.e. the law of conservation of angular momentum) in the case of two colliding helium atoms with electron spins in the same direction, since their combined spin is 2. As a result of the spin requirement the polarised helium atoms can only undergo elastic collisions, which do not lead to ionisation (in spite of the energy gain offered by the ionisation process). Thus the polarisation of the helium atoms results in a decrease in the density of free electrons and helium ions. Experimentally this effect is detected as a decrease in electrical conductivity and in luminescence intensity of the electron–helium plasma following optical orientation of the atoms.

A radio-frequency field affects the collisional ionisation of helium atoms by inducing resonant transitions between the Zeeman sublevels of the triplet state, thus lessening the polarisation of the atoms. The result is an increase in the number of collisions between metastable helium atoms, whose electron spins are in different orientations and for which inelastic processes are "allowed", leading to ionisation of one of the atoms. Therefore a radio-frequency field should increase the experimentally observed electrical conductivity of an electron–helium plasma. Formally this phenomenon can be described by postulating an additional participant to the reaction, whose presence ensures equality of the total spins of the reacting and the resulting particles. The role of this additional particle (with a spin $S = 1$) is played by the quantum of the radio-frequency field, whose absorption causes reorientation of the electron spins of the metastable helium atoms.

Very interesting experiments[28] on the influence of radio-frequency fields on the collisional ionisation of optically oriented alkali metal atoms (e.g. rubidium or caesium), and of excited helium atoms, have been reported. Since the ionisation potentials of alkali metal atoms are much lower than the excitation energy of the helium atom, inelastic collisions in the gas phase usually cause ionisation of the metal atoms and deactivation of the helium atoms:

$$\mathrm{He}\,(2^3S_1) + \mathrm{Rb}\,(5^2S_{1/2}) \rightarrow \mathrm{He}\,(1^1S_0) + \mathrm{Rb}^+(4^1S_0) + e^- \ .$$

The total spin of the resulting Rb^+ ion, helium atom in the ground state, and free electron is 1/2. However, if the magnetic moments of the colliding helium and rubidium atoms have the same orientation their total spin is 3/2. Therefore if the colliding helium and rubidium atoms have parallel spins the inelastic collisions accompanied by ionisation are spin-forbidden. Collisional ionisation is possible only when the spins of the colliding atoms are pointing in opposite directions. Indeed, it is experimentally found that the concentration of free electrons and ions decreases when the helium and alkali metal atoms have the same orientation. Perturbing the polarisation of these atoms by the application of a resonant radio-frequency field increases the number of inelastic collisions and the concentration of electrons and ions, as shown by a change in the observed electrical conductivity of the plasma.

However, the effect of radio-frequency fields on the spin systems of colliding and interaction atoms is not merely to equalise the occupancies of the Zeeman and hyperfine levels: these fields also create coherence in the spin systems. As we showed in Section II, coherence implies the existence of transverse components of the total magnetisation vector, precessing at the Larmor frequency around the direction of the external field H_0. It so happens that this radio-frequency coherence has the same effect as orientation on the collisional ionisation (atom polarisation). Since the transverse components of the electron spins of the helium and rubidium atoms have different Larmor precession frequencies, they will periodically show a parallel orientation, and under these conditions their collisional ionisation is spin-forbidden, only elastic collisions are possible, and the electrical conductivity of the plasma decreases. After some time the spins of the helium and rubidium atoms are found to point in opposite directions (owing to the difference in precession frequency), collisional ionisation is no longer forbidden by the law of conservation of spin (or of its transverse component), and the electrical conductivity of the plasma increases. The two types of process (elastic and inelastic collisions) alternate at a frequency equal to the difference between the precession frequencies of the magnetic moments of the excited helium and rubidium atoms. As a result the electrical conductivity of the plasma is modulated at this difference frequency. These experiments[28] are the first demonstration of the effect of electromagnetic fields and of radio-frequency spin coherence on the elementary acts of chemical reactions.

Various examples of the influence of variable electromagnetic fields on the rate and direction of chemical reactions have been considered above. In every case the chemical reaction acts as a "receiver" of electromagnetic radiation. The physical explanation of the change in reactivity of the atoms, triplet molecules, and ions lies in the partial relief from spin restrictions given by the external radio-frequency field. Similar effects should be observed in the interaction of alternating electromagnetic fields with nuclear (as opposed to electronic) spin systems. Partial control of the rate and direction of a chemical reaction should be possible by using a radio-frequency field to modulate the nuclear spin state of the participating radicals or radical pairs.

VII. CHEMICAL RADIOPHYSICS

Chemically induced radio-frequency emission is a new phenomenon, which allows the radiophysical properties of radical reactions to be observed. These properties allow new approaches to the study of the reactions themselves, and they offer new (radiophysical) methods of detecting the radical steps. They also suggest new ways of designing technological devices such as magnetometers and masers in which the working substance is the product of a chemical reaction incorporating an inverted population of Zeeman levels.

Radio-frequency emission can be generated, in principle, in a system of negatively polarised electrons and radicals. The special features and properties of this chemically induced emission of the energy of the Zeeman electronic reservoir are discussed in Ref.16.

The self-excitation of the precession of the nuclear magnetisation vector and the development of coherence in the nuclear spin system of the reaction products are equivalent to a transition from a disordered to an ordered state, i.e. to a non-equilibrium phase transition (similar to a phase transition of the second kind). In this transition the quantity equivalent to the order parameter is the modulus of the transverse components of the precessing nuclear magnetisation vector of the reaction products. The

observations reported in Refs.2, 11, and 12 are the first examples of magnetic phase transitions caused by chemical reactions.

The discovery of chemically induced radio-frequency emission and of the effect of radio-frequency electromagnetic fields on the elementary acts of chemical reactions has laid the foundation of a new branch of science: chemical radiophysics, whose object is to study the generation and detection of radio waves at the chemical (molecular) level, to investigate the radiophysical properties of chemical reactions, and to analyse the chemical and radiophysical consequences of coherence effects in spin systems[29]. Radiophysical properties may also be found, in future, in biochemical reactions and processes.

REFERENCES

1. V.V.Tal'roze and P.P.Baryshev, Zhur.Vses.Khim. Obshch.imeni Mendeleeva, 1973, **18**, 15.
2. A.G.Zhuravlev, V.L.Berdinskii, and A.L.Buchachenko, Zhur.Eksper.Teor.Fiz.Pis'ma, 1978, **28**(3), 150.
3. A.L.Buchachenko, "Khimicheskaya Polyarizatsiya Elektronov i Yader" (Chemical Polarisation of Electrons and Nuclei), Izd.Nauka, Moscow, 1974, 246 pp.
4. A.L.Buchachenko, R.Z.Sagdeev, and K.M.Salikhov, "Magnitnye i Spinovye Effeckty v Khimicheskikh Reaktsiyakh" (Magnetic and Spin Effects in Chemical Reactions), Izd.Nauka, Novosibirsk, 1978, p.296.
5. A.L.Buchachenko, Symposium "Fizicheskaya Khimiya. Sovremennye Problemy" (Modern Problems in Physical Chemistry) (Edited by Ya.M.Kolotyrkin), Izd. Khimiya, Moscow, 1980, p.3.
6. J.Bargon, H.Fischer, and U.Johnsen, Z.Naturforsch., 1967, **22a**, 1551.
7. H.R.Ward and R.G.Lawler, J.Amer.Chem.Soc., 1967, **89**, 5518.
8. Yu.A.Grishin, A.V.Dushkin, and R.Z.Sagdeev, Khim.Vys.Energii, 1978, **12**, 278.
9. Yu.A.Grishin, A.V.Dushkin, and R.Z.Sagdeev, Zhur.Fiz.Khim., 1979, **53**, 278 [Russ.J.Phys.Chem., 1979(2)].
10. A.Abragam, "The Principles of Nuclear Magnetism" (Translated into Russian), Inostr.Lit., Moscow, 1963, p.551.
11. V.L.Berdinskii and A.G.Zhuravlev, Khim.Fizika (in press).
12. V.L.Berdinskii and A.L.Buchachenko, Zhur.Fiz.Khim. 1981, **55**, 1827 [Russ.J.Phys.Chem., 1981(7)].
13. V.L.Berdinskii, A.L.Buchachenko, and A.D.Pershin, Teor.Eksper.Khim., 1976, **12**, 666.
14. N.M.Pomerantsev, V.M.Ryzhkov, and G.V.Skrotskii, "Fizicheskie Osnovy Kvantovoi Magnitometrii" (Physical Foundations of Quantum Magnetometry), Izd.Nauka, Moscow, 1972, p.448C.
15. V.L.Berdinskii and A.L.Buchachenko, Zhur.Fiz. Khim., 1980, **54**, 676 [Russ.J.Phys.Chem., 1980(3)].
16. L.D.Landau and E.M.Lifshits, "Teoriya Polya" (Field Theory), GIFML, Moscow, 1962, p.442.
17. E.L.Frankevich and A.I.Pristupa, Zhur.Eksper.Teor. Fiz.Pis'ma, 1976, **24**, 397.
18. E.L.Frankevich, A.I.Pristupa, and V.I.Lesin, Chem. Phys.Letters, 1978, **54**, 99.
19. E.L.Frankevich, Zhur.Eksper.Teor.Fiz., 1978, **75**, 397.
20. E.L.Frankevich, Vestnik Akad.Nauk SSSR, 1978(1), 80.
21. E.L.Frankevich, Khim.Vys.Energii, 1980, **14**, 195.
22. O.A.Anisimov, V.M.Grigoryants, and Yu.N.Molin, Zhur.Eksper.Teor.Fiz.Pis'ma, 1979, **30**, 589.
23. O.A.Anisimov, V.M.Grigoryants, V.K.Molchanov, and Yu.N.Molin, Chem.Phys.Letters, 1979, **66**, 265.
24. Yu.N.Molin, O.A.Anisimov, V.M.Grigoryants, and V.K.Molchanov, J.Phys.Chem., 1980, **84**, 1853.
25. M.K.Bowman, D.E.Budii, G.H.Closs, A.C.Kostka, C.A.Wraight, and J.R.Narris, Proc.Nat.Acad.Sci. USA, 1981, **78**, 3305.
26. R.A.Zhitnikov and B.N.Sevast'yanov, Zhur.Eksper. Teor.Fiz., 1969, **56**(5), 1508.
27. S.P.Dmitriev, R.A.Zhitnikov, and A.I.Okunev, Zhur.Eksper.Teor.Fiz., 1976, **70**, 69.
28. R.A.Zhitnikov, Vestnik Akad.Nauk SSSR, 1978(5), 3.
29. A.L.Buchachenko and V.L.Berdinskii, Vestnik Akad. Nauk SSSR, 1981(1), 91.

Institute of Chemical Physics of the
USSR Academy of Sciences, Moscow