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Dynamic and stimulated nuclear polarisation in photochemical radical reactions

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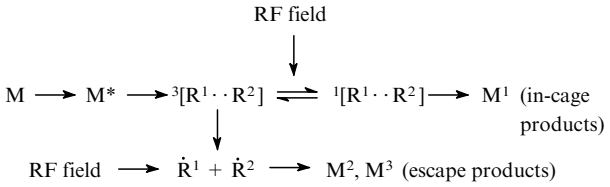
Abstract. Highly sensitive time-resolved magnetic resonance techniques based on the effect of variable radio-frequency and switched constant magnetic fields on the nuclear polarisation of diamagnetic products of radical reactions are considered. The applications of these methods to the investigation of short-lived radical intermediates (radical pairs, biradicals, free radicals and radical ions) formed in photochemical reactions in homogeneous and molecular-organised media are discussed. The bibliography includes 148 references.

I. Introduction

The review is devoted to the use of new time-resolved magnetic resonance techniques based on the detection of nuclear polarisation of diamagnetic products of radical reactions for the study of spin dynamics and chemical kinetics of short-lived radical species (free radicals, radical pairs and radical ion pairs) in photochemical radical reactions. The demand for investigation of fast photochemical reactions in solutions has stimulated the appearance and extensive development of methods for the detection of short-lived radical species, for example, laser flash photolysis, time-resolved EPR, reaction yield detected magnetic resonance methods (RYDMR), *etc*. The progress in the investigations into the mechanisms of photochemical radical reactions is largely associated with the use of magnetic resonance † because these methods provide information on the structure of radicals, the rates of chemical reactions, electron exchange interaction, the parameters determining the mobility of radical species in solutions.

Methods based on the application of variable resonance magnetic fields have been greatly developed during the last two decades.[1–12] A radio-frequency (RF) resonance field induces nuclear polarisation of in-cage (M^1) and escape (M^2, M^3) diamagnetic products of a photochemical reaction. Polarisation arises either upon RF-induced changes in the singlet – triplet conversion rate in radical pairs (selectively with respect to the orientation of nuclear spins) or upon electron or nuclear transitions in the free radicals R^1, R^2 (Scheme 1). The magnitude and the sign of nuclear polarisation induced by an RF field depend on the field frequency and on the type of resonance transition (nuclear or electronic) to which this frequency corresponds.

Scheme 1



There are several methods for detecting magnetic resonance spectra of short-lived radical species.

(i) Stimulation of nuclear transitions in polarised intermediate short-lived radicals with simultaneous recording of the NMR spectra of diamagnetic products.[13–18] This method was first proposed and implemented in a study by Sagdeev *et al.*[13] and was developed further by Trifunac *et al.*[14–18] An obvious advantage of the method is high sensitivity (below 10^8 spins in the sample) and simplicity of line assignment — the lines of the product detected by NMR correspond to a particular nucleus in the radical precursors. The main shortcoming of the method is that its scope is limited to radicals the lifetimes of which are not shorter than several microseconds.

(ii) The method of dynamic nuclear polarisation (DNP). Pumping of electron transitions in the intermediate short-lived radicals gives rise to nuclear polarisation, which is transferred to diamagnetic products after radical recombination.[12,19–22] The dependence of the signal intensity in the NMR spectrum of diamagnetic products on the external magnetic field is an EPR spectrum of the intermediate radicals. This method provides information on the mechanism of electron – nucleus interaction in short-lived radicals (contact or dipole – dipole); it opens the way for determining the relaxation times, the signs and the magnitudes of hyperfine coupling (HFC) constants and for investigation of the kinetics of these radicals in solution.

(iii) The method of stimulated nuclear polarisation (SNP). The effect of an RF field with a specified frequency on an ensemble of

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† The sensitivity of EPR (10^9 spins in a sample) does not always suffice for the investigation of fast radical processes.

radical pairs changes nuclear polarisation in the products formed.[12, 23–25] By investigating the dependence of nuclear polarisation of the diamagnetic products on the frequency of the saturating field, one can gain information on the EPR spectrum of the intermediate radical pair, exchange interaction, pathways to diamagnetic products, *etc*.

II. Experimental implementation of the methods

For recording the spectra of short-lived radicals, it was necessary to devise instruments which either produce a variable resonance magnetic field at radio frequency or ensure the possibility of switching an external magnetic field directly during a radical reaction with simultaneous recording of the NMR spectra of diamagnetic products. Coupling of a resonator or an oscillator circuit with the probe of a standard NMR spectrometer was a complicated engineering problem. This was done by Sagdeev *et al.*[13] in the first experiment on recording the NMR spectra of short-lived radicals. In scanning the resonance lines, the frequency sweep of the RF field was accomplished manually; due to the restrictions in the frequency range of the resonance circuit of the NMR spectrometer, only one resonance line was detected. The separate pumping of resonance transitions in radical pairs and recording the NMR spectra of the reaction products proved to be an easier procedure (Fig. 1). A fast-flow system is normally used to transfer the sample into the photolysis cell. A liquid is injected into the cell through a thin Teflon capillary either using a pump [17, 20, 26] or under a gas pressure.[12] The flow rate of the liquid should be such that the time it takes to transfer the sample from the reaction vessel to the probe of the NMR spectrometer be shorter than the nuclear relaxation time of diamagnetic products, *i.e*. this should require fractions of a second. An original setup for detecting SNP in weak magnetic fields of about 10.0 mT has been developed.[27] The transfer of a sample from the magnetic field in which the photochemical reaction took place to the probe of the NMR spectrometer was performed using the pneumatic system of the probe. The frequency of pumping of electron transitions (300 MHz) was equal to the resonance frequency of the NMR spectrometer. The limitations of this method include the use of only one resonance frequency of an RF field.

The magnetic flux chosen (B_0) is largely determined by the goals of the experiment. The resonance frequency employed in existing experimental setups ranges from 50 MHz to 10 GHz.

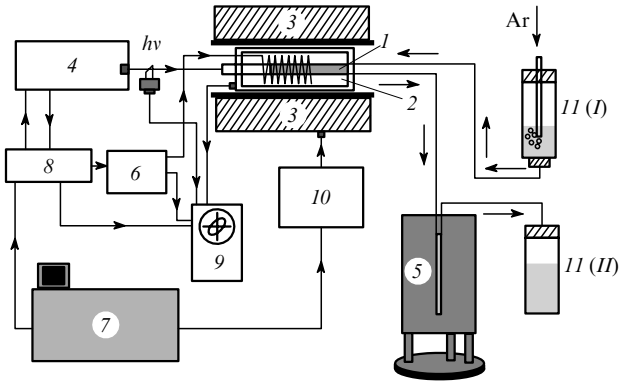


Figure 1. Block diagram of the setup for the study of SNP: (*1*) photolysis cell with a sample; (*2*) RF resonator or oscillating circuit; (*3*) electromagnet; (*4*) laser (308 nm); (*5*) superconductive magnet and the probe of a Bruker MSL-300 NMR spectrometer (300 MHz); (*6*) RF generator; (*7*) control computer of the NMR spectrometer; (*8*) pulse generator; (*9*) an oscilloscope; (*10*) power supply of the magnet and B_0 sweep; (*11*) fast-flow system consisting of a vessel (*I*) with the initial substances (argon feed under a pressure of $\sim$1.5 atm) and a vessel for the collection of the reaction products (*II*).

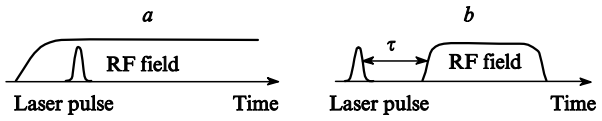


Figure 2. Schematic illustration of the two methods for recording the spectra: continuous (*a*) and pulse (*b*).

In pulse methods [28] (Fig. 2), the dependence of the intensity of NMR spectra on the time delay (τ) between the laser pulse and the RF pulse is studied. The main difference between the pulse and steady-state methods is as follows. When the continuous variant is used, radical pairs and the intermediate short-lived radicals exist throughout their lifetimes under the influence of an RF field, which induces the singlet – triplet conversion in radical pairs or the DNP. The use of pulse modification provides a new, in principle, opportunity to expose separate sub-ensembles of radical pairs (or radicals) with a particular lifetime to an RF field. The main advantages of the pulse variant over the steady-state method include differentiation of geminate and diffusion pairs by measuring the SNP for different delays τ; separation of the contributions of SNP and DNP to the RF field-induced nuclear polarisation; the possibility of obtaining information on the pattern of distribution of radical pairs and radicals over lifetimes. In the case of pulse method, time resolution is determined by the rise times of the microwave pulse and the laser pulse and equals 20 – 30 ns. High time resolution can be achieved by using either cavities with low Q-factors or cavities with high Q-factors but with a higher coupling constant between the resonator and the generator.[29] Upon mathematical processing of the data, the time resolution of the method can be improved to 5 ns.[27]

A substantial drawback of the above methods of recording the spectra is the necessity of using large samples. The use of deuterated solvents markedly increases the cost of the experiment; however, this problem can be solved by taking solvents containing no protons (CCl_4, C_6F_6 and so on) or by recording the spectra for other nuclei (^{13}C, ^{31}P, ^{19}F and so on.). In the case where the NMR chemical shifts of the solvent and the compound under study differ by several ppm (at least, by 1 ppm), the signal of the solvent should be suppressed.

III. Dynamic nuclear polarisation

The DNP effect means that saturation of the electron levels of free radicals in an external magnetic field gives rise to a non-equilibrium nuclear polarisation.[30, 31] A radio-frequency resonance magnetic field makes the occupancies of the electron levels equal and thus creates non-equilibrium occupation. Cross-relaxation transitions caused by hyperfine coupling of an electron with the nucleus are directed at restoring the thermal equilibrium between the electron levels. However, since cross-relaxation processes are accompanied by inversion of nuclear spins, polarisation arises on the radical nuclei,

$$p = \xi s f \frac{\gamma_e}{\gamma_n},$$

where, the parameter ξ is determined by the mechanism of the electron – nucleus coupling, $s = (S_0 - < S_z >)/S_0$ is the saturation factor of the electron spin system, f is the leakage factor determining the fraction of nuclear relaxation occurring without participation of electron spins, and γ_e and γ_n are gyromagnetic ratios of the electron and nuclear spins. For contact interaction [the change in the total spin of the electron and the nucleus (Δm) is equal to zero], $\xi = 1$, while for dipole interaction ($\Delta m = 2$), $\xi = -1/2$. Figure 3 illustrates qualitatively the mechanism of formation of the DNP upon non-equilibrium electron polarisation of a radical with two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) and positive

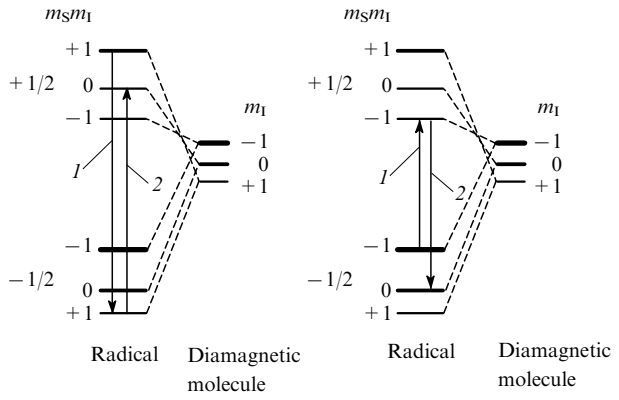


Figure 3. Schematic illustration for the mechanism of the generation of multiplet DPN of the diamagnetic products formed from short-lived radicals. The arrows show the resonance transitions induced by an RF field (*1*) and cross-relaxation transitions (*2*).

HFC constants ($A_1 = A_2$).[32] Cross-relaxation occurs by a contact mechanism ($\Delta m = 0$).

Study of the dependences of DNP of stable radicals of paramagnetic ions on the temperature, solvent viscosity, and the magnetic field strength makes it possible to solve diverse problems, for example, to study the effect of the medium on the interaction of various molecules with free radicals, to study the roles of the contact and dipole interactions during relaxation, to determine the mechanisms of interaction between radicals and nuclei, *etc*.‡

1. Dynamic nuclear polarisation of neutral intermediate short-lived radicals

Grishin *et al*.[19] was the first to consider the possibility of using the DNP effects for the investigation of intermediate short-lived radicals. Photolysis of benzaldehyde in CCl_4 affords the radical pairs [PhĊH(OH) PhĊO].[19] α-Hydroxybenzyl radicals are converted into the starting benzaldehyde upon hydrogen atom transfer. In strong magnetic fields (330 mT), DNP can be detected in the NMR signals of all the diamagnetic reaction products.[19, 33–35] The negative sign of DNP corresponds to a dipole mechanism of cross-relaxation in the intermediate α-hydroxybenzyl radical. In weak and medium magnetic fields (3 and 60 mT) in which the cross-relaxation efficiency is much lower, DNP is negligibly small, the predominant contribution to polarisation being made by SNP. As noted above, an RF field induces nuclear polarisation both by the DNP mechanism, due to cross-relaxation processes in free radicals, and by the SNP mechanism, due to the change in the rate of singlet–triplet transitions in radical pairs. The contributions of these mechanisms to the polarisation of the nuclei of diamagnetic products formed from short-lived radicals can be separated based on the dependence of the width of resonance lines and the SNP and DNP intensities on the RF field amplitude (B_1). For example, photolysis of benzaldehyde in $CHCl_3$ has been used to study the influence of the RF-field amplitude on the ratio of the SNP and DNP contributions and on the width of individual components of the spectrum.[20] This permitted the researchers to estimate the lifetime of the radical pairs (~ 20 ns).

The possibility of separating the contributions of DNP and SNP to the total polarisation by varying the external magnetic field, the RF-field amplitude and the lifetimes of radicals was demonstrated [12] in relation to the photolysis of benzoquinone in solutions. For semiquinoid radicals, the efficiency of cross-relaxation in 50.0 mT fields becomes substantial, and the observed DNP is comparable in magnitude with SNP. For durosemiquinoid radicals, cross-relaxation is due to the modulation of HFC caused by rotation of the methyl groups (*i.e*. cross-relaxation follows a contact mechanism); in this case, a positive DNP effect is observed.[20, 21, 31–36]

Information on electron relaxation times in short-lived radicals and on the rate of chemical reactions can be gained by using pulsed generation of radicals and by investigating the variation of DNP intensity in the magnetic field corresponding to the maximum of the resonance line *vs*. the time delay between the laser pulse and the leading edge of the RF pulse. These experiments for the neutral radicals generated upon photolysis of benzaldehyde in chloroform were first performed by Yamakage *et al*.[37] The experimental results were processed by calculations in terms of the kinetic scheme for the occupancies of the radical levels with allowance for cross-relaxation, electron transitions and the chemical reaction. It was shown that the DNP kinetics actually reflect the radical kinetics and do not depend on the cross-relaxation rate, while the DNP intensity is determined by the ratio of the cross-relaxation, electron relaxation and the chemical reaction rates. The results provided grounds for concluding that the cross-relaxation rate for the α-proton of the α-hydroxybenzyl radical is one or two orders of magnitude lower than that for aromatic protons.

Cross-relaxation processes influence substantially the chemically induced dynamic electron polarisation (CIDEP) of short-lived radicals [38–40] and, in some cases, account for the change in its sign. Thus McLauchlan *et al*.[39, 40] found the change in the CIDEP sign in the photolysis of aliphatic ketones and suggested that this is due to the cross-relaxation in the intermediate radical. Subsequently, in a theoretical study of the cross-relaxation processes, it was shown [41] that CIDNP and CIDEP are related in time and their kinetics should be considered jointly. Thus, the transfer of electron polarisation to the nuclei should substantially affect the CIDNP kinetics. Experimental research on photolysis of aliphatic ketones by the time-resolved CIDNP method gave ambiguous results. Tsentalovich *et al*.[42–46] concluded that, when analysing the kinetics of CIDNP detected during the photolysis of acetone in isopropanol and 2,4-dihydroxy-2,4-dimethylpentanone, one should take into account the contribution of the cross-relaxation mechanism. However, Fischer *et al*.[47] showed that the CIDNP kinetics can be adequately described without allowance for cross-relaxation; only two-photon processes resulting in CIDNP of some reaction products should be taken into account. In addition, CIDEP with a positive sign is observed in the photolysis of 2,4-dihydroxy-2,4-dimethylpentanone, which refutes the conclusions about generation of CIDNP by the cross-relaxation mechanism made by Salzmann.[45] The main difficulty in comparison of the results obtained by the CIDEP and CIDNP methods is that the fields used in CIDEP experiments are about 330 mT, while the operating fields of NMR spectrometers are usually in the range 3–7 T. The electron and cross-relaxation times are known to depend appreciably on the external magnetic field, while the processes of polarisation transfer are, in turn, determined by these times.

The use of the DNP method clarified the point concerning the nature of inversion of the CIDEP sign.[32] A study of the DNP in reactions involving $Me_2X\dot{C}$ radicals (X = Me, OH, D, COMe) demonstrated unambiguously the presence of effective scalar ($\Delta m = 0$) electron–nuclear cross-relaxation in the *tert*-butyl and 2-hydroxyprop-2-yl radicals and the absence of cross-relaxation in 2-acetyl and prop-2-yl radicals. Figure 4 shows the DNP and EPR spectra recorded in the X and L ranges for the $Me_2(OH)\dot{C}$ radical, resulting from photolysis of 2,4-dihydroxy-2,4-dimethylpentanone in benzene. It can be seen that the signs of polarisation coincide and the intensity ratios of the lines in the spectra are closely similar. Comparison of the obtained results with the results of time-resolved CIDNP studies led to the conclusion that the cross-relaxation is due to the modulation of the isotropic HFC with a characteristic correlation time of $\tau_c \gg 1$ ps.

‡ The DNP studies of stable radicals are surveyed comprehensively in Ref. 31.

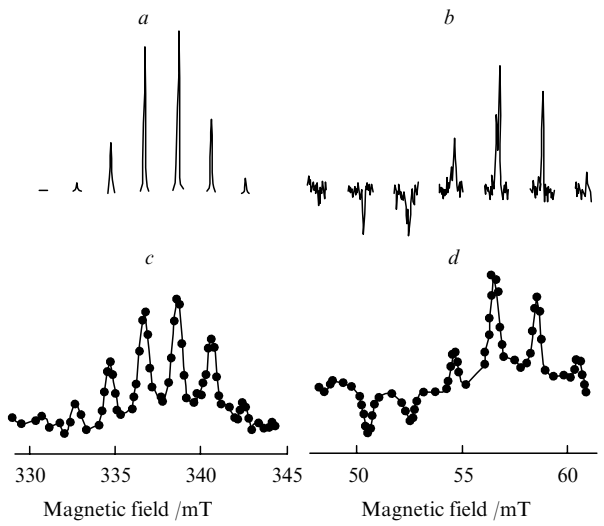


Figure 4. Spectra of 2-hydroxyprop-2-yl radical recorded in the X and L ranges by the time-resolved EPR (*a*, *b*) and DNP (*c*, *d*) methods. The resonance frequency is 10 (*a*, *c*), 1.6 (*b*) and 1.53 GHz (*d*).

2. Dynamic nuclear polarisation in radical ions

Radical-ion reactions are accompanied, in the majority of cases, by degenerate electron exchange (DEE) reactions

$$D^{\bullet} + D \rightleftharpoons D + D^{\bullet},$$

$$A^{\bullet} + A \rightleftharpoons A + A^{\bullet}$$

(D is donor, A is acceptor); therefore, the DNP in radical-ion reactions has several specific features.

In a study of the influence of an RF field on the nuclear polarisation of the products of radical-ion reactions in weak magnetic fields, a pronounced DNP effect was found.[48] Further studies demonstrated[22,49] that this effect is observed in the presence of DEE provided that the magnitide of the external magnetic field is comparable with the HFC constant of the radical ion.

Two different approaches have been proposed for quantitative description of DNP under the conditions of DEE in weak magnetic fields.[22,49] One approach is based on numerical solution of the Liouville equation for the spin density matrix of the radical with allowance for the spin dynamics in a weak magnetic field and the DEE process, while the other approach includes solution of the Bloch phenomenological equations with allowance for the relaxation times T_1^e, T_2^e

$$\frac{1}{T_1^e} = 2\Delta^2\tau_e\frac{1}{1+\omega_0^2\tau_e^2};$$

$$\frac{1}{T_2^e} = \Delta^2\tau_e\left(1+\frac{1}{1+\omega_0^2\tau_e^2}\right),$$

where $\Delta^2 = \frac{1}{3}\sum_i I_i(I_i+1)A_i^2$ is the second moment of the EPR spectrum of the radical ion for nuclei with spins I_i and HFC constants A_i, τ_e is the DEE time, and ω_0 is the Larmor frequency of electron spins.

The former approach is applicable to any DEE rates, while the latter one is suitable only for high exchange rates ($\Delta^2\tau_e^2 \ll 1$). The main advantages of the latter model include its simplicity and the possibility of using it to study radicals with complex EPR spectra. Comparison of the DNP spectra calculated in terms of these two models showed that at high rates of electron exchange, the spectral patterns are identical; in this case, the use of the phenomenological approach is quite justified. Note that both models take into account only processes which occur in radical ions, the influence of the RF field on the radical pairs being ignored. Of course, this assumption is rather simplified because the RF field induces singlet–triplet transitions in the radical ion pairs and, thus, it can, in principle, induce CIDEP.[50] The line shape in the DNP spectrum in the absence of CIDEP was compared to that obtained with the assumption that CIDEP does not depend on the fields B_1 and B_0. It was shown that the distinctions become significant in the case of DEE and large B_1 values, *i.e.* in those cases where the spectrum width becomes comparable with the field magnitude B_0.

The DNP effects have also been studied in the photolysis of anthracene with dimethyl- or diethyl-aniline and in the photosensitised *cis–trans* isomerisation of fumaronitrile in the presence of naphthalenes.[22,24,49,51] The researchers studied the influence of the electron exchange rate and the amplitude of the RF field on the pattern of DNP spectra; the results were in good agreement with theoretical predictions. The dependence of the half-width of the spectrum on the reciprocal concentration of diamagnetic molecules participating in the charge exchange was used to determine the rate constants for the electron exchange of the dimethyl- and diethyl-aniline radical cations.

The sign of CIDEP is known to be determined by the multiplicity of the radical pair and by the sign of exchange interaction.[52] Upon the change in multiplicity, the sign of CIDEP and, hence, the sign of DNP should be reversed. This was observed,[25,51] for example, in the photosensitised isomerisation of fumaronitrile in 1,4-dimethoxynaphthalene. The triplet state of the excited 1,4-dimethoxynaphthalene molecule is lower in energy than the radical-ion pair; therefore, by changing the concentration of fumaronitrile, one can change the multiplicity of the radical pair.[53]

The measurement of the DEE rate constants can be markedly simplified by proceeding from the dependence of the DNP kinetics on the concentration of the diamagnetic product. This method has advantages over investigation of the concentration dependence of the half-with of the DNP spectra because the half-width of the spectra depends appreciably on the amplitude of the RF field B_1, whereas the DNP kinetics do not. For the first-order reaction of radical decay, an analytical solution was found; for the second-order reaction, a numerical solution was obtained.[49] It was shown that the DNP kinetics are determined by the time of electron exchange τ_e, the time of electron relaxation T_1^e and the lifetime of radical ions τ_l. For high concentrations of diamagnetic molecules involved in DEE, the kinetics are described by an exponential function with a decay parameter equal to T_1^e. Figure 5 shows the experimental curves for the DNP kinetics of the photolysis of fumaronitrile with perdeuterated naphthalene. Any curve for $\tau_l > 100$ ns can be described by the exponential function $\exp(-k_{obs}\tau_l)$, where k_{obs} is the observed rate constant for the exponential decay. The initial pattern of the curve presented in Fig. 5*b* is due to the time for generation of radical ions. At high concentrations of molecules participating in charge exchange, *i.e.* at low times of DEE, the condition $T_1^e \ll \tau_l$ holds, T_1^e and the experimental dependences of k_{obs} on the concentration of fumaronitrile being adequately described by the formula

$$k_{obs} \simeq \frac{1}{T_1^e} = \frac{2\Delta^2\tau_e}{1+\omega_0^2\tau_e^2}.$$

The rate constant for DEE k_e is equal to $(4.52\pm0.23)\times10^9$ litre mol^{-1} s^{-1} and is close to the value estimated from the concentration dependence of the spectra.

In a series of studies,[25,54,55] the DNP method together with time-resolved EPR were employed to identify the radical species resulting from photolysis of heteroaromatic azines in the presence of dimethylaniline in polar solvents. In the DNP study of all the compounds, except for phenazine, the recorded spectra of the dimethylaniline radical cation were narrowed down due to the DEE reaction. This provided grounds for conclusion that the radical-ion pathway contributes to the formation of the compounds under consideration.

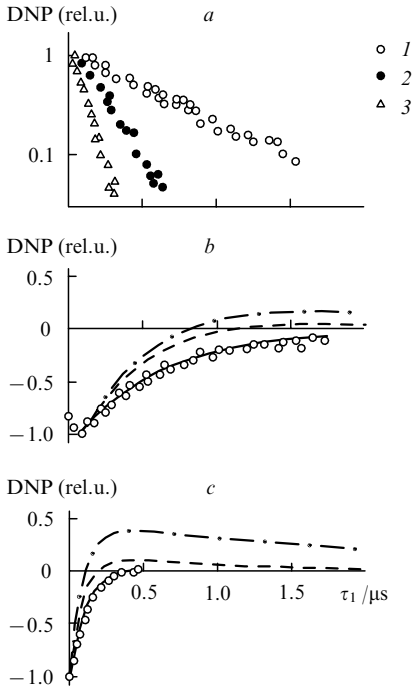


Figure 5. Time dependences of DNP obtained for the photolysis of naphthalene-d_8 ($c = 5\times10^{-4}$ mol litre^{-1}) with fumaronitrile in CD_3CN at different DEE rates. Fumaronitrile concentration (mol litre^{-1}): (*a*) 5×10^{-3} (*1*), 2×10^{-2} (*2*), 4×10^{-2} (*3*); (*b*) 5×10^{-3}; (*c*) 4×10^{-2}. The absolute magnitudes of DNP are plotted on a logarithmic scale (*a*). The continuous lines (*b*, *c*) correspond to the decay of radical ions by an exponential law, dashed lines show the second-order decay of radical ions and describe the contributions of the minor geminate (dashed line) and diffusion polarisations (chain line).

3. Electron – nuclei transitions in short-lived radicals in weak magnetic fields

The influence of an RF field on the nuclear polarisation of diamagnetic products of radical reactions in weak magnetic fields, whose magnitudes are comparable with the HFC constants of radicals, possesses several specific features: the intrinsic wave functions of radicals are no longer the products of the electronic and nuclear wave functions, and the resonance transitions are not purely electronic or nuclear transitions. Therefore, all transitions in these fields involve both the nuclear and the electronic spins. Therefore, the use of relatively low RF-field amplitudes results in substantial changes in the occupancy of the electron – nuclear levels. This effect was called NMR detected electron – nuclear transitions in short-lived radicals (NMR ENR).[56, 57]

The diagram of the electron – nuclear spin levels of a radical with one magnetic nucleus with the spin 1/2 is shown in Fig. 6. In a weak magnetic field, the probabilities (P) of transitions $n_1 \rightleftharpoons n_2$ and $n_3 \rightleftharpoons n_4$ on exposure to a resonance field are proportional to the expression

$$P_{n_i \rightleftharpoons n_j} \sim |<\Psi_{n_i}|\hat{B}_{1x}(\hat{S}_x + \hat{I}_x)|\Psi_{n_j}>|^2 = \\ = B_1^2[c_1^2(\gamma_e\beta_e)^2 + c_2^2(\gamma_n\beta_n)^2],$$

where n_i, n_j correspond in pairs to n_1, n_2 and n_3, n_4; $\Psi_{n_{i,j}}$ are the wave functions of the $n_{i,j}$ states; the coefficients c_1 and c_2 are determined by the relationship between the HFC constant and the B_0 value. When the magnetic field changes, the coefficients c_1^2 and c_2^2 change from 1 and 0, respectively, in strong magnetic fields (where $n_1 \rightleftharpoons n_2$ and $n_3 \rightleftharpoons n_4$ are purely nuclear transitions) to 0.5 and 0.5, respectively, in the zero magnetic field in which these transitions involve changes in the projections of both electron and nuclear spins. In a strong magnetic field ($c_1 = 1$, $c_2 = 0$), substantial amplitudes of the radio-frequency field are required to saturate these transitions in short-lived radicals

$$B_1 \approx \frac{1}{\gamma_n\tau^*},$$

where

$$\frac{1}{\tau^*} = \frac{1}{T_1^n} + \frac{1}{\tau_1} + \frac{1}{T_{cr}},$$

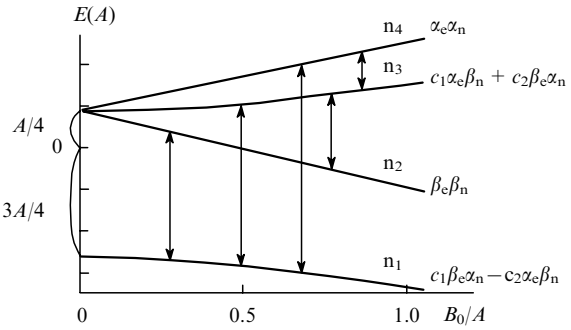


Figure 6. Scheme of the energy levels of a radical with one magnetic nucleus and the spin 1/2 in a magnetic field. The arrows show all the transitions allowed in a weak field.

T_1^n is the time of nuclear relaxation of the radical, τ_1 is the lifetime of the radicals and T_{cr} is the time of electron – nuclear cross-relaxation. With the real values $T_1^n \approx 10^{-4}$ s, $\tau_1 \approx 10^{-5}-10^{-6}$ s, $T_{cr} \approx 10^{-5}$ s, we have $B_1 \approx 1-10$ mT. In weak magnetic fields ($c_1^2 \approx c_2^2$), the probability of transitions is high even for much smaller amplitudes of the radio-frequency field

$$B_1 \sim \frac{1}{c_1\gamma_e\tau^*},$$

where

$$\frac{1}{\tau^*} = \frac{1}{T_1^e} + \frac{1}{\tau_1} + \frac{1}{T_{cr}},$$

T_1^e is the time of electron relaxation of the radical. Thus, in weak magnetic fields, the probability of transitions is high when radio-frequency fields of about 10^{-2} mT are used.

In radical reactions, the occupancies of electron–nuclear sublevels of radicals are usually non-equilibrated due to CIDNP. It is evident that saturation of transitions would result in equalisation of the occupancies and in a substantial change in the nuclear polarisation of the diamagnetic products. In weak magnetic fields, a radio-frequency field acting parallel to an external magnetic field induces the $n_1 \rightleftharpoons n_3$ transition (see Fig. 6), forbidden in strong magnetic fields. The probability of this transition is proportional to the value $(c_1c_2\gamma_eB_1)$.[2]

Theoretical description of the NMR ENR effect was made using the numerical solution of the Liouville equation for the spin density matrix of the radical with allowance for electron and nuclear relaxation. Theoretical analysis of the main features of this effect showed that its magnitude is determined by several factors, namely, by the amplitude of the applied radio-frequency field, the coefficients c_1 and c_2, the lifetime of radicals in solution and by the occupancy of the corresponding electron – nuclear levels (Fig. 7). It can be seen that at relatively small amplitudes of the radio-frequency field, the magnitude of this effect does not depend on the type of the transition excited, while at large amplitudes, it does depend on the type of transition. Thus, by comparing the polarisation intensities corresponding to different transitions in the same magnetic field, one can calculate the occupancies of all the electron – nuclear spin levels of free radicals; analysis of the line shape provides information concerning the

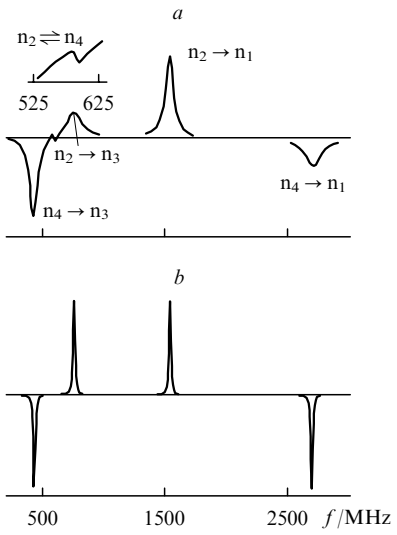


Figure 7. Theoretical NMR ENR spectra. Initial occupancies of the levels $n_1 = 0$, $n_2 = 1/2$, $n_3 = 0$, $n_4 = 1/2$. The multiplet CIDNP arises in a 42 mT magnetic field, $\tau_1 \ll T_{1,2}$, $A = 70$ mT, the amplitude of the applied radio-frequency field B_1 (mT): (*a*) 3, (*b*) 0.001.

relaxation times of radicals in a weak magnetic field and on their lifetimes.

Ananchenko *et al.*[56–58] were the first to carry out experiments on the study of the electron–nuclear transitions in phosphonyl radicals resulting from photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide and dimethyl 2,4,6-trimethylbenzoylphosphonic acid. Figures 8 and 9 present the NMR ENR spectra recorded upon photolysis of 2,4,6-(trimethylbenzoyl)diphenylphosphine oxide (B_1 is parallel to B_0, Fig. 8) and dimethyl

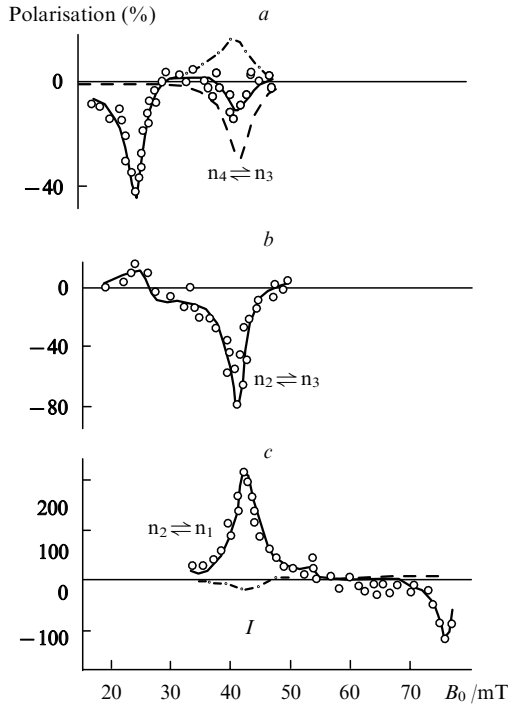


Figure 8. NMR ENR spectra of the diphenylphosphinyl radical $Ph_2(O)P^{\bullet}$. RF-field frequency ν (MHz): (*a*) 431, (*b*) 750, (*c*) 1530; RF-field amplitude B_1 (mT): (*a*, *c*) 1.1, (*b*) 1.2. Continuous lines are the simulated spectra constructed as the sum of the SNP contributions (chain line) and the theoretical NMR ENR spectra (dashed line).

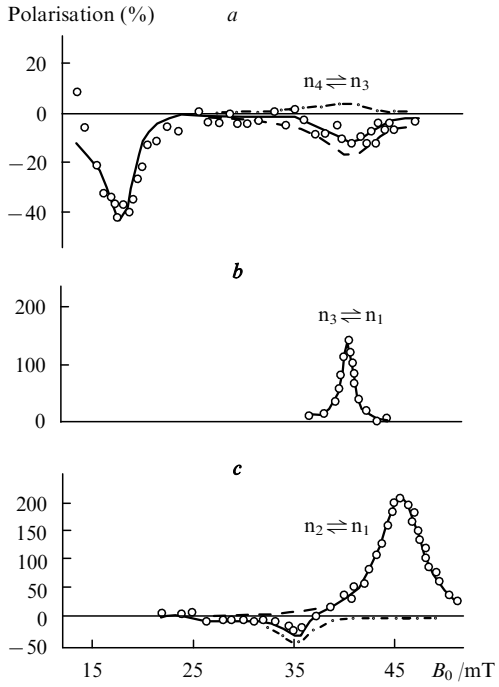


Figure 9. NMR ENR spectra of the dimethylphosphonyl radical $(MeO)_2(O)P^{\bullet}$. RF-field frequency ν (MHz): (*a*) 315, (*b*) 1530, (*c*) 694; RF-field amplitude B_1 (mT): (*a*) 1.2, (*b*) 0.7, (*c*) 0.9. For the designation of lines, see Fig. 8.

2,4,6-trimethylbenzoylphosphonate in dioxane (B_1 is perpendicular to B_0, Fig. 9). Polarisation was measured in percent of CIDNP for $B_0 = 42$ mT. It can be seen that the intensity of the $n_1 \rightleftharpoons n_2$ and $n_1 \rightleftharpoons n_3$ transitions exceeds the intensity of the $n_4 \rightleftharpoons n_3$ transitions by a large factor. Based on analysis of the intensities and the signs of resonance lines in the spectrum, it was shown that the initial occupancy of the level n_1 is negligibly small compared to that of the levels n_2, n_3 or n_4. Thus, it can be concluded that in weak magnetic fields, the magnitudes of which are lower than the HFC constants of radicals, intense electron polarisation should be observed. It is noteworthy that the results are in good agreement with the conclusions based on analysis of the field dependences of CIDNP for radical pairs with large HFC constants.[59, 60]

IV. Stimulated nuclear polarisation

Stimulated nuclear polarisation is a phenomenon tightly related to other magnetic and spin effects in radical reactions, in particular, to the chemically induced dynamic nuclear polarisation. The CIDNP method does not bear direct quantitative information about the magnetic-resonance parameters of radical pairs; therefore, it should be combined with other methods such as EPR, optical spectroscopy, *etc.* For example, the use of time-resolved CIDNP, first proposed and implemented by Closs *et al.*,[61] provides quantitative information on the kinetics of the intermediate radical species, the lifetimes of triplet molecules, *etc.*[62–64]

The SNP method is a combination of CIDNP with the RYDMR principles,[1–10, 65, 66] based on the selective influence of a variable field on the probability of recombination of separate sub-ensembles of radical pairs. The influence of an RF field on the yield of the reaction products is detected from the change of parameters of the system under study (for example, the resonance photoconductivity of organic semiconductors, the intensity of the recombination fluorescence, the optical absorption of the products, the EPR spectra of stable radicals,[67] *etc.*).

We shall consider the mechanism of SNP in relation to a radical pair with one magnetic nucleus in strong magnetic fields. Let us assume that the pair has formed in the triplet state and

recombination from the triplet state is forbidden. In the case of strong magnetic fields, the S and T_0 states are degenerate and, therefore, transitions from the non-reactive T_0 state to the reactive S state occur efficiently due to hyperfine coupling. However, transitions from the T_- and T_+ states to the S state are supressed due to the great energy gap between these states. The CIDNP effect is known to be based on the fact that the probabilities of the S–T transitions are different for radical pairs with different orientations of the nuclear spin. Let the *g*-factors of the radicals be equal. In this case, the CIDNP effect for a radical pair with one magnetic nucleus is equal to zero. The resonance RF field mixes the T_0 state of the radical pair with the T_- and T_+ states, which accelerates the S–T conversion at small amplitudes of the RF field ($\omega_1 < |\Delta\omega|$) and decelerates it at great amplitudes ($\omega_1 > |\Delta\omega|$). [Here, ω_1 is the amplitude of the RF field, $\Delta\omega = \omega_\alpha - \omega_0 = \omega_0 - \omega_\beta$ is the difference between the resonance frequencies of the radicals R^1 and R^2 (partners of the $R^{1\bullet}{}^{\bullet}R^2$ radical pairs), R^1 contains the magnetic nucleus (ω_α, ω_β) and R^2 contains no nuclei with a non-zero HFC constant (ω_0).] We assume that $\omega_1 < |\Delta\omega|$. If the resonance-field frequency is equal to the resonance frequency ω_α of electron transitions in the radical R^1 with α-orientation of the nuclear spins, the acceleration of S–T transitions would involve only the sub-ensemble of radical pairs with this spin orientation and the products of recombination of radical pairs would mainly contain nuclei with the α-projection of spins. This would result in enhanced absorption in the NMR line of in-cage products. The nuclei of the escape products of the recombination of the radical pair would be mainly characterised by the β-projection of spins and the corresponding line in the NMR spectrum would be an emission line (Fig. 10). If the frequency of the RF field is equal to the ω_β frequency of the electron transitions in the R^1 radical with the β-orientation of nuclear spins, emission would be observed in the NMR lines of the in-cage products and absorption would be observed in the spectra of escape products. The effect of the RF field on the resonance frequency of the R^2 radical (ω_0) will induce acceleration of the S–T conversion with the same efficiency for both sub-ensembles of radical pairs and, hence, will not change the nuclear polarisation of the products. Thus, the positions of the resonance lines in the SNP spectrum correspond to the resonance frequencies in the EPR spectrum of the radical pair, and the signs of the resonance lines are determined by the signs of the HFC constants and by the pathways to diamagnetic products the NMR spectrum of which is used to detect the SNP.

In the case where $\omega_1 > |\Delta\omega|$, *i.e.* under spin-locking conditions, the RF field retards the S–T conversion and, hence, the signs of SNP would be opposite to those observed in the case described above. On the basis of these considerations, Mikhailov *et al.*[68] formulated the rule for determining the sign of polarisation of the products for the case of net SNP

$$\Gamma = \mu\varepsilon\psi\eta A_k ,$$

where $\Gamma > 0$ corresponds to the positive (absorption) and $\Gamma < 0$, to the negative SNP effect (emission), $\mu = 1$ or -1 for a triplet or a singlet radical pair; $\varepsilon = 1$ or -1 for the in-cage or escape product; $\psi = 1$ or -1 for low- or high-field component of the HFC spectrum of the chosen nucleus; $\eta = 1$ for $\omega_1 < |\Delta\omega|$ and $\eta = -1$ for $\omega_1 > |\Delta\omega|$, A_k is the isotropic HFC constant at the *k*-th nucleus polarisation of which is considered.

For radical pairs with any number of magnetic nuclei, the SNP spectrum is a superposition of the spectra of separate sub-ensembles of radical pairs with fixed configurations of nuclear spins. In a real situation when the spin dynamics of radical pairs are overlapped by the molecular motion of radicals, the spectral lines have a finite width and, in the general case, for several nuclei with different HFC constants, the SNP spectral pattern is markedly complicated. Therefore, to analyse the experimental SNP spectra, one should compare them with the theoretical spectra.

Exchange interaction markedly influences the pattern of the SNP spectra. We shall consider this influence qualitatively in relation to a biradical with one magnetic nucleus (Fig. 11 *a*,*b*). The relative positions of the energy levels are determined by the ratio of the HFC constants *A*, the effective exchange interaction J_0 and the external magnetic field B_0. The effects of nuclear polarisation, both chemically induced and stimulated, depend substantially on the ratio of the intersystem crossing rates (K_{S-T_0}, K_{S-T_-}). In the case where the average exchange interaction $\gamma_e B_0 < 2|J_0|$ (Fig. 11 *a*), the rate of intersystem crossing *via* the S–T_- channel is higher than that *via* other channels ($K_{S-T_-} > K_{S-T_0}$, K_{S-T_+}); therefore, the occupancy of the T_-^α state is lower than those of the T_+^α or T_0^α states. Radio frequency pumps the T_-^α level and thus increases the number of radical pairs recombining upon $T_-^\alpha \rightarrow S^\beta$ transitions. As a consequence, the products of recombination become enriched in the nuclei with the β-projection of nuclear spins. The SNP spectrum of radical pairs is an emission line. Otherwise, $\gamma_e B_0 > 2|J_0|$ ($K_{S-T_0} > K_{S-T_-}$, K_{S-T_+}) (Fig. 11 *b*) and the occupancy of the T_0^α state is lower than that of the T_-^α or T_+^α states. In this case, the number of radical pairs recombining *via* the S–T_0 channel of intersystem crossing increases under the action of the RF field. The SNP spectral pattern is normal — the signs of polarisation of the spectral lines depend on the signs of the projection of the nuclear spins, the exchange interaction being manifested as a change in the line splitting in the spectrum. Thus,

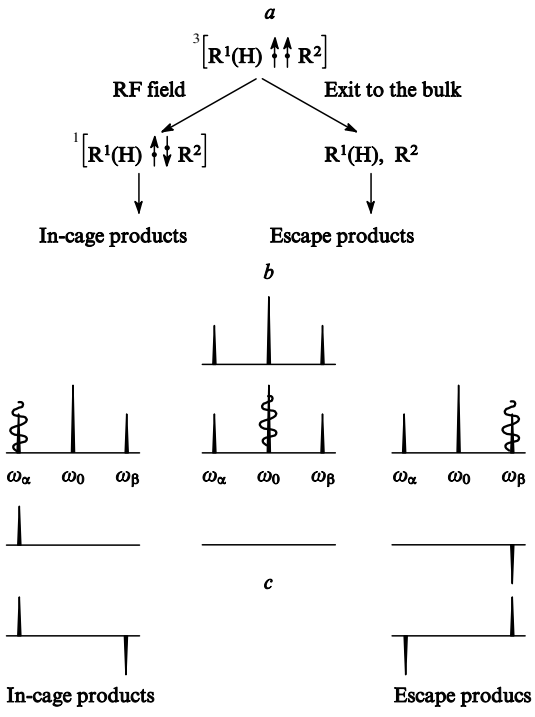


Figure 10. Scheme for the generation of SNP for a radical pair with one magnetic nucleus (*a*) and its EPR (*b*) and SNP (*c*) spectra.

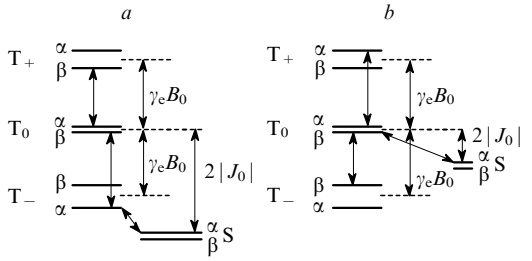


Figure 11. Diagram of the electron levels of a biradical with one magnetic nucleus for strong (*a*) and weak (*b*) exchange interaction.

the magnitude of exchange interaction can be judged both from the pattern of the $S-T_0$ or $S-T_-$ type spectrum and from the splitting in the $S-T_0$ type SNP spectrum. Apart from the exchange interaction, splitting in the SNP spectra is influenced by spin-selective decay of radical pairs, which can diminish splitting even in the absence of exchange interaction.[69] It was shown [69, 70] that exchange interaction, electron relaxation and fast decay of the singlet state are factors influencing the splitting of lines in the SNP spectra because they all result in dephasing of the singlet – triplet transitions.

Theoretical description of the SNP effects has been the object of a number of studies [69–81] in which various approaches were employed. Thus Mikhailov *et al.*[68] developed a theory of SNP for reactions of neutral radicals with isotropic reactivity in strong magnetic fields based on the mathematical apparatus used traditionally to study the geminate recombination of radicals with allowance for the $S-T_0$ transitions in radical pairs. The SNP effects were calculated in this study by summing the contributions to recombination of all the radical re-encounters.[82] This method is based on the assumption that the spin dynamics in radical pairs and relative molecular motion of radicals in solution are completely separate and implies the use of numerical calculations. However, numerical analysis of the SNP effects in systems with many magnetic nuclei is highly time-consuming. Analytical expressions have been obtained [72, 83] for the calculation of the probability of recombination of radical pairs with a specified configuration of nuclear spins and of the SNP effects on the assumption of low efficiency of singlet – triplet transitions in radical pairs.

The effects of various parameters on the line intensity and the pattern of the SNP spectrum have been studied theoretically.[68] It was shown that the intensity and the sign of SNP as well as the spectral pattern depend substantially on many molecular-kinetic and magnetic-resonance parameters of the radical pair, solvent viscosity, reactivity of radicals, the occurrence of reactions of the radicals with acceptors, the amplitude and the frequency of a microwave field, the HFC constants and *g*-factors of radicals. Therefore, detailed interpretation of experimental data can only be performed resorting to calculations of the SNP effects.

Osintsev *et al.*[84] used the kinematic approach to derive the analytical expressions for calculating the SNP effects of radical pairs with one HFC constant in arbitrary magnetic fields. In another study,[73] these reseachers analysed the line profile in the SNP spectra in weak magnetic fields, comparable with the HFC constant, for different RF-field amplitudes. It was shown that in weak fields, additional lines which are missing in strong fields appear in the spectrum.

The effect of a powerful RF field during recording of the SNP spectra in weak magnetic fields gives rise to new resonance characteristics in the spin dynamics of radical pairs, which are multi-quantum resonances from the standpoint of quantum theory.[74] Experimentally, this shows itself as the appearance of signals in the SNP spectra in the Zeeman fields B_0 approximately divisible by the field of the main resonance.[25] The kinematic approximation has also been used successfully [73] to design the theory of multi-quantum resonances under the conditions of SNP.

Characteristic features of the SNP spectra for spin-correlated radical pairs in strong magnetic fields have been considered taking a two-position model as an example.[81] It was found that narrow lines the nature of which is due to the degeneracy of two electron transition frequencies appear in the SNP spectra under definite conditions. From the width of these lines, the lifetime of spin-correlated radical pairs can be determined. Note that similar features are characteristic of the spectra of radical pairs measured using the optically detected electron paramagnetic resonance (OD EPR) technique.[85]

The SNP effects in systems with non-zero exchange interaction depending on the distance between the radical sites (short-lived biradicals,[69] radical pairs in micelles [75–78]) can be described using an approach based on the numerical solution of the stochastic Liouville equation.

1. Stimulated nuclear polarisation of radical pairs in homogeneous solutions

The SNP effects were first observed experimentally for recombination of the biradicals formed upon photolysis of cyclododecanone.[86] Subsequently, it has been shown in relation to the photolysis of benzoyl peroxide in various solvents [87] that recombination of radicals in the liquid phase proceeding *via* the formation of radical pairs consisting of the phenyl and phenacyl radicals [Ph$^{\bullet}$ $^{\bullet}$OC(O)Ph] is accompanied by substantial polarisation. Bagryanskaya *et al.*[87] carried out experiments in weak magnetic fields ($B_0 = \sim 3.0$ mT, $\nu = 94.5$ MHz), the magnitudes of which are comparable with the HFC constants in the phenyl radical. The pattern of the SNP spectrum was complex, which substantially hampered interpretation of the data obtained, especially for $B_1 \approx A$. Subsequently, the main regularities of SNP have been investigated in the photolysis of *p*-benzoquinone and duroquinone in CD_3CN, $CDCl_3$ and CD_3OD in weak and strong magnetic fields.[12, 20, 21, 34, 88] Photolysis of benzoquinone in CD_3CN has been used as an example to study [86] the effect of spin locking, which was then employed to estimate the amplitude of the RF field when working in a high-frequency resonator. By comparing the dependences of SNP on the amplitude of the radio-frequency field in weak magnetic fields in the case of low pumping frequency (100 MHz, when measurements of the B_1 value are rather simple) and in strong magnetic fields in the case of high pumping frequency (1.6 GHz), one can determine the amplitude B_1 in the resonator for the high-frequency case. Multi-quantum resonances were detected experimentally in the high-field region of the SNP spectra measured at great RF field amplitudes ($B_1 \gg A$).[25]

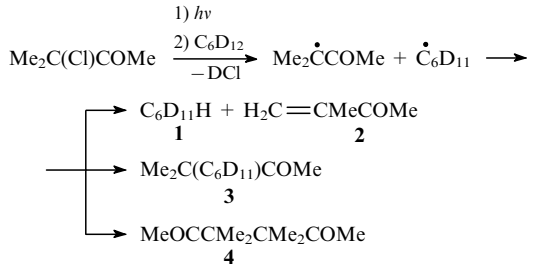
As noted above, the method of SNP permits identification of intermediate short-lived species (radical and radical-ion pairs) and also provides information on the pathways of formation of the reaction products. For example, SNP has been used [89] to study elementary steps in the photolysis of anthraquinone (AQ) with triethylamine in solvents with different polarities. For the reaction carried out in polar solvents (CD_3CN, CD_3OD), the spectrum of triethylamine radical cation was measured using the NMR line of the triethylamine CH_2 group. Based on the sign of the spectrum, it was concluded that triethylamine is an in-cage product of recombination of the radical-ion pair $\{[AQ]^{-\bullet}\cdots^{+}[Et_3N]\}$. For the photolysis of triethylamine and anthraquinone in CD_3OD, the SNP spectrum was measured based on the NMR signal of the proton of the hydroxy group in CD_3OH. This spectrum differed from the SNP spectrum recorded using the signal of the triethylamine CH_2 group only by the sign; hence, it corresponds to an escape product of transformation of the triethylamine radical cation. This fact indicates that the hydroxyl proton of the alcohol has come from the CH_2 group of the triethylamine escape radical cation. Thus, the authors concluded that the reaction takes place between hydroxyalkyl and aminoalkyl radicals. In non-polar solvents, in particular, in benzene, the SNP spectrum corresponds to the EPR spectrum of the aminoalkyl radical Me$\dot{C}$HNEt. In medium-polarity solvents (cyclohexane and isopropanol), both pathways are effective (the radical-ion and radical pathways).

It should be borne in mind that signals in the SNP spectra can differ substantially for continuous and pulse photolysis modes.[28, 90] For example, the intensity of signals recorded during pulse laser photolysis of benzoquinone and benzaldehyde decreases by a factor of dozens when a mercury light is used as a continuous source of light. The signal intensity in the SNP spectra does not change if the radicals decay in a first-order reaction, for example, in the photolysis of benzoyl peroxide, cyclic ketones, *etc.* In the steady-state photolysis, the lifetime of radicals normally exceeds the time of nuclear relaxation of the intermediate radicals (10^{-4} s), the observed polarisation being due to the contribution of the polarisation of the in-cage recombination products. In the

case of pulse generation of radicals, the opposite situation is observed, *i.e.* the lifetime of radicals is usually shorter than the nuclear relaxation time. Hence, the total polarisation of diamagnetic products formed both in the cage and as a result of radical recombination in the bulk markedly decreases or disappears.

In a study of laser photolysis of *p*-benzoquinone in methanol by SNP, it has been found [25,91] that cyclohexadienyl type radicals with methoxy- or hydroxymethyl groups participate in the reaction. The SNP spectra based on the signals present in the NMR spectra of benzoquinone, hydroquinone and the alcohol (the hydroxyl-proton signal) differ appreciably from the SNP spectra of radical pairs of semiquinoid radicals measured for continuous photolysis under the same conditions. The distance between the terminal lines in the spectrum (4.5 mT) indicates that the reaction involves radicals with the high HFC constants of the ring protons. Comparison of experimental SNP spectra with those calculated for several assumed radical species with allowance for HFC constants (calculated by the MNDO method) made it possible to establish the structure of the intermediate radical.

Figure 12 *a*,*b* shows the NMR and SNP spectra recorded for the photolysis of 2-chloro-2-methylbutan-3-one in C_6D_{12}.[32]



Stimulated nuclear polarisation is observed for all diamagnetic products **1**–**4**. The experimental spectra of in-cage products are in good agreement with the spectra calculated for the $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C_6D_{11}]$ radical pair. To attain agreement between the theoretical and experimental SNP spectra of escape products, contributions of both radical pairs, $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C_6D_{11}]$ and $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C(COMe)Me_2]$, should be taken into account.

The influence of the DEE rate on the pattern of SNP spectra has been studied.[48] It was shown that, since DEE results in frequency exchange between the components of the spectrum with opposite polarisation signs, the narrowing of lines is accompanied by a decrease in their intensities; in the limit, the lines disappear.

The influence of DEE on the SNP effect has been studied in detail both experimentally and theoretically.[92] The researchers used two approaches to the theoretical description of the SNP spectra with allowance for DEE. In the former case, the spectra were calculated using the theory of uncorrelated frequency migration for a radical pair with two magnetic nuclei. In the latter case, for a weak RF field ($B_1 \ll A$), a two-position model was proposed. In the case of low DEE rates $\{A\tau_e \gg 1$, where τ_e is the time of DEE, $\tau_e = 1/k_e[A]$ (or [D]), [A] or [D] is the concentration of the acceptor or the donor participating in the DEE reaction$\}$, this model provides an analytical expression describing the variation of the SNP amplitude *vs.* the exchange time τ_e. Photoinduced isomerisation of fumaronitrile in the presence of deuterated naphthalene in acetonitrile was chosen as the model reaction for experimental investigations. Figure 13 shows the SNP spectra of radical pairs resulting from photolysis of fumaronitrile with naphthalene over broad ranges of DEE rates and RF-field amplitudes. At low fumaronitrile concentrations when the influence of DEE is negligibly small, the SNP spectra resemble the spectra based on calculations for neutral radical pairs without

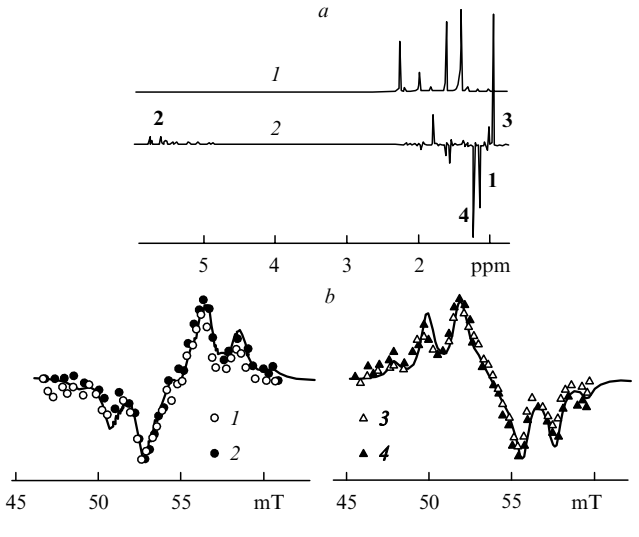


Figure 12. NMR spectra recorded for the photolysis of 2-methyl-2-chlorobutan-3-one in C_6D_{12} (*a*) [(*1*) spectrum in the dark, (*2*) CIDNP spectrum] and experimental and simulated SNP spectra for reaction products (*b*);
(*1*) product **1**, (*2*) product **2**, (*3*) product **4**, (*4*) product **3**. The continuous lines are simulated spectra. (*1*, *2*) with allowance for the contributions to SNP of the escape products of the geminate radical pair $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C_6D_{11}]$ and in-cage products of the diffusion radical pair $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C(COMe)Me_2]$; (*3*, *4*) calculations of the SNP of the in-cage products from the geminate radical pair $[Me_2(COMe)C^{\bullet}\ {}^{\bullet}C_6D_{11}]$.

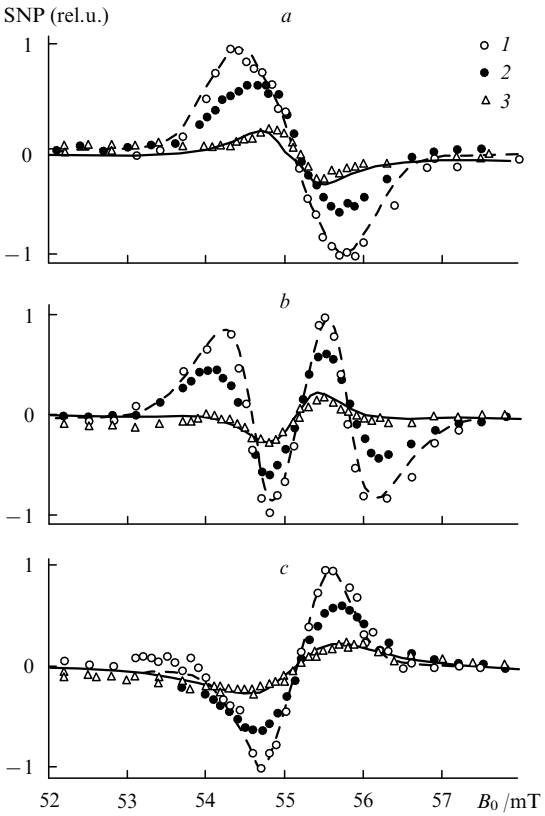


Figure 13. SNP spectra recorded for the photolysis of naphthalene-d_8 (2×10^{-3} mol litre^{-1}) with fumaronitrile and detected from the NMR signal of the fumaronitrile protons. Fumaronitrile concentration (mol litre^{-1}): (*1*) 10^{-3}, (*2*) 10^{-2}, (*3*) 5×10^{-2}. RF-field amplitudes (mT): (*a*) 0.25, (*b*) 0.67, (*c*) 1.2. The dashed lines correspond to the spectra calculated with allowance for all the HFC constants using the theory of SNP for neutral radical pairs without DEE. The continuous lines are the spectra calculated using the theory of uncorrelated frequency migration for a radical pair with two magnetic nuclei.

allowance for charge exchange. The calculation was carried out taking into account all the HFC constants in radical pairs in terms of the theory of SNP in strong magnetic fields. It can be seen from Fig. 13 that the pattern of the SNP spectra is extremely sensitive to the RF-field amplitude. As the concentration of fumaronitrile increases, SNP sharply decreases; line splitting in the spectra also decreases. To measure the rate constant for DEE in radical-ion reactions by comparison of the theoretical and experimental SNP spectral patterns, the dependence of the SNP intensity on the exchange time τ_e at low RF-field amplitudes in the absence of fast trapping of radical ions was used.

The SNP method was utilised to study the photoinduced electron transfer from quadricyclanes to tetrafluorobenzoquinone. It was shown[93] that the radical-ion pair in this reaction incorporates the quadricyclane radical cation. Isomerisation of quadricyclane into norbornadiene takes place in the free radical ion rather than in the step of formation of the radical-ion pair.

The majority of researchers studied reactions in homogeneous solutions by ^{1}H NMR spectroscopy. However, detection of SNP using other nuclei (^{13}C, ^{31}P, ^{19}F, *etc*.) appears quite promising. Figure 14 presents the ^{31}P SNP spectrum of the radical pair formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. Splitting in the spectrum corresponds to the HFC constant at the phosphorus nucleus. A specific feature of SNP at the ^{31}P nuclei is large HFC constants comparable with the magnitude of the external magnetic field. Therefore, calculations cannot be carried out using the strong magnetic field approximation. In addition, for radical pairs with large HFC constants, contributions of $S-T_-$ transitions occurring in the area of intersection of terms should be taken into account.[59,60]

The potential and advantages of the time-resolved SNP method were verified experimentally[28] taking photolysis of benzoyl peroxide (in CD_3OD or CD_3CN) as an example. It was shown that the delay (τ) between the laser pulse and the RF pulse inverts the observed SNP spectrum. A study of the dependence of SNP on τ in different magnetic fields for different resonance lines demonstrated that the inversion of the spectrum takes place at $\tau > 50$ ns, and subsequently the spectral pattern changes only slightly. Apparently, the spectrum corresponds to the [Ph$^{\bullet}$ $^{\bullet}$Ph] and [Ph$^{\bullet}$ $^{\bullet}CD_2OD$] pairs.

Osintsev *et al*.[84] have considered theoretically the problem of the line shape in the SNP spectra recorded in time-resolved experiments and the dependence of SNP on the character of motion of the partners of radical pairs. From the theoretical standpoint, consideration of these processes is reduced to the calculation of the probability of recombination of geminate radical pairs. (The theory of recombination of radical pairs with a Hamiltonian changing abruptly with time has been formulated.[94,95]) It was shown[84] that the width of the SNP line at small amplitudes of the RF field is determined by the amplitude of the RF field, while the intensity of the SNP spectral line depends on this amplitude according to a law describing diffusion motion. The use of a delay between the laser and RF pulses should not result in a substantial narrowing of SNP lines. This is due to the fact that the re-encounter of partners in radical pairs which takes place after a prolonged diffusion walk contributes significantly to the SNP. As long as the delay τ differs from zero, this contribution remains crucial. The variation of the intensity of the SNP line in the magnetic field corresponding to the resonance line maximum *vs*. the delay τ appears the most informative. For great delays, the dependence typical of diffusion motion should be observed. The SNP kinetics calculated using the two-position model is described by an exponential curve with a characteristic exponent parameter equal to the constant for the irreversible decay of radical pair τ_c. The expected line widths in the SNP spectrum should not depend on the amplitude of the RF field and are determined by the reciprocal time $1/\tau_c$.

Time-resolved SNP experiments for geminate radical pairs in homogeneous solutions are currently impossible because the characteristic lifetime of radical pairs is about several nanoseconds and, to obtain real kinetics, it would be necessary to initiate the reaction by lasers with nanosecond pulse duration. In addition, it would be necessary to create a rise time of about 1 ns for the RF pulse, which is a difficult engineering problem. However, the lifetimes of short-lived biradicals and micellised radical pairs lie in the range from tens to hundreds of nanoseconds; the kinetics of these systems can be studied experimentally.

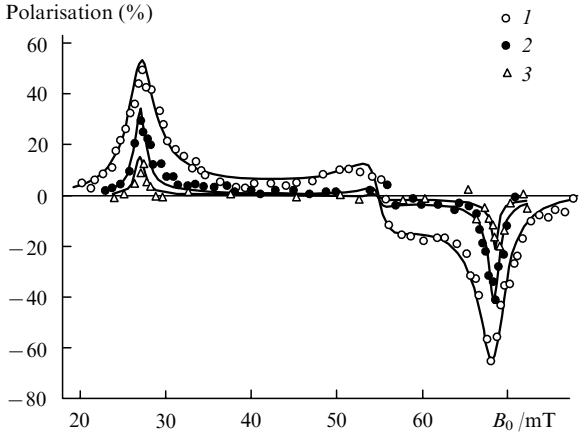


Figure 14. ^{31}P SNP spectra of radical pairs formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. The spectra were detected using the NMR signal of diphenylphosphine oxide. Polarisation was measured in percent of the CIDNP for $B_0 = 43$ mT. B_1 (mT): (*1*) 1, (*2*) 0.6, (*3*) 0.4. The continuous lines are the spectra simulated using the analytical formula for weak magnetic fields.[73]

2. Stimulated nuclear polarisation of short-lived biradicals

Biradicals are formed as intermediates in many photochemical processes; therefore, it is important to investigate them in order to elucidate reaction mechanisms. As a rule, the lifetimes of flexible biradicals are about 0.1 – 1 μs. They are determined by the rates of intersystem crossing from the non-reactive triplet state to the singlet state, recombination from the singlet state and the conformational motion of radical centres. Photolysis of aliphatic cyclic ketones with rupture of the α-bond is a perfect method for the investigation of short-lived biradicals. The α-bond rupture occurs from the excited triplet state almost in all cases. The introduction of methyl or phenyl groups in the α-position decreases the activation energy and increases the rate of α-rupture to 10^9 s^{-1} or more. The acylalkyl biradical thus formed can be decarbonylated giving rise to alkyl biradicals. The rate of decarbonylation increases substantially upon α-substitution. For biradicals formed in the photolysis of aliphatic cyclic ketones, the rate of molecular motion in non-viscous solutions at room temperature is much higher than the rate of spin dynamics. In the absence of steric hindrance, recombination from the singlet state is not the rate-determining step either; thus, the lifetime of biradicals is determined by the rate of the triplet – singlet conversion, which depends on the hyperfine electron-exchange and spin-orbital interactions and on the electron spin relaxation.

The main features of the generation of SNP in biradicals have been studied experimentally in relation to the photolysis of several aliphatic cyclic ketones $O=C(CH_2)_n$ ($n = 10-13$).[86,96–99] As noted above, the major pathway of the photolysis of cycloalkanones is α-rupture in the triplet-excited ketone, resulting in the formation of an acylalkyl biradical. Variation of the length of the polymethylene chain of the ketone, the HFC constants (by using ketones in which the protons in the α-position have been replaced by D or CH_3) and the external magnetic field, as well as detection of SNP from ^{1}H and ^{13}C NMR spectra make it possible to vary the ratio of A, J and B_0 over a broad range.

For biradicals with $n = 10-13$ in weak magnetic fields (3–12 mT), the S–T$_-$ channel of intersystem crossing predominates. Both emission CIDNP and emission SNP can be observed in the NMR signals of all groups of protons of ketones and aldehydes. Polarisation on the ketone γ-protons, for which the HFC constant in the biradical is close to zero, arises due to the transfer of the nuclear polarisation from the α-CH_2 groups of the ketone, induced by the transfer of the sample from a weak to a strong magnetic field. For ketones with $n = 11-13$ in a ~50 mT field, the main intersystem crossing channel is S–T$_0$; no signals for the ketone protons are observed in the SNP spectra in this field because the HFC constants of α- and β-protons in biradicals have different signs, and the lines for opposite signs overlap. When the chain length decreases, the effective value of exchange interaction increases; an emission SNP spectrum is obtained in a 50 mT field for biradicals formed in the photolysis of cyclodecanone ($n = 10$). Koptyug *et al.*[96] reported calculations of SNP of short-lived biradicals performed for a realistic model, which had been used previously[100] to describe the field dependences of CIDNP. Presumably, exchange interaction occurs through the spatial overlap of the orbitals of unpaired electrons and is attenuated according to an exponential law as the distance r between the electrons increases

$$J(r) = J_0 \exp(-\alpha r),$$

the interaction anisotropy being averaged due to the fast rotations of the terminal groups of the polymethylene chain. Two mechanisms of electron spin relaxation were taken into account, one due to fluctuation of local magnetic fields and one, due to dipole–dipole interaction of the spins of the unpaired electrons. The pattern of the calculated SNP spectra is highly sensitive to the exchange interaction constant J_0. Using experimental and theoretical spectra obtained for different radio frequencies, the optimal values for J_0 and α were found. Koptyg *et al.*[96] studied theoretically the influence of several parameters, namely, the diffusion coefficient, the rate of trapping of biradicals, the rate of decay of the triplet biradical due to the spin-orbital interaction, and the electron spin relaxation, on the pattern of the SNP spectra. It is significant that all parameters, except the diffusion coefficient, have little influence on the shape of spectral lines but can only cause a decrease in the signal intensity. As noted above, the dependence of the signal intensity in the SNP spectrum on the delay τ bears information on the lifetimes of radical pairs. For instance, this dependence has been used[96] to estimate the lifetimes of short-lived biradicals formed upon photolysis of cyclododecanone. The characteristic times of SNP decay were ~ 80 ns. Due to the lack of a theory of time-resolved SNP for biradicals, the researchers could not use the experimental data to perform a profound analysis or to gain new information.

The kinetics of SNP of short-lived acylalkyl biradicals in homogeneous solutions in weak magnetic fields (~ 10 mT) have been studied.[27,101] Two types of radio-frequency pulses were used, a long pulse (~ 2 μs) and a short pulse with a duration at half-height of 15 ns. It was shown that the kinetic dependences of SNP pass through a maximum when the delay between the laser pulse and the RF pulse is 40 ns and then decay by an exponential law. The appearance of the maximum is due to the competition between spin-dependent and spin-independent channels of the triplet–singlet conversion. The kinetics of SNP were described using a simple kinetic model. From comparison of the experimental data with the calculated data, the researchers estimated the rate of spin-orbital interaction, the electron relaxation rate and the lifetimes of the excited triplet molecules of ketones. Upon the addition of a quencher for triplet states (*cis*-piperylene), the time for attenuation of the SNP signal diminishes to reach a limiting value equal to the lifetime of the biradical. Proceeding from these results, the lifetimes of biradicals (80 ns for cyclododecanone and 50 ns for cycloundecanone) and of triplet molecules (250 ns for cycloundecanone and 150 ns for cyclododecanone) were estimated.

The ^{13}C SNP spectra of acylalkyl biradicals with $n = 11$, in which the ^{13}C isotope occurs in the carbonyl position or in the α-position, differ significantly. This is due to the difference between the HFC constants and, correspondingly, different ratios of the external magnetic field to the HFC constants, resulting in dissimilar efficiencies of the competing intersystem crossing channels.[102] As shown by calculations performed in terms of the two-position model in weak and zero magnetic fields, the pattern of the SNP spectra of short-lived biradicals is exceptionally sensitive to the rate of spin-non-selective intersystem crossing; this can be used to measure their rates.

The main regularities of the origination of SNP in the consecutively formed biradicals were studied experimentally and theoretically[103] in relation to the acylalkyl and bisalkyl biradicals formed in the photolysis of tetramethyl-substituted cycloalkanones with $n = 11-15$. A specific feature of the consecutive biradicals, as well as of the consecutive radical pairs, is the 'memory effect', which implies that nuclear polarisation of the diamagnetic products of the secondary radical pairs or biradicals reflects the spin dynamics processes in both the primary and the secondary pair (biradical). Due to the high spectral selectivity, typical of the NMR method, when recording the NMR spectra of various recombination products, the authors were able to obtain simultaneously the SNP spectra of primary and secondary biradicals arising during photolysis. A model for the calculation of SNP for the consecutive biradicals was developed; the generation of SNP was studied both experimentally and theoretically. The main characteristics influencing the line intensity and the pattern of the SNP spectra of secondary biradicals are the rate constant for the electron relaxation of both biradicals, the time required for relaxation processes, the rate constant for the spin-orbital interaction, parameters of the exchange interaction of both primary and secondary biradicals, the rate constant for decarbonylation, the type of the main intersystem crossing channel in the biradicals, and the ratio of the polarisation intensities for the first and the second biradicals. Note that for the symmetrical biradicals, in which the HFC constants for various radical centres are equal, the SNP spectral pattern differs appreciably from the case considered above. This is due to the fact that, in symmetrical biradicals or radical pairs in strong magnetic fields, the SNP effect is equal to zero. This fact can be easily understood from a qualitative consideration. Saturation of the electron transitions in radical pairs with identical orientations of nuclear spins does not accelerate the intersystem crossing. In the radical pairs with the opposite orientation of nuclear spins, the S–T conversion is accelerated for both sub-ensembles of radical pairs. Thus, the overall polarisation induced by a microwave field would be equal to zero. When calculating the SNP in symmetrical biradicals in weak magnetic fields, it is necessary to take into account both HFC constants in the secular approximation. If one HFC constant is taken into account in the secular approximation, while the second, is in a non-secular approximation, a non-symmetrical radical pair is actually considered and an S–T$_0$ type spectrum appears in the calculated SNP spectra. Unlike biradicals with different HFC constants, for which the spectral pattern is determined by the major channel of the singlet–triplet conversion, for symmetrical biradicals, the SNP spectra would always correspond to the S–T$_-$ type even in those cases where S–T$_0$ is the major channel of intersystem crossing.

Study of the SNP of acylalkyl and bisalkyl biradicals in different magnetic fields (Fig. 15) allowed the authors to determine the J_0 value, which describes adequately all the experimental data. In the photolysis of ketones with $n = 11$, on the basis of the NMR signals of the products resulting from the bisalkyl biradicals, the S–T$_-$ type spectra represented by one emission line ($B_0 = 54.6$ mT) were observed (Fig. 15*c*). For $n = 12$, inverted S–T$_0$ type spectra were recorded (Fig. 15*d*). The lower limit of the J_0 range was established by comparing the calculated and experimental SNP spectra of biradicals with $n = 11$ (S–T$_-$ type), while

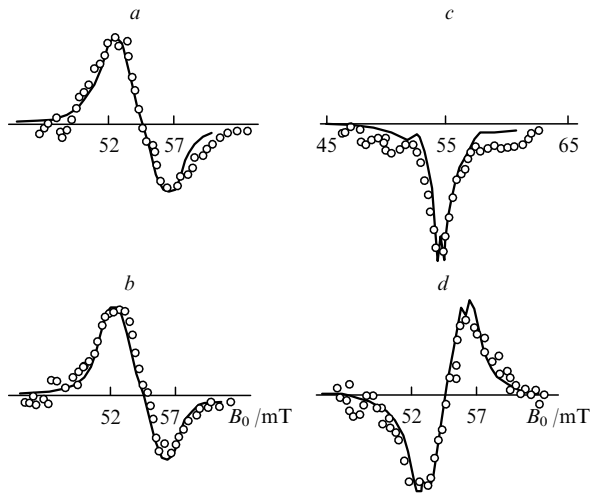


Figure 15. Experimental (dots) and calculated (continuous lines) SNP of acylalkyl [$OC^{\bullet}CMe_2(CH_2)_{n-2}C^{\bullet}Me_2$, $n = 11$ (*a*), 12 (*b*)] and bisalkyl [$MeC^{\bullet}(CH_2)_{n-2}C^{\bullet}Me_2$, $n = 11$ (*c*), 12 (*d*)] biradicals formed in the photolysis of tetramethyl-substituted cycloalkanones.

the upper limit was found by comparing the spectra of biradicals with $n = 12$ ($S-T_0$ type) in a 27 mT field.

In the literature, the short lifetime of the acylalkyl biradicals is attributed most often to the presence of spin-orbital interaction between the radical centres of the biradical (see, for example, Ref. 104). This statement is true for biradicals with relatively short chains ($n = 5, 6$). Evidently, the influence of spin-orbital interaction on the lifetime of the biradical depends on the residence time of radical centres in the reaction volume. For biradicals with long chains, the residence time of the radical centres in the reaction area is short; therefore, the role of relaxation occurring due to spin-orbital interaction should markedly decrease. On the basis of analysis of the SNP experimental kinetics for biradicals with $n = 12-15, 17$, it was concluded that in addition to the spin-orbital interaction, spin-rotational relaxation also plays an important role.[103]

The influence of temperature and viscosity on the spin and molecular dynamics of short-lived alkylacyl and bisalkyl biradicals formed successively has been studied both experimentally and theoretically.[105] The ^1H and ^{13}C CIDNP and SNP effects were studied in the temperature range from 200 to 360 K for magnetic fields varying from 0 to 0.1 T. The investigators found a unified set of parameters that describe adequately the nuclear polarisation effects for both protons and ^{13}C atoms with different HFC constants in the biradical. The introduction of a temperature dependence of the biradical reactivity proved especially important for attaining quantitative agreement between the calculated and experimental data in the low-temperature range. Comparison of the experimental data with the results of model calculations showed that broadening of the field dependence of CIDNP and slowing down of the decay of SNP signals at temperatures below 240 K is due both to the retardation of the molecular mobility of the polymethylene chain and to the decrease in the reactivity of the acylalkyl biradicals. For the bisalkyl biradicals, spin-orbital interaction is less important for the spin dynamics than in the acylalkyl radicals. The effect of molecular dynamics on the field dependences of the CIDNP of the products formed from bisalkyl biradicals with the change in temperature is more pronounced. Since the lifetime of bisalkyl biradicals is much longer than the lifetime of acylalkyl biradicals, the intensity of nuclear polarisation of the products formed from bisalkyl biradicals is much higher.

3. Stimulated nuclear polarisation of micellised radical pairs

Micellar solutions as a specific microstructured medium have been drawing attention of photochemists during the last decades. Numerous publications[106–115] are devoted to the detection and investigation of extremal magnetic effects and magnetic isotope effects, nuclear and electron polarisation and other effects in radical pairs located in micelles. In micelles, radical pairs are isolated; this enables detailed investigation of the geminate recombination of radicals and spin and molecular dynamics of radical pairs. Since in radical pairs occurring in micelles, the partners are located at short distances from each other throughout their whole lifetime, the electron exchange interaction has a considerable influence on the intersystem crossing in these radical pairs. The field dependences of ^{13}C CIDNP of radical pairs formed upon photolysis of dibenzyl ketone in sulfate micelles of different sizes have been studied.[108] The polarisation of the ^{13}C nuclei in both strong and weak fields (irrespective of the sign of the HFC constant) was found to be emission polarisation. The 'maximum' of the field dependence of CIDNP shifts upfield as the size of micelles decreases. On the basis of experimental data, it was concluded that CIDNP is mainly due to $S-T_-$ transitions. The effective exchange interaction estimated from the field dependence of CIDNP was ~ 30 mT. However, the results obtained by CIDEP for a number of systems are at variance with the conclusion concerning large values for average exchange interactions. In the EPR spectra of micellised radical pairs, each hyperfine-structure line is split into two. This splitting can be described by including a constant exchange interaction $|J| \approx 5-10$ MHz into the Hamiltonian in model calculations.[115] Similar estimates were obtained in RYDMR experiments in micelles.[114] Later, it was shown that modulation of the exchange interaction due to the mutual motion of radicals should be taken into account in the description of the spectral patterns and the CIDEP kinetics of spin-correlated pairs in micelles.[116] The use of the SNP method for the investigation of the effect of exchange interaction on the intersystem crossing in radical pairs confined in micelles proved quite effective.[75–78,117–123] Stimulated polarisation is detected from the NMR signals of the diamagnetic products of recombination of radical pairs; therefore, it reflects the influence of the exchange interaction on the intersystem crossing in radical pairs localised in micelles to a greater extent than CIDEP, in which the predominant contribution to the spectral signal is made by free radicals.

The ^{13}C and ^{31}P SNP techniques were used to study the radical pairs resulting from photolysis of α-methyldeoxybenzoin,[77,119,122,123] dibenzyl ketone,[76,78,117,118,122] benzoin,[78] deoxybenzoin,[124] benzophenone in the presence of *tert*-butylphenol[121] and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide[120] in the sulfate micelles $Na^+SO_3^-O(CH_2)_nMe$ of various sizes ($n = 6-11$). The significant differences in the ratios of the HFC constants and the lifetimes of these radical pairs permitted the researchers to examine the influence of the exchange interaction on the pattern of the SNP spectra. It was discovered that line splitting and line width in the spectra depend on the size of micelles. From comparison of the spectra recorded in strong and weak magnetic fields and the field dependences of CIDNP with the spectra calculated theoretically, parameters of the molecular and spin dynamics of micellised radical pairs were found.

The dynamics of radical pairs in micelles were described using a microreactor model — one radical was fixed in the centre of a spherical micelle, whereas the other was moving inside the micelle core.[75–78] In addition, a diffusional character of the motion was assumed. The electron spin relaxation due to the dipole–dipole interaction and due to modulation of the anisotropic part of HFC was taken into account.[77] The allowance for the dipole–dipole relaxation was made by two methods. One approach is similar to that described previously[69] for the calculation of the field dependences of CIDNP and SNP in short-lived biradicals. The other approach is more consistent; it was used (in combination with the Monte Carlo method)[125] to calculate the correlation function of

the dipole–dipole interactions in radical pairs for micelles of different sizes. Subsequently, an analytical expression describing the dipole–dipole relaxation was obtained.[126] The main parameters determining the molecular dynamics of radicals are the coefficient of mutual diffusion D, the micelle radius L, the reaction radius and the rate constant for the radical exit to the bulk k_{ex}. Splitting in the SNP spectra depends on the ratio of the following values: the HFC constants, the characteristic time between the collisions of radicals inside the micelle

$$\tau_2 = \frac{L^3 - R^3}{3RD} \sim \frac{L^3}{3RD},$$

the exchange interaction and the rate of the spin-selective decay. Upon a decrease in the micelle size, the time the radical pair spends in the reactive state increases relative to the time spent in the non-reactive state. Thus, the time-average exchange interaction and the time-average recombination rate increase.

The experimental implementation of the SNP method for the investigation of radical pairs in micelles has several specific features. On the one hand, due to the higher viscosity of micellar media compared to homogeneous solutions, the nuclear relaxation time of diamagnetic products decreases, resulting in a less intense signal in the SNP spectra. On the other hand, the lifetime of radical pairs in micelles ($\sim 0.1-1$ μs) is commensurable with the characteristic time of RF transitions ($\sim 10-100$ ns), which is calculated from the expression

$$\omega_1 = \gamma_e B_1$$

(the B_1 value lies in the range 0.1–1 mT). This results in a pronounced increase in the intensity of spectral lines and provides the possibility of measuring ^{13}C SNP spectra for samples with natural abundance of ^{13}C. An advantage of the ^{13}C SNP method is that the spectra of radical pairs containing ^{13}C magnetic nuclei are recorded on the basis of the corresponding lines in the ^{13}C NMR spectrum; therefore, the splitting in the SNP spectrum is equal to the HFC constant for this nucleus in the radical.

In small micelles ($n = 7-9$) for $A = 2-10$ mT, the decrease in the spectral splitting is due to both the exchange interaction J and the rate of spin-selective decay of the radical pair. In larger micelles ($n = 11, 12$) for $A > 2.0$ mT, splitting in the spectrum is equal to the HFC constant, exchange interaction influencing only the widths of individual lines.

The ^{13}C SNP effects involved in the photolysis of α-methyldeoxybenzoin enriched to 96% in the ^{13}C isotope at the carbonyl position have been studied in micelles of different sizes.[51,77] The splitting in the SNP spectrum for sodium dodecyl sulfate micelles amounts to 12.4 mT; it is equal to the HFC constant for the carbonyl carbon atom in the benzoyl radical (Fig. 16 *a*). A decrease in the length of the polymethylene chain of the detergent molecule results in a shorter spacing between the lines in the SNP spectrum and in a changed width of individual lines. From calculations of the SNP spectra and field dependences of CIDNP, the optimal parameters of the electron exchange interaction and spin-selective decay were found ($k_s\tau$): $J_0 = 50$ mT (the parameter for the decay of exchange interaction α is 2 Å) and $k_s\tau = 8$. It is noteworthy that the high sensitivity of the SNP spectra to the change in the rate of re-encounters of radicals in the micelles and, hence, to the change in the intra-micellar viscosity and micelle size can be used to investigate the dependence of the properties of micelles on the temperature and on salt additives (see Fig. 16).[123]

Parnachev *et al.*[121] studied experimentally the SNP of radical pairs formed in the photolysis of benzophenone-d_{10} in sodium dodecyl sulfate micelles in the presence of 2,4,6-tri-*tert*-butylphenol with the natural abundance of the ^{13}C isotope. On exposure to a 0.03 mT radio-frequency field, the NMR spectrum exhibits signals from six radical pairs differing in the position of ^{13}C (denoted by the Roman numerals I–VI) (Fig. 17 *a*).

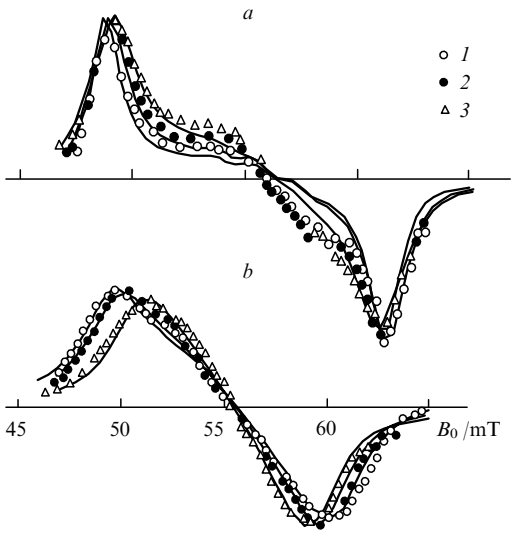
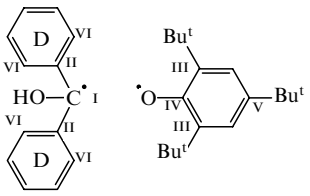


Figure 16. Temperature dependence of the SNP spectra of the radical pairs formed in the photolysis of α-methyldeoxybenzoin in sodium dodecyl sulfate (*a*) and sodium octyl sulfate (*b*) micelles. The spectra were detected using the NMR signal of the carbonyl carbon atom of α-methyldeoxybenzoin. The continuous lines are the calculated SNP spectra. T (°C): (*1*) 12, (*2*) 29, (*3*) 45 (*a*) and (*1*) 10, (*2*) 17, (*3*) 45 (*b*).



The SNP spectra were obtained for all the six radical pairs with different positions of ^{13}C. Figure 17 *b* shows the SNP spectra for pairs with the ^{13}C isotope in positions I and II. The opposite phases of these spectra are due to the different signs of the HFC constants for the corresponding ^{13}C nuclei. Measurement of the SNP kinetics makes it possible to determine the lifetimes of radical pairs and to draw conclusions about the mechanisms of their relaxation. The value of the contact electron exchange interaction estimated from comparison of the experimental and theoretically calculated spectra is $|J_0| > 40$ mT. The HFC constants in radical pairs with different positions of the ^{13}C isotope were calculated from analysis of the SNP spectra.

In the limiting case, where the characteristic time of intersystem crossing markedly exceeds the characteristic time period between the re-encounters in the micelle ($A\tau_2 \gg 1$), splitting of lines in the SNP spectra does not depend on the micelle size, and the effect of the exchange interaction reduces to line broadening.[120] For example, this is the case in the radical pairs formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. In accordance with theoretical predictions, the experimental SNP spectra of radical pairs in sodium octyl sulfate micelles and in sodium dodecyl sulfate micelles show the same splitting; however, agreement between experimental and theoretical spectra is attained only when sodium dodecyl sulfate micelles with a radius of 17–21 Å or sodium octyl sulfate micelles with a radius of 13–15 Å are used. Thus, it was concluded that the effective radius of micelles varies depending on the compounds involved in the reaction.

As noted above, in measuring the EPR spectra, the observed polarisation contains contributions of both radical pairs in micelles and free radicals, whereas SNP arises only in the presence of radical pairs. For example, using SNP and time-resolved EPR, the spectra of the radical pairs formed in the photolysis of α-methyldeoxybenzoin and benzoin in micelles of various size

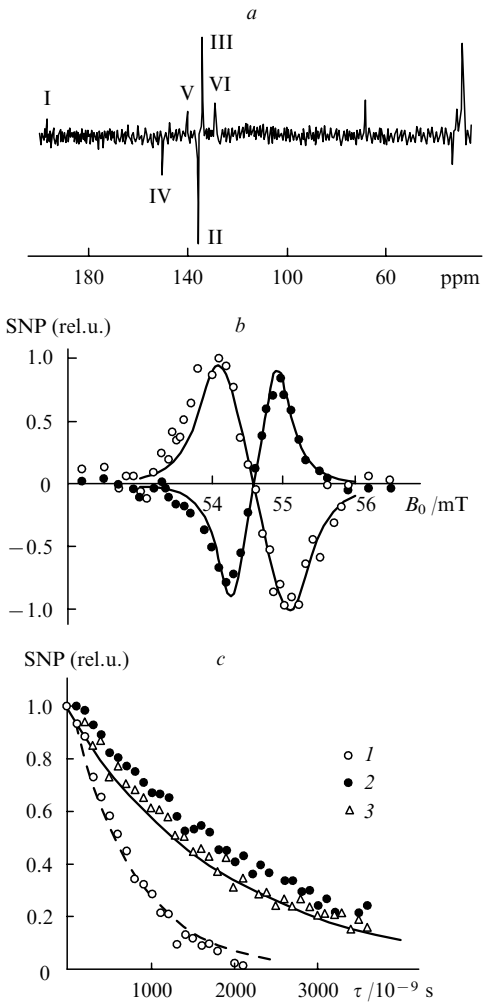


Figure 17. NMR spectrum of radical pairs formed in the photolysis of benzophenone-d_{10} with 2,4,6-tri-*tert*-butylphenol in the micelles on exposure to a 0.03 mT RF field (*a*); SNP spectra of radical pairs labelled at position I (*1*) and II (*2*) (*b*) and the kinetic curves of SNP of the radical pairs labelled at positions I–III (*1–3*, respectively) (*c*) in different magnetic fields. B_0 (mT): (*1*) 53.5; (*2*), (*3*) 54.1. The calculated relaxation constants k_{rel} 1.2×10^6 (dashed line) and 3.0×10^5 s^{-1} (continuous line).

were recorded. The SNP spectra measured for micelles with different sizes are closely similar because the HFC constants, electron relaxation parameters, radical size, and the reactivity of radical pairs are very close. Meanwhile, the EPR spectra recorded for the photolysis of α-methyldeoxybenzoin and benzoin are different in principle. Whereas the RP formed in α-methyldeoxybenzoin is responsible for an antiphase structure of the spectrum depending on the micelle size, in the case of benzoin, no line splitting due to exchange interaction is observed.[116] The radical pairs consisting of hydroxybenzyl radicals formed in benzoin photolysis leave the micelles at a markedly higher rate than the radical pairs consisting of benzyl and benzoyl radicals. As shown by Tarasov *et al*,[116] within 200 ns after the photolysis of α-methyldeoxybenzoin, 70% of the radicals are located in micelles, while in the case of benzoin, this value is only 5%.

The kinetics of micellised radical pairs have been studied by time-resolved SNP. It is obvious that the coherent transitions between singlet and triplet sublevels in radical pairs cannot be described within the framework of a kinetic scheme.[124] However, since for most radical pairs, the rate of recombination markedly exceeds the relaxation rate, the experimental kinetic dependences of SNP are well described by an exponential curve and are consistent with the calculation based on the simple kinetic scheme.

Yet another approach to the theoretical description of the dynamics of radical pairs is numerical solution of the Liouville equation for the density matrix.[78] The kinetic curves for time-resolved SNP measured for the photolysis of α-methyldeoxybenzoin and dibenzyl ketone in sodium dodecyl sulfate micelles are described adequately by an exponential function in accordance with the kinetic scheme.

Figure 17 *c* shows the kinetic curves of SNP obtained for the photolysis of benzophenone-d_{10} with 2,4,6-tri-*tert*-butylphenol in sodium dodecyl sulfate micelles. The SNP kinetic curves for radical pairs labelled in positions I–V bear information on the relaxation in various radical pairs. The decay of SNP for the pairs labelled in positions II–V is due to the exit of radicals from the micelle and dipole–dipole relaxation. For a pair labelled in position I, relaxation caused by the modulation of the anisotropic part of HFC plays an important role.

In the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, the rate of the decay of SNP kinetics for sodium dodecyl sulfate micelles is 2.5 times higher than that for sodium octyl sulfate; meanwhile, in the case of photolysis of ketones, this difference was not more than 20%–30%. Analysis of the resulting time dependences in terms of the kinetic model made it possible to estimate the relaxation and recombination rates for the radical pair in this reaction. For sodium octyl sulfate micelles, the relaxation rate is only 1.8 times lower than that for sodium dodecyl sulfate micelles. Thus, the SNP kinetics observed in sodium octyl sulfate micelles is determined by both recombination and relaxation. Note that the parameters determining the kinetics of radical pairs and those determined from theoretical and experimental SNP spectra are in good agreement with the data from the time-resolved EPR spectra.[127, 128]

The use of the SNP methods in investigating micellised radical pairs provides unique information on their spin dynamics and kinetics. This possibility is due to the high sensitivity of the SNP method and to its selectivity with respect to radical pairs. The information obtained in SNP studies of micellised radical pairs was used in experiments on the measurement of the magnetic isotope effect (MIE) induced by a resonance RF field. The reaction investigated in these experiments was photolysis of dibenzyl ketone.[129] Saturation of the electron transitions in radical pairs can give rise to enhanced MIE in two different regimes: at small amplitudes of the RF field ($B_1 \ll A$), the S–T conversion in one sub-ensemble of radical pairs containing a magnetic isotope is accelerated, while at large amplitudes of the RF field ($B_1 \gg A$), closing of the S–T conversion for radicals devoid of a magnetic isotope takes place. Tarasov *et al.*[129] used the former regime but the latter appears to be more promising as regards enhancement of MIE.[130, 131] The SNP method can provide exact information on the RF-field amplitude that ensures the maximum MIE value.

V. Chemically induced dynamic nuclear polarisation in switched external magnetic fields

The method of time-resolved CIDNP permits one to obtain quantitative information about the kinetics of radical reactions, lifetimes of triplet molecules and electron–nuclear cross-relaxation processes.[132–135] The procedure involved in the time-resolved CIDNP method is the measurement of the dependence of CIDNP intensity on the variable delay τ between the laser pulse and the detecting radio-frequency pulse (90-degree pulse of an NMR spectrometer) (Fig. 18 *a*). CIDNP arises in the strong magnetic field of the NMR spectrometer; as a rule, this is not the optimal field for observing this effect when many photochemical reactions take place. The time resolution of the method is determined by the duration of the radio-frequency pulse and is equal to 40 ns at best (normally, it is of the order of microseconds). It is often necessary to study CIDNP in weak and medium magnetic fields [52] because this method can provide information about the exchange interaction, exchange reactions and so on. When measuring CIDNP in

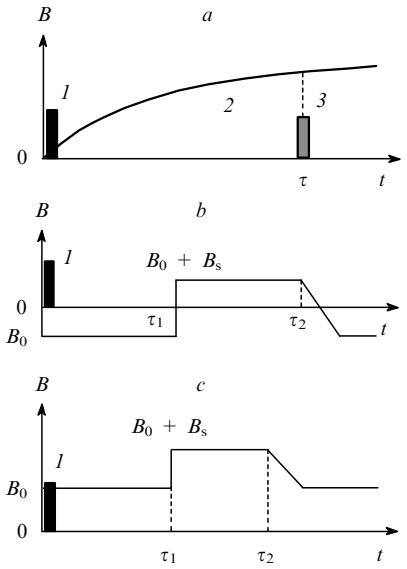


Figure 18. Schematic illustration of time-resolved CIDNP (*a*) and switched external magnetic field CIDNP (*b*, *c*); (*1*) laser, (*2*) region of CIDNP generation, (*3*) detecting radio-frequency pulse. Field switching can occur both with (*b*) and without (*c*) change in its direction.

weak and medium magnetic fields, photolysis is normally carried out in the field of a separate magnet and then the sample is transferred into the probe of an NMR spectrometer to record the spectrum. Photolysis can be performed directly in the probe of an NMR spectrometer with detection in weak magnetic fields;[136] however, in this case, spectral resolution and the sensitivity are very low, which restricts the scope of this method to systems with abnormally high CIDNP intensity. It is evident that time resolution by a traditional time scheme cannot be used in the experiments with transfer of the sample from the field of an individual magnet to the probe of an NMR spectrometer. This opportunity appears in the case of fast switching of the magnetic field within a variable period after the laser pulse initiating the radical reaction (Fig. 18 *b*, *c*). The idea of switching the external magnetic field (SEMF) during a photochemical reaction was first proposed and implemented by Lavrik *et al.*[137] The authors studied the effect of magnetic field switching on the intensity of fluorescence of excimers in radical-ion reactions. On the basis of the results obtained, estimates were made of the lifetimes of radical pairs.

The potential of the methods based on the SEMF during the lifetime of radical pairs was studied theoretically.[83] The researchers considered the influence of SEMF on both the probability of recombination of radical pairs and the nuclear polarisation of diamagnetic products in strong magnetic fields (*i.e.* with allowance for only $S-T_0$ transitions). Three different modes of radical recombination were chosen. In the first mode, the singlet–triplet transitions occur in the period between two contacts. This is accompanied by quantum oscillations. In the second mode, the $S-T_0$ transitions do not have time to take place in the interval between two contacts but do occur effectively over the lifetime of the pair in the cage. In this case, no quantum oscillations are displayed; however, the recombination kinetics depend on the frequency of $S-T_0$ transitions. Finally, in the third mode, the singlet–triplet transitions are relatively ineffective. This mode of recombination is of interest because it permits one to determine the lifetime of the pair in the cage. It should be noted that in experiments, the recombination mode is largely 'controllable'. It can be changed, for example, by changing the solution viscosity.

Bagryanskaya *et al.*[138–140] carried out experiments based on switching of the external magnetic field within a variable period after a laser pulse followed by recording of the CIDNP effect (the SEMF CIDNP method). It was found that the change of nuclear polarisation of the products of radical reactions upon switching the external magnetic field can be induced both by the change in the conditions of spin dynamics of radical pairs and intermediate short-lived free radicals and by the change in the electron and nuclear polarisation at the instant of switching. On the one hand, this treatment substantially complicates interpretation of the experimental results but, on the other hand, it opens the following ways for the investigation of the chemical kinetics and spin dynamics of radical species.

(i) Study of the dependence of polarisation on the delay τ between the laser pulse and the instant of magnetic field switching allows one to explore the kinetics of CIDNP of geminate radical pairs. The time it takes to switch a magnetic field by 10^{-3} T equals 1–3 ns. The time resolution is determined by the accuracy of synchronisation of the laser pulse and the instant of magnetic field switching (20–30 ns). Unlike the traditional time-resolved CIDNP, this method allows investigation of the CIDNP kinetics in weak and medium magnetic fields. This time resolution in NMR spectrometers is, in principle, impossible in weak fields because it is determined by the duration of the radio-frequency pulse, which lies in the millisecond time interval for weak and medium fields.

(ii) Variation of the delay τ permits one to change selectively the conditions of spin dynamics for geminate and diffusion radical pairs and thus to study the chemical kinetics of radical species.

(iii) Switching of the magnetic field changes the electron and nuclear polarisation of free radicals; this makes it possible to study the mechanisms of electron relaxation and the electron–nuclear cross-relaxation and CIDEP in weak magnetic fields.

Since the change in the magnetic field by $\sim 10^{-2}$ T causes only a minor change in the CIDNP in strong magnetic fields, realisation of the SEMF CIDNP technique in strong magnetic fields requires that a pulsed magnetic field of a substantial magnitude be created. This is a complex engineering problem. In weak magnetic fields, CIDNP changes quite substantially as the magnetic field changes by $\sim 10^{-3}$ T. The SEMF CIDNP method in weak and medium magnetic fields was implemented using a setup in which photolysis was carried out in the field of a separate magnet and, subsequently, after polarisation appeared, the polarised diamagnetic product was rapidly (over a period shorter than the characteristic time of nuclear relaxation) delivered *via* a fast-flow system to the probe of an NMR spectrometer in which CIDNP was recorded. The magnetic field is switched by use of Helmholtz coils, which create an additional field in the magnet with a switching amplitude of ± 7 mT. This markedly restricts the range of fields in which the SEMF CIDNP kinetics can be measured and is due to a requirement of the method according to which the absolute magnitudes of CIDNP in the initial and the final fields should be substantially different. Therefore, the highest sensitivity of the method is attained in those fields, in which the curve for the field dependence of CIDNP has 'steep slopes'.

1. Chemically induced nuclear polarisation under conditions of non-adiabatic switching of the magnetic field

The time of electron relaxation of free radicals does not actually depend on the switching of the external magnetic field. However, the situation changes if the chemical processes, for example DEE, influence the electron relaxation. For radical-ion reactions with DEE, the relaxation times in weak fields can be markedly dependent on the external magnetic field. As has been shown above, CIDNP in radical-ion reactions is influenced substantially by DEE reactions. The dependence of CIDNP kinetics on the concentration of the donor or acceptor molecules can be used to measure the DEE rate and to study the electron polarisation in weak magnetic fields.

The utility of the SEMF CIDNP method for measurement of DEE rates has been demonstrated in relation to the photoisomerisation of fumaronitrile with naphthalene in polar solvents.[139] Figure 19 presents the kinetic curves for the SEMF CIDNP of fumaronitrile and maleonitrile recorded for magnetic fields

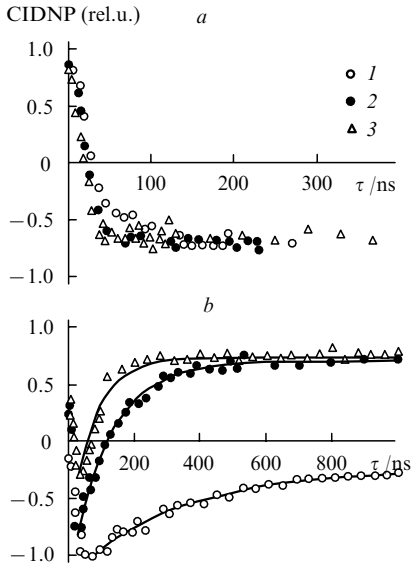


Figure 19. Kinetic curves of the SEMF CIDNP for the photoisomerisation of the fumaronitrile with naphthalene constructed using the NMR signals of maleonitrile (B_0 = 1 mT, B' = −1 mT) (*a*) and fumaronitrile (B_0 = 3 mT, B' = 5 mT) (*b*). Fumaronitrile concentration (mol litre^{-1}): (*1*) 5×10^{-3}, (*2*) 2×10^{-2}, (*3*) 4×10^{-2}.

switched either with or without inversion of their direction. The kinetics of CIDNP detected based on an in-cage reaction product, maleonitrile, are determined by the time required for the formation of radical pairs. For the escape reaction product, fumaronitrile, the kinetics are stipulated by the time of electron relaxation of the intermediate radical anion. The characteristic time of the decay of the CIDNP signal (of maleonitrile) is determined by the time of formation of geminate radical pairs; at high fumaronitrile concentrations [$(2-4)\times10^{-2}$ mol litre^{-1}] it amounts to 15–20 ns, while at low concentrations (5×10^{-3} mol litre^{-1}), it is 30–40 ns. On the basis of analysis of the kinetic curves of CIDNP constructed using the signals of maleonitrile in the NMR spectra, it was concluded that the time it takes for CIDNP in geminate radical pairs to appear is either shorter than or comparable with the duration of a laser pulse. Meanwhile, the kinetic curves of CIDNP detected from the NMR signal of fumaronitrile depend substantially on the rate of DEE. In the case of fast exchange, the obtained values coincide with the times of electron relaxation due to DEE, while for slow exchange, the CIDNP kinetics are determined by both the rate of DEE and the lifetime of free radicals.

It is worth noting that the typical lifetimes of radical pairs in homogeneous solutions are in the nanosecond range. Lasers with a pulse duration of 10–20 ns are used to initiate photochemical reactions; this stipulates the characteristic time of formation of the radical pair. Thus, experimental kinetic curves for CIDNP constructed for geminate radical pairs in homogeneous solutions are expected to reflect the kinetics of formation rather than the lifetime of the pair. The main advantage of the method discussed here is separation of the contributions of geminate and diffusion radical pairs to CIDNP.

The high time resolution and the possibility of investigating the kinetics of CIDNP in weak magnetic fields makes this method attractive for the investigation of spin dynamics of micellised radical pairs and short-lived biradicals. However, an attempt to carry out SEMF CIDNP experiments in micellised radical pairs demonstrated that, to obtain a satisfactory signal-to-noise ratio, the experiments should be carried out in fields whose magnitudes are close to the CIDNP maximum intensity. The field dependence of CIDNP for micellised radical pairs has almost in all cases the characteristic emission appearance, indicating the predominant contribution of the S–T$_-$ transitions to CIDNP. Thus, the kinetics of SEMF CIDNP should also be calculated with allowance for S–T$_-$ transitions. This brought about the necessity of modifying the theory of CIDNP under conditions of SEMF for the case of radical pairs with limited mobility. This problem was successfully solved [140, 141] on the basis of a kinematic approach. The time of switching of the magnetic field was assumed to be shorter than the time of intersystem crossing, electron relaxation and the exit of radicals from the micelles. To describe the motion of a micellised radical pair, the model for motion in the confined space was utilised. The calculation of the CIDNP effect as a function of the instant t_0 when the magnetic field is switched using typical parameters of a micellised radical pair showed that no quantum oscillations occur and the effect decays monotonically. The value by which the field changes has no influence on the pattern of time dependence, which is determined by the viscosity of the solution inside the micelle, but influences only the scale of the CIDNP effect. An interesting result is drawn if singlet–triplet transitions in one sub-ensemble of radical pairs stop after the magnetic field switching. In this case, quantum oscillations are observed on the time dependence of the effect. An expression was derived describing averaging of the S–T$_0$ transitions in the absence of relaxation and at low reactivity of the radical pair. In this case, conclusions about the character of movement of radicals in the radical pair can be drawn from the shape of the kinetic curve of SEMF CIDNP.

The purpose of the work by Fedin *et al.*[140] was to test the SEMF CIDNP method on a series of model reactions involving micellised radical pairs, to study the correspondence between the theoretical and experimental data, and to study the possibility of using this method for determination of the parameters of molecular and spin dynamics of micellised pairs. The researchers chose three photochemical reactions corresponding to different limiting cases of the ratio of the rates of radical exit from the micelles (k_{ex}), electron relaxation (k_{rel}) and S–T$_-$ conversion (k_{lc}) and conforming to the approximation at which only one magnetic nucleus is taken into account. In relation to these reactions, it was demonstrated that approximation of the kinetics by numerical calculations can provide information on the exit rate of the radicals from the micelle, the rate of decarbonylation, the rate of dipole–dipole electron relaxation, the rate of electron relaxation caused by anisotropy of HFC, and the rate of S–T$_-$ transitions occurring in the area of energy level crossing. Estimation of the rates of S–T$_-$ transitions for the systems studied suggested strong anisotropy of the exchange interaction.

The capacity of the SEMF CIDNP method for the investigation into short-lived biradicals has been evaluated [142] taking photolysis of acylalkyl cyclic ketones as an example. The use of substituted ketones allowed the researchers to compare the CIDNP kinetics for biradicals differing only in HFC constants and to estimate the lifetime of the triplet molecule. The measurement of the lifetimes of short-lived biradicals formed upon photolysis of α,α-diphenylcyclododecanone showed that the kinetic curves of CIDNP for this reaction in weak magnetic fields are described with rather high accuracy by an exponential curve and the characteristic time of the curve decay coincides with the data obtained from the optical absorption of biradicals.

2. Chemically induced nuclear polarisation under conditions of adiabatic switching of the external magnetic field

Switching of magnetic field can be accompanied by the transfer of electron polarisation to the nuclei and *vice versa*. The time and conditions of magnetic field switching are important factors determining the type of polarisation transfer (adiabatic or non-adiabatic). It has been shown [143] that adiabatic switching of the magnetic field with the change in its direction results in the transfer of the integral electron polarisation to the nuclei. The effect of the adiabatic change of the external magnetic field on the transfer of integral CIDEP on the radical nuclei and the subsequent transfer to the diamagnetic products of radical chemical

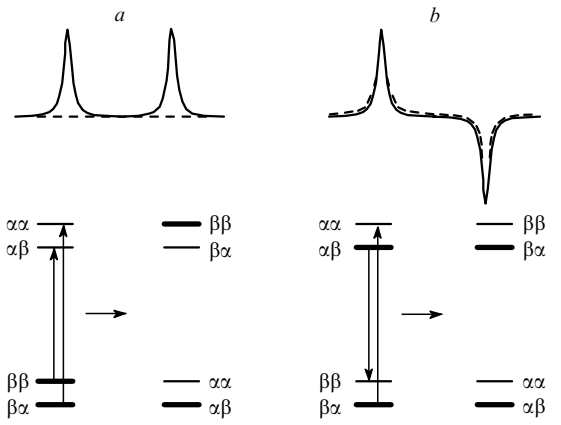


Figure 20. Schematic illustration of the effect of adiabatic switching of the external magnetic field on the nuclear polarisation of radicals; (*a*) the initial integral electron polarisation completely disappears after adiabatic switching of the magnetic field, (*b*) the initial multiplet electron polarisation does not change after the magnetic field switching.

reactions was studied. The limits of the adiabatic character of magnetic field switching were found from the Landau–Zener formula [144] to be 45–1100 nm. The lower limit is determined by the elucidation of time evolution of the spin system under adiabatic conditions, while the upper limit results from the requirement that radicals should react to give a diamagnetic product over a period of time shorter than the time of nuclear relaxation. The switching of the field was supposed to take place after the appearance of CIDEP. The adiabatic field switching is selective with respect to the mechanism of the appearance of CIDEP; the triplet and radical-pair mechanisms were considered as examples (Fig. 20). Passage through the zero magnetic field is accompanied by the transfer of the occupancy of levels: $\beta_e\alpha_n \rightleftharpoons \alpha_e\beta_n$ and $\alpha_e\beta_n \rightleftharpoons \beta_e\alpha_n$. It was found that the integral CIDEP is completely transferred to the radical nuclei and, after radical recombination, it can be detected in diamagnetic products. In the case of multiplet CIDEP, switching of the field does not influence the polarisation of the diamagnetic products. The optimal conditions for the transfer of electron polarisation were analysed numerically in the study cited as functions of the instant the field switching starts, of the duration of its front and of the velocity of passage through the zero-field region.

Evidently, non-zero nuclear polarisation is also transferred on electrons upon switching the magnetic field. This may result in the decay of escape nuclear polarisation. Since most radical reactions in weak magnetic fields are usually accompanied by substantial CIDNP, adiabatic change of the magnetic field can be used to separate the contributions of in-cage and escape polarisations. It has been shown [139] that transfer of electron polarisation to the nuclei takes place in weak magnetic fields even in the case of non-adiabatic switching of the magnetic field.

The potential of the SEMF ^{1}H CIDNP method as applied to short-lived radical species in a homogeneous solution has been analysed.[145] For this purpose, several photochemical reactions with participation of alkyl radicals $PhCH_2$, Me_3C and $PhC(O)CH_2$ in magnetic fields of 0.5–2.5 mT were studied. From analysis of experimental data, it was concluded that the kinetics of polarisation is determined by the electron–nuclear relaxation in the intermediate radicals. The measured relaxation times of the $PhCH_2$, Me_3C and $PhC(O)CH_2$ radicals in benzene were 2.2 ± 0.3, 7.1 ± 0.3 and 1.2 ± 0.2 μs. Figure 21 shows the kinetic curves of CIDNP for the photolysis of dibenzyl ketone constructed using the NMR signals of dibenzyl ketone. The CIDNP kinetics for dibenzyl ketone is determined by the rate of decarbonylation of the phenacyl radical, whereas for dibenzyl, the decay of the kinetic curve does not depend on the initial concentration of radicals and is equal to the electron relaxation time of the benzyl radical. The decays of the kinetic curves found for the photolyses of other compounds involving the benzyl radical do not depend on the initial concentration of the radicals either (Fig. 22).

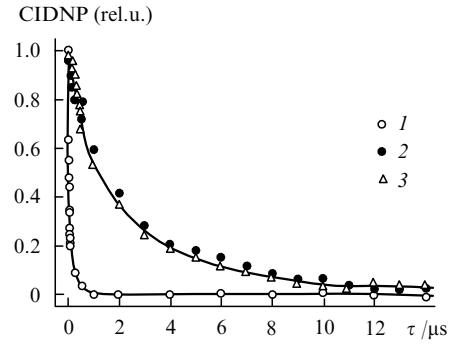


Figure 21. Experimental kinetic curves of SEMF CIDNP for the photolysis of dibenzyl ketone detected using the NMR signals of dibenzyl ketone (*1*) and dibenzyl: (*2*) I_1, (*3*) $I_2 = 3I_1$.

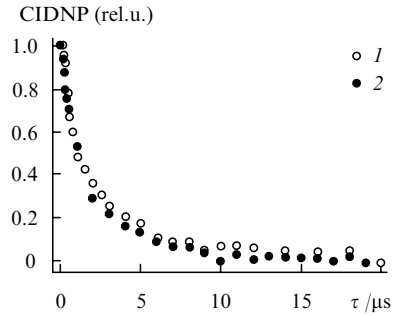


Figure 22. Kinetic curves of SEMF CIDNP for the photolysis of dibenzyl ketone (*1*) and deoxybenzoin (*2*).

The SEMF ^{31}P CIDNP method was used to determine the spin relaxation times for a series of phosphonyl radicals O=P(O)XY (X, Y are various substituents) in a 5 mT field in acetonitrile and in dioxane. If the anisotropy of HFC is modulated only by the rotation of the radical as a whole with characteristic times of the order of several picoseconds, the relaxation time in acetonitrile should be shorter than that in dioxane. However, an opposite relationship was found in the experiment, which was explained by the occurrence of deformation vibrations with characteristic periods of several nanoseconds. It was found that, if the relaxation time of the radical is shorter than its lifetime, the kinetics of SEMF CIDNP are determined by relaxation.

3. Polarisation under conditions of double switching of the external magnetic field

Recently, further updating of the SEMF CIDNP method was proposed, which implies the use of two non-adiabatic magnetic field switchings separated in time during the reaction.[146] The researchers considered the variation of the polarisation of free short-lived radicals induced by double switching of the magnetic field and determined the dependence of CIDNP of the diamagnetic products on the delay between the switchings. The time diagram of the experiment is shown in Fig. 23 *a*. In the first stage when $0 < t < t_1$, the radicals are formed under the action of a laser pulse in the external magnetic field H_1^0. It is assumed that by the time instant t_1, the primary polarisation of the radicals has arisen and they have moved out of the cage to the bulk. In the second stage when $t_1 < t < t_2$, the magnetic field undergoes a

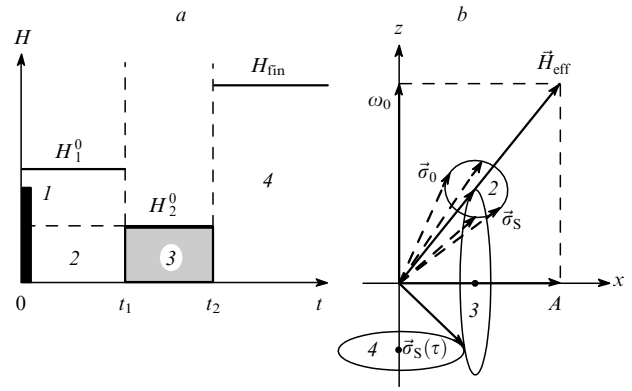


Figure 23. Time diagram (*a*) and vector model (*b*) in CIDNP experiments with double switching of the external magnetic field; (*1*) laser pulse, (*2*) preparation, (*3*) evolution; (*4*) recording.

non-adiabatic change to reach the value H_2^0. The radical polarisation starts to oscillate, the characteristic frequencies of oscillation being dependent on the structure of the spin levels of the radicals in the field H_2^0 and on the level occupancies. Finally, in the third stage when $t_2 < t$, the field undergoes a non-adiabatic change to reach the value $H_{fin} \gg H_2^0$. The nuclear polarisation of the radicals ceases to change and, upon recombination, passes to the diamagnetic products. Thus, the polarisation of oscillations in the intermediate radicals can be recorded using the dependence of the CIDNP intensity of the recombination products on the delay $\tau = t_2 - t_1$.

The appearance of beats of the CIDNP of radicals and their diamagnetic products can be illustrated using a vector model (Fig. 23 *b*). For the case of radical with one magnetic nucleus with the spin $I = 1/2$, the two-level approximation $|\alpha\beta N>, <\beta\alpha N|$ and the vector model are applicable. According to Adrian's approach,[147] we consider the operators of the projections $\hat{F}_z$, $\hat{F}_x$ of the effective spin, which act on the basis functions $|\alpha\beta N>, <\beta\alpha N|$ as the corresponding Pauli matrices

$$\hat{F}_z|\alpha\beta_N> = \frac{1}{2}|\alpha\beta_N>;$$

$$\hat{F}_z|\beta\alpha_N> = -\frac{1}{2}|\beta\alpha_N>;$$

$$\hat{F}_x|\alpha\beta_N> = \frac{1}{2}|\beta\alpha_N>;$$

$$\hat{F}_x|\beta\alpha_N> = \frac{1}{2}|\alpha\beta_N>.$$

Then the Hamiltonian

$$\hat{H} = \omega_0 \hat{S}_z + A(\hat{S}\,\hat{I})$$

for the radical in question in a weak field determined in the subspace Ω with the basis set $|\alpha\beta N>, <\beta\alpha N|$ assumes the form

$$\hat{H} = A\,\hat{F}_x + \omega_0\,\hat{F}_z = (\vec{H}_{eff}, \hat{F}),$$

where $\vec{H}_{eff} = (A, 0, \omega_0)$.

Thus, evolution of the state $|\Psi>$ from the subspace Ω can be represented as precession of the effective spin $\vec{\sigma}$ in an effective magnetic field with the z component ω_0, the x component A and the frequency $\sqrt{\omega_0^2 + A^2}$ (see Fig. 23 *b*). The projection of the vector $\vec{\sigma}$ on the z axis is equal to the difference between the occupancies of the levels $|\alpha\beta N>, <\beta\alpha N|$. The nuclear polarisation corresponding to the state $|\Psi>$ is proportional to this value. The permanent generation of effective spins at the preparation stage results in the vectors $\vec{\sigma}_0$ covering uniformly the surface of the cone, so that the average vector $\vec{\sigma}_S$ is directed along the cone axis, *i.e.* along the vector $\vec{H}_{eff}$. After non-adiabatic switching of the magnetic field to reach, for example, a zero magnitude, the vector $\vec{H}_{eff}$ is directed along the x axis and has the length A. At the initial instant, the vector $\vec{\sigma}_S$ remains constant then it starts to precess along the x axis with a frequency equal in magnitude to the HFC constant. The projection of the vector $\vec{\sigma}_S$ on the z axis varies periodically with the same frequency. If the magnetic field switches from the zero value to the value $H_{fin} \gg A$ after a time τ, the nuclear polarisation of radicals stops changing and passes to the diamagnetic reaction products after recombination. The vector $\vec{\sigma}_S$ would precess about the z axis and its projection on this axis would remain constant. Thus, by applying a second switching of the magnetic field after different delays τ, one can record the dependence of the oscillation of the CIDNP of diamagnetic products on τ. The paramagnetic relaxation in the radicals would result in a decrease in the length of the vector $\vec{\sigma}_S$ with an increase in the time t_1 and in a decrease in the amplitude of beats with an increase in the delay τ. When $t_1 \gg T_1$ (T_1 is the spin–lattice relaxation time), all the spin levels of the radical are almost equally occupied, which corresponds to the decrease in the length of the vector $\vec{\sigma}_S$ to zero. Evidently, in this case, the CIDNP of the diamagnetic products of the reaction does not oscillate. Thus, for high-quality recording of the oscillation, it is requited that T_1 be much longer than t_1.

Data on the oscillation of the CIDNP of the diamagnetic products bear information on the short-lived intermediates from which these products are formed. The amplitude, the frequency and the phase of oscillations depend on the structure and occupancy of the spin levels in the short-lived intermediate species. The method described above was first implemented by Makarov *et al.*[148] in relation to the photolysis of *p*-benzoquinone with 2-propanol-d_8 and to sensitised photoisomerisation of fumaronitrile. The oscillations of the CIDNP of the reaction products were

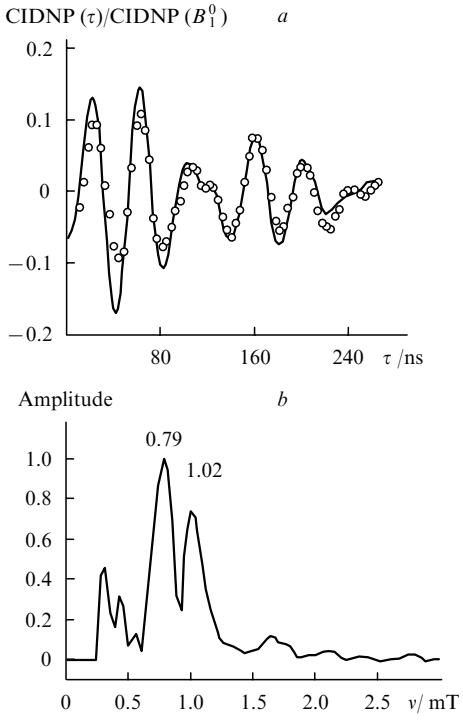


Figure 24. Oscillation of the CIDNP of the products of photolysis of *p*-benzoquinone with isopropanol-d_8 in acetonitrile in experiments with double switching of the external magnetic field (*a*) and Fourier spectrum of the resulting kinetic curve (*b*). The experimental positions of the resonance frequencies in the spectrum are given (the calculated positions are 0.76 and 1.04).

recorded as functions of the delay τ between the magnetic field switchings (Fig. 24). It was found that the amplitude, phase and the frequency of CIDNP beats are determined by the hyperfine structure and by the occupancies of the spin levels in the intermediate radicals. It was concluded from comparison of the experimental and theoretical data that the electron polarisation of semiquinoid radicals and fumaronitrile radical ions in weak magnetic fields is negative. It appears promising to use this method for investigating electron polarisation and the times of electron – nuclear relaxation of short-lived radicals in weak magnetic fields to which conventional time-resolved EPR is inapplicable.

VI. Conclusion

A vast body of experimental information has been accumulated on the use of high-sensitivity magnetic-resonance techniques based on the influence of variable resonance magnetic fields and switched constant magnetic fields on the nuclear polarisation of the products of radical reactions. The examples given in this review demonstrate the applicability of these methods to the study of the mechanism of radical reactions, identification of latent radical stages and measurement of DEE rates. The main regularities of polarisation of radical species with a broad range of lifetimes and in homogeneous and molecular-organised media have been elucidated. By now, the theory of the influence of RF fields on the nuclear polarisation in radical reactions has been thoroughly developed and employed to gain information on short-lived radical species — their spin dynamics and chemical kinetics.

The time-resolved SNP method can be used to separate the contributions to the polarisation of geminate and diffusion radical pairs and to obtain quantitative data on their kinetics. The SEMF CIDNP technique provides the possibility of measuring the rates of DEE, the kinetics of radicals, the lifetimes of short-lived biradicals and micellised radical pairs. This can prove useful in those cases where the use of flash photolysis is difficult due to the overlap of optical absorption bands. An additional advantage of the SEMF CIDNP method is the spectral resolution of NMR, which allows one to follow the transformation of biradicals into diamagnetic products. The DNP method provides the possibility of measuring the electron relaxation times for short-lived radicals and the signs and magnitudes of their HFC constants. Detection of DNP of the final reaction products can be used to investigate the mechanisms of radical processes. Unlike the CIDNP method, in the case of DNP, the formation of radical pairs in solution is not necessary. The doubly switched external magnetic field CIDNP method is supposed to be suitable for measuring the kinetics and the spin relaxation times of radicals, for investigating the CIDEP in weak magnetic fields, and for gaining information on the occupancy of the spin levels in the radicals.

Thus, nowadays, there exists a basis for the use of highly sensitive magnetic-resonance methods in the studies of complex photochemical reactions. The highest efficiency in the application of these methods can be attained by combining them with the techniques of laser flash photolysis and time-resolved EPR.

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References

1. V M Grigoryants, O A Anisimov, Yu N Molin *Zh. Strukt. Khim.* **23** (3) 4 (1982) [a]
2. Yu N Molin, O A Anisimov, V I Melekhov, S N Smirnov *Faraday Discuss. Chem. Soc.* **78** 1 (1984)
3. E L Frankevich, A I Pristupa *Pis'ma Zh. Techn. Fiz.* **24** 397 (1976)
4. E L Frankevich, S I Kubarev, in *Triplet State ODMR Spectroscopy* (Ed. R H Clarke) (New York: Wiley, 1982) p. 137
5. V I Lesin, V P Sakun, A I Pristupa, E L Frankevich *Phys. Status Solidi B* **84** 513 (1977)
6. M K Bowman, D E Budil, G L Closs, A G Kostka, C A Wraight, J R Norris *Proc. Natl. Acad. Sci. USA* **78** 3305 (1981)
7. J R Norris, M K Bowman, D E Budil, J Tang, C A Wraight, G L Closs *Proc. Natl. Acad. Sci. USA* **79** 5532 (1982)
8. A I Grant, K A McLauchlan, S R Nattrass *Mol. Phys.* **55** 557 (1985)
9. K W Moehl, E J Lous, A J Hoff *Chem. Phys. Lett.* **121** 22 (1985)
10. E L Frankevich *Zh. Eksp. Teor. Fiz.* **50** 1139 (1993)
11. H Murai, A Matsuyma, Y Iwasaki, K Enjo, K Maeda, T Azumi *Appl. Magn. Reson.* **12** 411 (1997)
12. E G Bagryanskaya, Yu A Grishin, N I Avdievich, R Z Sagdeev, Yu N Molin *Chem. Phys. Lett.* **128** 162 (1986)
13. R Z Sagdeev, Yu A Grishin, A Z Gogolev, A V Dushkin, A G Semenov, Yu I Molin *Zh. Strukt. Khim.* **20** 1132 (1979) [a]
14. A D Trifunac, W T Evanochko *J. Am. Chem. Soc.* **102** 4598 (1980)
15. R H D Nuttall, A D Trifunac *Chem. Phys. Lett.* **81** 151 (1981)
16. R H D Nuttall, A D Trifunac *J. Phys. Chem.* **86** 3963 (1982)
17. R H D Nuttall, A D Trifunac *J. Magn. Reson.* **51** 118 (1983)
18. A D Trifunac, R G Lawler, D M Bartels, M C Thurnauer *Prog. React. Kinet.* **14** 43 (1986)
19. Yu A Grishin, A Z Gogolev, E G Bagryanskaya, A V Dushkin, A G Semenov, R Z Sagdeev, Yu N Molin *Dokl. Akad. Nauk SSSR* **255** 1160 (1980) [b]
20. K Maeda, Q-X Meng, Y Yamakage, T Azumi *Z. Phys. Chem.* **182** 99 (1993)
21. Q Meng, Y Yamakage, K Maeda, T Azumi *Phys. Chem.* **180** 95 (1993)
22. E G Bagryanskaya, N N Lukzen, I V Koptyug, R Z Sagdeev, M N Usacheva *Appl. Magn. Reson.* **1** 431 (1990)
23. R Z Sagdeev, Yu N Molin, K M Salikhov, Yu A Grishin, A V Dushkin *Bull. Magn. Reson.* **2** 66 (1980)
24. R Z Sagdeev, E G Bagryanskaya *Pure. Appl. Chem.* **62** 1547 (1990)
25. E G Bagryanskaya, R Z Sagdeev *Prog. React. Kinet.* **18** 63 (1993)
26. Y Yamakage, Q Meng, K Maeda, T Azumi *Chem. Phys. Lett.* **204** 411 (1993)
27. S V Dvinskikh, A V Yurkovskaya, H-M Vieth *J. Phys. Chem.* **100** 8125 (1996)
28. N I Avdievich, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *Chem. Phys. Lett.* **155** 141 (1989)
29. V P Ivannikov, Yu D Chernousov, I V Shebolaev *Vopr. At. Nauki Tekhn.* **6** 55 (1989)
30. A L Buchachenko, A M Vasserman *Stabil'nye Radikaly* (Stable Radicals) (Moscow: Nauka, 1973)
31. K H Hausser, D Stelik *Adv. Magn. Reson.* **3** 1772 (1070)
32. E G Bagryanskaya, G S Ananchenko, T Nagashima, K Maeda, S Milikisyants, H Paul *J. Phys. Chem. A* **103** 1127 (1999)
33. S Nagakura, H Hayashi, T Azumi (Eds) *Dynamic Spin Chemistry. Magnetic Controls and Spin Dynamic of Chemical Reactions* (Tokyo: Kodansha, 1998)
34. K Maeda, Y Yamakage, K Shindo, T Azumi *Appl. Magn. Reson.* **5** 177 (1993)
35. Y Yamakage, Q Meng, S S Ali, K Maeda, T Azumi *Indian Acad. Sci.* **105** 629 (1993)
36. Q Meng, Y Yamakage, T Aizawa, K Maeda, T Azumi *Indian Acad. Sci.* **105** 619 (1993)
37. Y Yamakage, K Maeda, T Azumi *Mol. Phys.* **90** 3 (1997)
38. K A McLauchlan, in *Modern Pulsed and Continuous Wave Electron Spin Resonance* (Eds L Kevan, M K Bowman) (New York: Wiley, 1990) p. 285
39. K A McLauchlan, D G Stevens *Mol. Phys.* **57** 223 (1986)
40. F Jent, H Paul, K A McLauchlan, D G Stevens *Chem. Phys. Lett.* **141** 443 (1987)
41. V I Valyaev, Yu N Molin, R Z Sagdeev, P J Hore, K A McLauchlan, N J K Simpson *Mol. Phys.* **63** 891 (1988)
42. A V Yurkovskaya, Yu P Tsentalovich, R Z Sagdeev *Chem. Phys. Lett.* **171** 406 (1990)
43. Yu P Tsentalovich, A A Frantsev, A B Doctorov, A V Yurkovskaya, R Z Sagdeev *J. Phys. Chem.* **97** 8900 (1993)
44. Yu P Tsentalovich, A V Yurkovskaya, A A Frantsev, A B Doctorov, R Z Sagdeev *Z. Phys. Chem.* **182** 119 (1993)
45. M Salzmann, Yu P Tsentalovich, H Fischer *J. Chem. Soc., Perkin. Trans. 2* 2119 (1994)
46. O Morozova, Yu P Tsentalovich, A V Yurkovskaya, R Z Sagdeev *Chem. Phys. Lett.* **246** 499 (1995)

47. S N Batchelor, H Fischer *J. Phys. Chem.* **100** 556 (1996)
48. E G Bagryanskaya, N I Avdievich, Yu A Grishin, R Z Sagdeev *Chem. Phys.* **135** 123 (1989)
49. V R Gorelik, E G Bagryanskaya, N N Lukzen, I V Koptyug, V V Perov, R Z Sagdeev *J. Phys. Chem.* **100** 580 (1996)
50. K M Salikhov, C H Boch, D Stehlik *Appl. Magn. Reson.* **1** 195 (1990)
51. E G Bagryanskaya, R Z Sagdeev *Z. Phys. Chem.* **80** 63 (1993)
52. K M Salikhov, Yu N Molin, R Z Sagdeev, A L Buchachenko, in *Spin Polarization and Magnetic Effects in Radical Reactions* (Ed. Yu N Molin) (Amsterdam: Elsevier, 1984)
53. E Schaffner, H Fischer *J. Phys. Chem.* **100** 1657 (1996)
54. M N Usacheva, E G Bagryanskaya, T I Viktorova, I V Drozdenko, in *Mezhdunarodnaya Konferentsiya po Fotokhimii (Tez. Dokl.), Kiev, 1992* [International Conference on Photochemistry (Abstracts of Repots), Kiev, 1992] p. 170
55. E G Bagryanskaya, V R Gorelik, R Z Sagdeev, M N Usacheva, H Paul, in *The Xth International Conference 'Magnetic Resonance in Chemistry and Biology' (Abstracts of Reports), Suzdal, 1998* p. 49
56. G S Ananchenko, E G Bagryanskaya, R Z Sagdeev *Chem. Phys. Lett.* **282** 450 (1998)
57. E G Bagryanskaya, G S Ananchenko, A P Parnachev, P A Purtov, R Z Sagdeev, in *Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena (Abstracts of Reports), Ierusalim, 1997* p. 49
58. G S Ananchenko, Candidate Thesis in Chemical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1999
59. G S Ananchenko, P A Purtov, E G Bagryanskaya, R Z Sagdeev *J. Phys. Chem. A.* **101** 3848 (1997)
60. G S Ananchenko, P A Purtov, E G Bagryanskaya, R Z Sagdeev *J. Phys. Chem. A.* **103** 3430 (1999)
61. G L Closs, R J Miller, O D Redwein *Acc. Chem. Res.* **18** 196 (1985)
62. J K Vollenweider, H Fischer *Chem. Phys.* **108** 365 (1986)
63. N J Turro, M B Zimmt, I R Gould *J. Am. Chem. Soc.* **105** 6347 (1983)
64. Yu P Tsentalovich, A V Yurkovskaya, R Z Sagdeev, A A Obynochny, P P Purtov *Chem. Phys.* **139** 307 (1989)
65. S I Kubarev, E A Pshenichnov *Chem. Phys. Lett.* **28** 66 (1974)
66. S N Batchelor, K A McLauchlan, I A Shkrob *Chem. Phys. Lett.* **181** 327 (1991)
67. M Okazaki, S Sakata, R Konaka, T Shiga *J. Chem Phys.* **86** 6792 (1987)
68. S A Mikhailov, K M Salikhov, A M Plato *Chem. Phys.* **117** 197 (1987)
69. I V Koptyug, N N Lukzen, E G Bagryanskaya, A B Doktorov *Chem. Phys. Lett.* **175** 467 (1990)
70. A I Shushin *Chem. Phys. Lett.* **181** 274 (1991)
71. S M Mikhailov, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1988
72. S M Mikhailov, P P Purtov *Teor. Eksp. Khim.* **24** 519 (1988) [c]
73. A M Osintsev, P P Purtov, K M Salikhov *Chem. Phys.* **174** 237 (1993)
74. V A Morozov, A B Doktorov, R Z Sagdeev *Chem. Phys.* **179** 287 (1994)
75. I A Shkrob, V F Tarasov, E G Bagryanskaya *Chem. Phys.* **153** 427 (1991)
76. E G Bagryanskaya, V F Tarasov, N I Avdievich, I A Shkrob *Chem. Phys.* **162** 213 (1992)
77. V F Tarasov, E G Bagryanskaya, I A Shkrob, N I Avdievich, N D Ghatlia, N N Lukzen, N J Turro, R Z Sagdeev *J. Am. Chem. Soc.* **117** 110 (1995)
78. A P Parnachev, E G Bagryanskaya, V F Tarasov, N N Lukzen, R Z Sagdeev *Chem. Phys. Lett.* **244** 245 (1995)
79. A I Shushin *Chem. Phys. Lett.* **282** 413 (1998)
80. P A Purtov, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1982
81. K M Salikhov, R T Galeev *Mol. Phys.* **99** 1005 (1998)
82. J B Pedersen *Chem. Phys. Lett.* **52** 333 (1977)
83. A B Doktorov, S A Mikhailov, P P Purtov *Chem. Phys.* **160** 223 (1992)
84. A M Osintsev, P A Purtov, A B Doktorov *Chem. Phys.* **185** 281 (1994)
85. K M Salikhov, Y Sakaguchi, H Hayashi *Chem. Phys.* **220** 355 (1997)
86. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *Chem. Phys. Lett.* **113** 234 (1985)
87. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, Yu A Molin *Chem. Phys. Lett.* **114** 138 (1985)
88. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, T V Leshina, N E Polyakov, Yu A Molin *Chem. Phys. Lett.* **117** 220 (1985)
89. Yu P Tsentalovich, E G Bagryanskaya, Yu A Grishin, A A Obynochny, R Z Sagdeev, H-K Roth *Chem. Phys.* **142** 75 (1990)
90. I V Koptyug, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1990
91. N I Avdievich, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1992
92. V R Gorelik, N N Lukzen, A V Morozov, E G Bagryanskaya, R Z Sagdeev *Chem. Phys.* **224** 229 (1997)
93. Y Yamakage, T Nagashima, K Maeda, H Murai, T Azumi *Appl. Magn. Reson.* **12** 441 (1997)
94. A B Doktorov, S A Mikhailov, P P Purtov *Chem. Phys.* **160** 239 (1992)
95. S A Mikhailov, P P Purtov, A B Doktorov *Chem. Phys.* **166** 35 (1992)
96. I V Koptyug, N N Lukzen, E G Bagryanskaya, A B Doktorov, R Z Sagdeev *Chem. Phys.* **162** 165 (1992)
97. I V Koptyug, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev *Chem. Phys.* **145** 375 (1990)
98. I V Koptyug, E G Bagryanskaya, R Z Sagdeev *Chem. Phys. Lett.* **163** 503 (1989)
99. R Z Sagdeev, E G Bagryanskaya, I V Koptyug, Yu P Tsentalovich, A V Yurkovskaya, in *Spin Chemistry (Oji International Conference on Spin Chemistry)* (Ed. Y J I'Haya) (Tokyo: University of Electro-Communications, 1991) p. 138
100. F J J De Kanter, R Kaptein, R A von Santen *Chem. Phys. Lett.* **45** 575 (1977)
101. A V Yurkovskaya, O B Morozova, R Z Sagdeev, S V Dvinskikh, G Buntkowsky, H M Vieth *Chem. Phys.* **197** 157 (1995)
102. S V Dvinskikh, G Buntkowsky, K M Salikhov, H-M Vieth *Chem. Phys. Lett.* **268** 401 (1997)
103. N V Lebedeva, E G Bagryanskaya, I V Koptyug, R Z Sagdeev, M D E Forbes *Chem. Phys. Lett.* **308** 295 (1999)
104. J C Scaiano *Acc. Chem. Res.* **15** 252 (1982)
105. A Yurkovskaya, S Grosse, S Dvinskikh, O Morozova, H M Vieth *J. Chem. Phys.* **103** 980 (1999)
106. A L Buchachenko, R Z Sagdeev, K M Salikhov *Magnitnye i Spinovye Effekty v Khimicheskikh Reaktsiyakh* (Magnetic and Spin Effects in Chemical Reactions) (Novosibirsk: Nauka, 1978) p. 296
107. N J Turro, W R Cherry *J. Am. Chem. Soc.* **100** 7431 (1978)
108. M B Zimmt, C Doubleday Jr , N J Turro *J. Am. Chem. Soc.* **106** 3363 (1984)
109. I R Gould, M B Zimmt, N J Turro, B H Baretz, G F Lehr *J. Am. Chem. Soc.* **107** 4607 (1985)
110. P P Levin, V A Kuzmin *Chem. Phys.* **162** 79 (1992)
111. T Ulrich, U E Steiner *Chem. Phys. Lett.* **112** 365 (1984)
112. E N Step, V F Tarasov, A Z Yankelevich *Khim. Fiz.* **7** 1487 (1988) [d]
113. I A Shkrob, V F Tarasov, A L Buchachenko *Chem. Phys.* **153** 443 (1991)
114. K A McLauchlan, S R Nattrass *Mol. Phys.* **65** 1483 (1988)
115. G L Closs, M D E Forbes, J R Noris Jr *J. Phys. Chem.* **91** 3592 (1987)
116. V V Tarasov, H Yashiro, K Maeda, T Azumi, I A Shkrob *Chem. Phys.* **212** 353 (1996)
117. E G Bagryanskaya, A P Parnachev, G S Ananchenko, V F Tarasov, N N Lukzen, R Z Sagdeev, in *The VIth Chianti Workshop on Magnetic Resonance (Abstracts of Reports), San Miniato, 1995* p. 3
118. E G Bagryanskaya, N V Lebedeva, M V Fedin, in *The 17th IUPAC Symposium on Photochemistry (Abstracts of Reports), Barcelone, 1998* p. 53
119. E G Bagryanskaya, M V Fedin, N V Lebedeva, in *International Conference on Reactive Intermediates and Reaction Mechanisms (Abstracts of Reports), Ascone, 1998* p. 31
120. G S Ananchenko, E G Bagryanskaya, V F Tarasov, R Z Sagdeev, H Paul *Chem. Phys. Lett.* **255** 267 (1996)
121. A P Parnachev, E G Bagryanskaya, R Z Sagdeev *J. Phys. Chem. A* **101** 3854 (1997)

122. E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, V F Tarasov, I A Shkrob, A L Buchachenko *Khim. Fiz.* **10** 1365 (1991) [d]
123. N V Lebedeva, E G Bagryanskaya, V R Gorelik, I V Koptyug, R Z Sagdeev, in *The VIth International Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena (Abstracts of Reports), Emmetten, 1999* p. 76
124. N I Avdievich, E G Bagryanskaya, V F Tarasov, R Z Sagdeev *Z. Phys. Chem.* **182** 107 (1993)
125. U E Steiner, J R Wu *Chem. Phys.* **162** 53 (1992)
126. V A Morozov, S V Isakov, R Z Sagdeev *Chem. Phys. Rep.* **16** 559 (1997)
127. V F Tarasov, M D Forbes *Spectrochim. Acta, Part A* **56** 245 (2000)
128. V V Tarasov, H Yashiro, K Maeda, T Azumi, I A Shkrob *Chem. Phys.* **212** 253 (1996)
129. V F Tarasov, E G Bagryanskaya, Yu A Grishin, R Z Sagdeev, A L Buchachenko *Mendeleev Commun.* 85 (1991)
130. M Okazaki, Y Tamimoto, Y Konishi, K Toriyama *J. Phys. Chem.* **100** 9403 (1996)
131. Y Konishi, M Okazaki, K Toriyama *Appl. Magn. Reson.* **11** 135 (1996)
132. G L Closs, R J Miller *J. Am. Chem. Soc.* **101** 1639 (1979)
133. R J Miller, G L Closs *Rev. Sci. Instr.* **52** 1876 (1981)
134. J-K Vollenweider, H Fischer, J Hennig, R Leuschner *Chem. Phys.* **97** 217 (1985)
135. J-K Vollenweider, H Fischer *Chem. Phys.* **124** 333 (1988)
136. Yu A Grishin, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1978
137. N L Lavrik, V E Khmelinsky *Chem. Phys. Lett.* **140** 582 (1987)
138. A P Parnachev, E G Bagryanskaya, V F Tarasov, N N Lukzen, N I Avdievich, R Z Sagdeev, in *The IIIrd International Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena (Abstracts of Reports), Chicago, 1994* p. 69
139. E G Bagryanskaya, V R Gorelik, R Z Sagdeev *Chem. Phys. Lett.* **264** 655 (1997)
140. M V Fedin, P A Purtov, E G Bagryanskaya *J. Chem. Phys.* **111** 5491 (1999)
141. A P Parnachev, P A Purtov, E G Bagryanskaya, R Z Sagdeev *J. Chem. Phys.* **107** 9942 (1997)
142. E G Bagryanskaya, V R Gorelik, A P Parnachev, R Z Sagdeev, in *The 28th Congress on Magnetic Resonance and Related Phenomena (Abstracts of Reports), Canterbury, 1996* p. 79
143. N N Lukzen, U E Steiner *Mol. Phys.* **86** 1271 (1995)
144. L D Landau, E M Lifshits *Teoreticheskaya Fizika* (Theoretical Physics) Vol. 3 (Moscow: Nauka, 1998)
145. M V Fedin, E G Bagryanskaya, in *Vseros. Shkola-Simpozium po Khimicheskoi Fizike (Tez. Dokl.), Tuapse, 1999* [All-Russian School-Symposium on Chemical Physics (Abstracts of Reports), Tuapse, 1999] p. 42
146. N N Lukzen, V A Morozov, R Z Sagdeev *Chem. Phys.* **241** 193 (1999)
147. F J Adrian *J. Chem. Phys.* **54** 3918 (1971)
148. T N Makarov, E G Bagryanskaya, S R Shakirov, N N Lukzen, R Z Sagdeev *Chem. Phys. Lett.* **317** 252 (2000)

[a] — *Russ. J. Struct. Chem. (Engl. Transl.)*
[b] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[c] — *Theor. Exp. Chem. (Engl. Transl.)*
[d] — *Russ. J. Chem. Phys. (Engl. Transl.)*