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Electron spin relaxation of radicals in weak magnetic fields

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The review summarizes the results of studies on specific features of spin relaxation of radicals in liquids in weak magnetic fields.

Key words: electron spin relaxation, weak magnetic field, free radicals, electron paramagnetic resonance, spin polarization, chemically induced dynamic electron polarization.

Many photochemical reactions involve radical stages. The interaction of external constant and alternating magnetic fields with electron and nuclear spins of intermediate radicals is the reason for the magnetic field and spin effects in radical chemical reactions. One of the key parameters determining the magnitude of the magnetic field effects is the spin relaxation rate of the intermediate radicals.[1,2] In the case of long-lived radical pairs (RPs), *e.g.*, RPs in micellar solutions,[2] radical ion pairs,[3] biradicals,[4] *etc.*, the spin relaxation is one of the main processes determining the probability of RP recombination. The spin relaxation rate is an important parameter used in calculations of the magnetic field effect,[2] EPR spectra,[5] kinetics of chemically induced dynamic electron polarization (CIDEP),[1,6] optically detected EPR spectra,[3] stimulated nuclear polarization (SNP) spectra and kinetics,[7] *etc.* Usually, the magnetic field effects and the CIDEP, SNP, and optically detected EPR spectra are calculated assuming additive contributions of (i) electron relaxation in individual radicals due to the interaction between an electron in a given radical and surrounding nuclei (modulation of anisotropic or isotropic HFI constant) or with the angular momentum of this radical (spin-rotational relaxation) and (ii) dipole-dipole and exchange relaxations due to the interaction between electrons in the radicals within the RP. Methods for the description of electron relaxation in the interacting radicals are not available as yet.

To date, the electron spin dynamics and relaxation of free radicals have been well studied in strong magnetic fields that much exceed typical HFI constants of organic radicals. Various experimental techniques were elaborated and detailed theoretical concepts were proposed, which makes it possible to determine the spin relaxation rates by analyzing experimental data.[8,9] Recently, there has been increasing literature on the behavior of radicals in weak magnetic fields whose magnitude is at most equal to the HFI constants of the radicals. Spin relaxation in weak magnetic fields has long been poorly studied both experimentally and theoretically. Experimental studies are scarce because of relatively small number of methods of measuring the relaxation times of radicals in weak magnetic fields. L-Band time-resolved EPR investigations of the radicals characterized by high HFI constants (30—70 mT) allow one to obtain information on the spin relaxation of radicals in weak and zero magnetic fields.[10,11] Because the sensitivity of c.w. EPR in weak magnetic fields is low (~10^{15} spins per sample), in this case information on electron spin relaxation can be extracted using indirect magnetic resonance methods, namely, the MARY (magnetic field effect on the reaction yield),[3] switched external magnetic field chemically induced dynamic nuclear polarization (CIDNP),[12,13] double-switched external magnetic field CIDNP,[14,15] and electron-nuclear transitions detected using the CIDNP of diamagnetic products.[16,17] In all these methods the CIDEP is formed in geminal or diffusion RPs on time scales of a few nanoseconds, whereas relaxation of the electron polarization occurs in free radicals and takes a few microseconds. Thus, spin relaxation in free radicals is an important parameter governing the kinetics of the signals detected by the methods mentioned above.

This work summarizes the results of our experimental and theoretical studies of spin relaxation in free radicals in weak magnetic fields.[10,11,18—21] We established that the spin relaxation rates in weak and strong magnetic fields can differ by a few orders of magnitude; this feature can not be explained in the framework of the high-field theory. The main relaxation mechanisms of radicals in liquids are

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considered, the laws of the process are analyzed, and the results obtained were compared with the available experimental data.

Spin relaxation in radicals: main computational methods

Electron spin relaxation of radicals in solutions can be due to modulation of 1) anisotropic hyperfine interaction; 2) isotropic hyperfine interaction; 3) spin-rotational interaction; and 4) anisotropy of the *g*-tensor. When studying magnetically concentrated solutions or long-lived RPs, one should take into account 5) electron spin exchange and 6) electron dipole-dipole interaction. The first four mechanisms correspond to relaxation due to intra-radical interactions, whereas the last two mechanisms correspond to radical-radical interactions. Because of this calculations for particular spin relaxation mechanisms are carried out by different methods.

Among theoretical approaches to the relaxation problem, Redfield´s theory[8,9] is applicable to any magnetic fields and allows the probabilities of relaxation transitions between arbitrary spin states to be calculated. This theory uses the correlation function of a stochastic process

$$G_{\alpha\beta,\gamma\delta}(\tau) = \overline{\left\langle\alpha\middle|\hat{H}_1(t-\tau)\middle|\beta\right\rangle\left\langle\gamma\middle|\hat{H}_1^*(t)\middle|\delta\right\rangle}, \tag{1}$$

where α, β, γ, and δ denote the stationary states of the system and the Hamiltonian $\hat{H}_1(t)$ describes a stochastic perturbation. The average value of $\hat{H}_1(t)$ is zero; the bar denotes the averaging over an ensemble of species with all possible realizations of the Hamiltonian $\hat{H}_1(t)$. The correlation function characterizes system´s "memory" and shows how the observed $\hat{H}_1(t)$ value depends on the $\hat{H}_1(t-\tau)$ value. The correlation function of a Markov process is independent of *t*. The correlation function decay is often described by an exponent

$$G_{\alpha\beta,\gamma\delta}(\tau) = \overline{\left\langle\alpha\middle|\hat{H}_1(t)\middle|\beta\right\rangle\left\langle\gamma\middle|\hat{H}_1^*(t)\middle|\delta\right\rangle}\cdot\exp(-|\tau|/\tau_c), \tag{2}$$

where τ_c is the correlation time. The spectral density of noise at frequency ω is calculated by integrating the correlation function

$$\begin{aligned} J_{\alpha\beta,\gamma\delta}(\omega) &= \frac{1}{2}\int_{-\infty}^{\infty} G_{\alpha\beta,\gamma\delta}(\tau)\exp(-i\omega\tau)\mathrm{d}\tau = \\ &= \overline{\left\langle\alpha\middle|\hat{H}_1(t)\middle|\beta\right\rangle\left\langle\delta\middle|\hat{H}_1(t)\middle|\gamma\right\rangle}\cdot\frac{\tau_c}{1+\omega^2\tau_c^2}. \end{aligned} \tag{3}$$

Then, the elements of the matrix of relaxation transitions can be determined using the following expression:

$$\begin{aligned} R_{\alpha\beta,\gamma\delta} &= J_{\alpha\gamma,\beta\delta}(E_\beta - E_\delta) + J_{\alpha\gamma,\beta\delta}(E_\alpha - E_\gamma) - \\ &- \delta_{\beta\delta}\sum_\sigma J_{\sigma\gamma,\sigma\alpha}(E_\sigma - E_\gamma) - \delta_{\alpha\gamma}\sum_\sigma J_{\sigma\beta,\sigma\delta}(E_\sigma - E_\delta), \end{aligned} \tag{4}$$

where E_i are the energies of the corresponding nondegenerate eigenstates. Otherwise, this relationship should be modified.

Spin levels of radicals in weak magnetic fields

From Eqs (3) and (4) it follows that the spin relaxation rate should depend on external magnetic field. Main differences from the case of strong magnetic fields are due to changes in the eigenstates of radicals, which causes significant changes in the relaxation transition probabilities. Consider the simplest model systems, namely, a radical containing one magnetic nucleus with spin $I = 1/2$ and a radical containing two equivalent magnetic nuclei with spins $I_{1,2} = 1/2$. The last-mentioned system is suitable for describing a particular case of a radical containing one nucleus with spin $I = 1$.

The spin-Hamiltonian of a radical containing one magnetic nucleus ($I = 1/2$) has the form

$$\hat{H}_0 = \omega_e\hat{S}_z - \omega_n\hat{I}_z + a\hat{S}_z\hat{I}_z + \frac{a}{2}(\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+), \tag{5}$$

where ω_e and ω_n are the electron and nuclear Zeeman frequencies, respectively; $\hat{S}$ and $\hat{I}$ are the electron and nuclear spin operators, respectively, and *a* is the isotropic HFI constant. The eigenfunctions (wave functions) and energy levels can be found using the Breit—Rabi relationships[5,22] in which we neglect ω_n (Fig. 1)

$$\begin{array}{ll} |1\rangle = |\alpha_e\alpha_n\rangle, & E_1 = \omega_e/2 + a/4, \\ |2\rangle = C_1|\alpha_e\beta_n\rangle + C_2|\beta_e\alpha_n\rangle, & E_2 = -\dfrac{a}{4} + \dfrac{\sqrt{\omega_e^2 + a^2}}{2}, \\ |3\rangle = |\beta_e\beta_n\rangle, & E_3 = -\omega_e/2 + a/4, \\ |4\rangle = C_2|\alpha_e\beta_n\rangle - C_1|\beta_e\alpha_n\rangle, & E_4 = -\dfrac{a}{4} - \dfrac{\sqrt{\omega_e^2 + a^2}}{2}, \end{array} \tag{6}$$

where

$$C_1^2 = \frac{1}{2}\left(1 + \frac{\omega_e}{\sqrt{\omega_e^2 + a^2}}\right), \quad C_2^2 = \frac{1}{2}\left(1 - \frac{\omega_e}{\sqrt{\omega_e^2 + a^2}}\right).$$

Here α_e and β_e are the electron spin projections on the *z* axis and α_n and β_n are the nuclear spin projections on the *z* axis.

The spin-Hamiltonian of a radical containing two equivalent HFI constants *a* has the form

$$\begin{aligned} \hat{H}_0 &= \omega_e\hat{S}_z - \omega_n(\hat{I}_{1z} + \hat{I}_{2z}) + a\hat{S}_z(\hat{I}_{1z} + \hat{I}_{2z}) + \\ &+ \frac{a}{2}\left[\hat{S}_+(\hat{I}_{1-} + \hat{I}_{2-}) + \hat{S}_-(\hat{I}_{1+} + \hat{I}_{2+})\right]. \end{aligned} \tag{7}$$

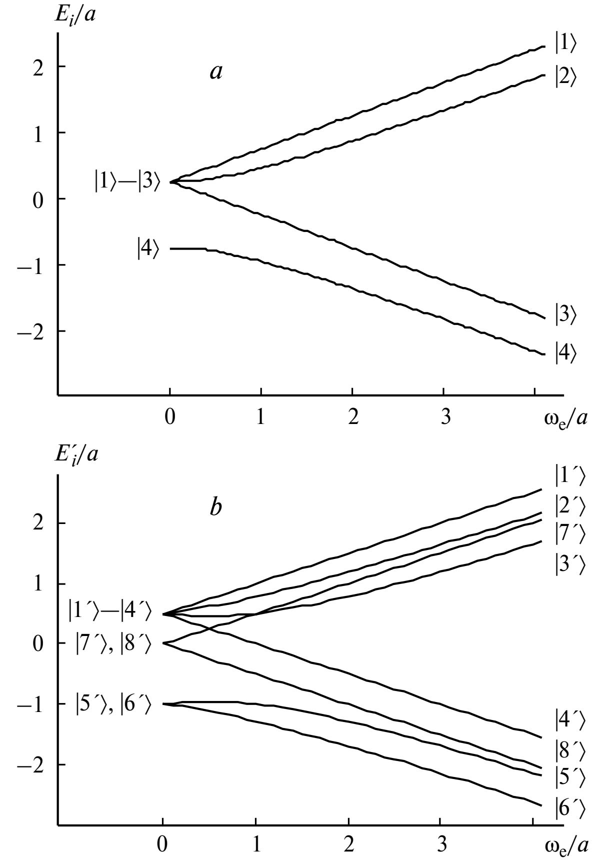

Fig. 1. Calculated scheme of the energy levels of radicals with one magnetic nucleus ($I = 1/2$) (*a*) and with two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) (*b*) plotted in the coordinates E_i/a *vs.* ω_e/a.

Neglecting ω_n compared to ω_e, one gets the corresponding eigenvalues and eigenfunctions

$$|1'\rangle = |\alpha_e\alpha_{1n}\alpha_{2n}\rangle, \qquad E_1' = (1/2)(a + \omega_e),$$

$$|2'\rangle = \frac{C_1'}{\sqrt{2}}\Big(|\alpha_e\alpha_{1n}\beta_{2n}\rangle + |\alpha_e\beta_{1n}\alpha_{2n}\rangle\Big) + C_2'|\beta_e\alpha_{1n}\alpha_{2n}\rangle,$$

$$E_2' = \frac{1}{4}\left(-a + \sqrt{9a^2 + 4a\omega_e + 4\omega_e^2}\right),$$

$$|3'\rangle = \frac{C_3'}{\sqrt{2}}\Big(|\beta_e\alpha_{1n}\beta_{2n}\rangle + |\beta_e\beta_{1n}\alpha_{2n}\rangle\Big) + C_4'|\alpha_e\beta_{1n}\beta_{2n}\rangle,$$

$$E_3' = \frac{1}{4}\left(-a + \sqrt{9a^2 - 4a\omega_e + 4\omega_e^2}\right),$$

$$|4'\rangle = |\beta_e\beta_{1n}\beta_{2n}\rangle, \qquad E_4' = (1/2)(a - \omega_e), \tag{8}$$

$$|5'\rangle = \frac{C_4'}{\sqrt{2}}\Big(|\beta_e\alpha_{1n}\beta_{2n}\rangle + |\beta_e\beta_{1n}\alpha_{2n}\rangle\Big) - C_3'|\alpha_e\beta_{1n}\beta_{2n}\rangle,$$

$$E_5' = \frac{1}{4}\left(-a - \sqrt{9a^2 - 4a\omega_e + 4\omega_e^2}\right),$$

$$|6'\rangle = -\frac{C_2'}{\sqrt{2}}\Big(|\alpha_e\alpha_{1n}\beta_{2n}\rangle + |\alpha_e\beta_{1n}\alpha_{2n}\rangle\Big) + C_1'|\beta_e\alpha_{1n}\alpha_{2n}\rangle,$$

$$E_6' = \frac{1}{4}\left(-a - \sqrt{9a^2 + 4a\omega_e + 4\omega_e^2}\right),$$

$$|7'\rangle = \frac{1}{\sqrt{2}}\Big(|\alpha_e\alpha_{1n}\beta_{2n}\rangle - |\alpha_e\beta_{1n}\alpha_{2n}\rangle\Big), \qquad E_7' = \omega_e/2,$$

$$|8'\rangle = \frac{1}{\sqrt{2}}\Big(|\beta_e\alpha_{1n}\beta_{2n}\rangle - |\beta_e\beta_{1n}\alpha_{2n}\rangle\Big), \qquad E_8' = -\omega_e/2,$$

where

$$(C_1')^2 = \frac{1}{2}\left(1 + \frac{a + 2\omega_e}{\sqrt{9a^2 + 4a\omega_e + 4\omega_e^2}}\right),$$

$$(C_2')^2 = \frac{1}{2}\left(1 - \frac{a + 2\omega_e}{\sqrt{9a^2 + 4a\omega_e + 4\omega_e^2}}\right),$$

$$(C_3')^2 = \frac{1}{2}\left(1 + \frac{a - 2\omega_e}{\sqrt{9a^2 - 4a\omega_e + 4\omega_e^2}}\right),$$

$$(C_4')^2 = \frac{1}{2}\left(1 - \frac{a - 2\omega_e}{\sqrt{9a^2 - 4a\omega_e + 4\omega_e^2}}\right).$$

The spin level scheme is shown in Fig. 1, *b*. The states $|1'\rangle$—$|6'\rangle$ correspond to the total nuclear spin $I_\Sigma = 1$ while the states $|7'\rangle$ and $|8'\rangle$ correspond to the total nuclear spin $I_\Sigma = 0$. The dependence of the mixing coefficients C_1, C_2, and C_1'—C_4' on the magnetic field governs the changes in the eigenfunctions (wave functions) on going from a strong ($\omega_e > a$) to a weak ($\omega_e < a$) magnetic field.

Spin relaxation due to modulation of anisotropic hyperfine interaction

Anisotropic hyperfine interaction is one of the key mechanisms of spin relaxation of radicals in solutions. The time T_1 of the electron relaxation due to anisotropic hyperfine interaction in strong magnetic fields ($\omega_e \gg a$) can be calculated using the Redfield theory[5,23]

$$1/T_1 = (1/6)([A:A]\tau_c)/(1 + \omega_e^2\tau_c^2), \tag{9}$$

where $[A:A] = \sum\limits_{x,y,z}(a_i - a)^2$ is the HFI anisotropy and a_x, a_y, and a_z are the principal values of the HFI tensor.

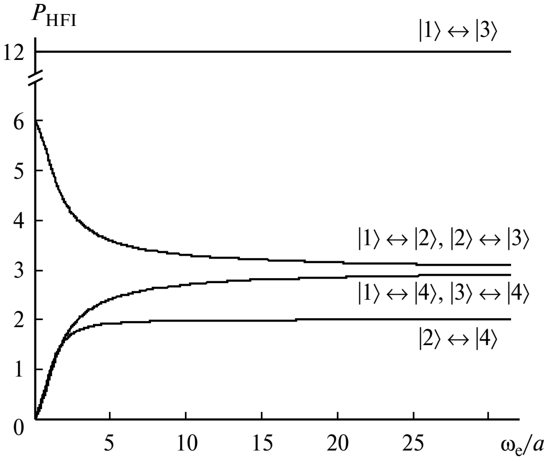

Fig. 2. Probabilities of relaxation transitions $|i\rangle \leftrightarrow |j\rangle$ induced by modulation of anisotropic hyperfine interaction (P_{HFI}) plotted *vs.* magnetic field (in units of ω_e/a) for a radical containing one magnetic nucleus ($I = 1/2$); $\Delta E_i^2\tau_c^2 \ll 1$.[19]

Usually, the time T_1 in a weak magnetic field was estimated using the same expression.[23–27] On going to the weak field[28] the parameter ω_e was replaced by the exact value of the splitting between the energy levels, but the T_1 value changed insignificantly. However, this treatment ignores the fact that HFI-induced relaxation of the radical containing one magnetic nucleus in zero magnetic field causes no transitions between states with different total spins. Thus, it is of crucial importance to allow for the changes in the wave functions in weak magnetic fields, because they lead to large differences between the relaxation transition rates of the high-field and low-field components of the EPR spectrum.

Radical with spin $S = 1/2$ ($I = 1/2$). The Hamiltonian of the dipole-dipole electron—nuclear interaction in a radical containing one magnetic nucleus ($I = 1/2$) can be written as follows[29–31]:

$$\hat{H}^{\mathrm{d}} = \left[\hat{S}_z\hat{I}_z - (1/4)(\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+)\right]\cdot F_0 + (\hat{S}_+\hat{I}_z + \hat{S}_z\hat{I}_+)\cdot F_1 + (\hat{S}_-\hat{I}_z + \hat{S}_z\hat{I}_-)\cdot F_1{}^* + (\hat{S}_+\hat{I}_+)\cdot F_2 + (\hat{S}_-\hat{I}_-)\cdot F_2{}^*, \qquad (10)$$

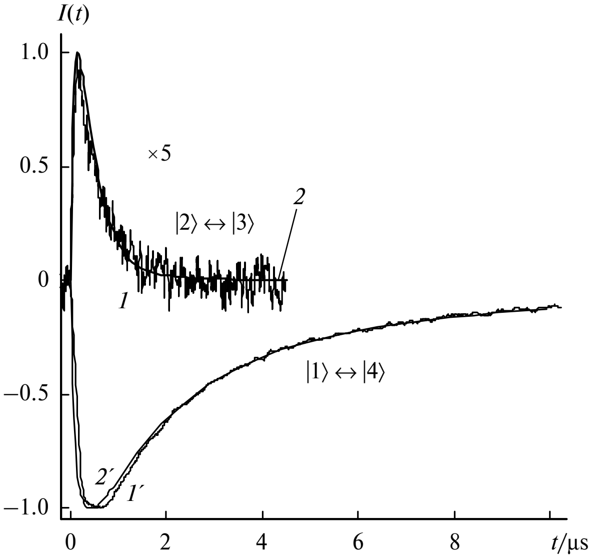

Fig. 3. Experimental CIDEP kinetics (*1, 1′*) of dimethoxyphosphonyl radical $(MeO)_2(O)P^{\bullet}$ in MeCN (L-band EPR; room temperature; *I*(*t*) is the signal intensity) and its simulation (*2, 2′*).[10]

where the random functions *F* are given by

$$F_0(t) = q[1 - 3\cos^2\vartheta(t)],$$
$$F_1(t) = -(3q/2)\sin\vartheta(t)\cos\vartheta(t)\exp[-i\varphi(t)], \qquad (11)$$
$$F_2(t) = -(3q/4)\sin^2\vartheta(t)\exp[-2i\varphi(t)],$$

and

$$\overline{F_0(t)F_0(t)} = \frac{4}{5}q^2, \qquad \overline{F_1(t)F_1{}^*(t)} = \frac{3}{10}q^2,$$
$$\overline{F_2(t)F_2{}^*(t)} = \frac{3}{10}q^2, \qquad (12)$$
$$q^2 = \frac{1}{6}[A:A] = \frac{1}{6}\sum_{i=x,y,z}(a_i - a_{\mathrm{iso}})^2.$$

Here $\vartheta(t)$ and $\varphi(t)$ are the azimuthal and polar angles in the polar laboratory system of coordinates, respectively, and a_{iso} is the isotropic HFI constant.

The Hamiltonian (see Eq. (10)) in the basis of the states described by Eqs (6) has the form

$$\hat{H}^{\mathrm{d}} = \begin{bmatrix} \dfrac{F_0}{4} & \dfrac{(C_1 + C_2)F_1}{2} & F_2 & \dfrac{(C_2 - C_1)F_1}{2} \\ \dfrac{(C_1 + C_2)F_1{}^*}{2} & -\dfrac{(1 + 2C_1C_2)F_0}{4} & -\dfrac{(C_1 + C_2)F_1}{2} & \dfrac{(C_1^2 - C_2^2)F_0}{4} \\ F_2{}^* & -\dfrac{(C_1 + C_2)F_1{}^*}{2} & \dfrac{F_0}{4} & \dfrac{(C_1 - C_2)F_1{}^*}{2} \\ \dfrac{(C_2 - C_1)F_1{}^*}{2} & \dfrac{(C_1^2 - C_2^2)F_0}{4} & \dfrac{(C_1 - C_2)F_1}{2} & -\dfrac{(1 - 2C_1C_2)F_0}{4} \end{bmatrix}. \qquad (13)$$

Then one should calculate the spectral density of noise (see Eq. (3)) in the framework of Redfield's theory taking into account expressions (12). The correlation time can be estimated using the Debye relationship

$$\tau_c = (4\pi r^3\eta)/(3kT), \tag{14}$$

where τ_c is the rotational correlation time of a spherical particle of radius r in isotropic liquid of viscosity η at temperature T.

The elements of the matrix, $R^{\mathrm d}_{ij,kl}$, of HFI-induced relaxation are calculated using relation (4). The structure of the matrix $\hat{\hat{R}}^{\mathrm d}$ and the expressions for calculating its elements at $(\omega_i\tau_c)^2 \ll 1$, where ω_i denotes all possible energy splittings between the intrinsic energy levels, are presented in Ref. 18. To illustrate the laws of HFI-induced relaxation in a weak magnetic field, we will describe the relaxation of spin states for the limiting cases of strong ($\omega_e \gg a$) and zero ($\omega_e = 0$) magnetic fields.

At $\omega_e \gg a$, the matrix $\hat{\hat{R}}^{\mathrm d}$ in the high-field basis set $|\alpha_e\alpha_n, \alpha_e\alpha_n\rangle$, $|\alpha_e\beta_n, \alpha_e\beta_n\rangle$, $|\beta_e\beta_n, \beta_e\beta_n\rangle$, and $|\beta_e\alpha_n, \beta_e\alpha_n\rangle$ has the form

$$\hat{\hat{R}}^{\mathrm d} = \begin{bmatrix} -3-15\nu & 3 & 12\nu & 3\nu \\ 3 & -3-5\nu & 3\nu & 2\nu \\ 12\nu & 3\nu & -3-15\nu & 3 \\ 3\nu & 2\nu & 3 & -3-5\nu \end{bmatrix} \frac{1}{120}[A:A]\tau_c, \tag{15}$$

where $\nu = 1/(1 + \omega_e^{\,2}\tau_c^{\,2})$. This expression coincides with the published ones.[30,32,33] Expression (9) for $1/T_1$ can be derived with ease by summing the probabilities of all electron spin-flip transitions, namely: $|\alpha_e\alpha_n\rangle \leftrightarrow |\beta_e\alpha_n\rangle$, $|\alpha_e\beta_n\rangle \leftrightarrow |\beta_e\beta_n\rangle$, $|\alpha_e\beta_n\rangle \leftrightarrow |\beta_e\alpha_n\rangle$ and $|\alpha_e\alpha_n\rangle \leftrightarrow |\beta_e\beta_n\rangle$.

At $\omega_e = 0$, the matrix $\hat{\hat{R}}^{\mathrm d}$ in the basis of the states $|1, 1\rangle$, $|2, 2\rangle$, $|3, 3\rangle$, and $|4, 4\rangle$ has the form:

$$\hat{\hat{R}}^{\mathrm d} = \begin{bmatrix} -18 & 6 & 12 & 0 \\ 6 & -12 & 6 & 0 \\ 12 & 6 & -18 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \frac{1}{120}[A:A]\tau_c. \tag{16}$$

The relaxation transition probabilities are plotted *vs.* magnetic field in Fig. 2. It is important that in zero magnetic field the modulation of anisotropic hyperfine interaction causes no relaxation transitions between the proper levels $|1\rangle$—$|3\rangle$ corresponding to the energies $E_{1-3} = a/4$, and the level $|4\rangle$ corresponding to the energy $E_4 = -3a/4$ (see Fig. 1). (Strictly speaking, this approximation is incorrect in zero magnetic field due to degeneration of the $|1\rangle$—$|3\rangle$ levels.) However, it can be shown that in weak magnetic fields ($\omega_e \ll a$) the relaxation transitions are allowed, although their probabilities are low, namely, of the order of $(\omega_e/a)^2$. A similar situation is also observed if a radical is characterized by one high HFI constant and a number of much lower HFI constants (such systems are much more often to occur compared to the radicals characterized by a single HFI constant). For instance, in the case of two HFI constants ($a_1 \gg a_2$) the probabilities of the relaxation transitions analogous to the $|1\rangle$—$|3\rangle \leftrightarrow |4\rangle$ transitions in a single-nucleus system are of the order of $a_2^{\,2}/(\omega_e a_1)$ and thus the conclusions drawn above remain valid.

Earlier,[18] the effect of spin relaxation of the populations of electron-nuclear levels in weak magnetic fields on the magnetic field and spin effects was studied theoretically. According to model calculations, taking into account the magnetic-field dependence of HFI-induced relaxation can significantly affect the magnetic field dependence of the CIDNP and magnetic field effect in the RPs with restricted mobility.[18] Additionally, it was shown that the inclusion of the magnetic field dependence of HFI-induced relaxation is critical to calculations of the CIDEP kinetics in weak magnetic fields. This was experimentally confirmed in the time-resolved X-, S-, and L-band EPR studies of the photolysis of phosphine oxides[10,11] (Fig. 3). The CIDEP kinetics determined by the electron relaxation rate, the reaction rate, and the formation of the CIDEP by the S—T_-mechanism in diffusion RPs were measured in different magnetic fields taking diphenyphosphonyl (a = 36.5 mT) and dimethoxyphosphonyl (a = 69.5 mT) radicals as examples. For both radicals the experimental CIDEP kinetics measured using the low-field spectral line ($|1\rangle \leftrightarrow |4\rangle$) at $\omega_e \approx 0$ were an order of magnitude slower than the CIDEP kinetics measured using the high-field line ($|2\rangle \leftrightarrow |3\rangle$) at $\omega_e \approx 4a/3$. According to calculations with inclusion of all contributions, the electron relaxation rate in weak magnetic field is much lower than the rate of the chemical decay of radicals that makes the major contribution to the CIDEP kinetics. In strong magnetic fields, the CIDEP kinetics is governed by HFI-induced spin relaxation whose rate is much higher than the rate of the chemical decay of radicals (see Fig. 3).

Now we will consider the HFI-induced phase relaxation in weak magnetic fields. Calculations predict different EPR linewidths in weak and strong fields.[18] Although the HFI-induced population relaxation between the states $|1\rangle$ and $|4\rangle$ becomes almost forbidden in weak magnetic fields, the phase relaxation differs from zero in zero magnetic field.[18] From this, in particular, it follows that the phase relaxation time and the population relaxation time due to anisotropic hyperfine interaction become different in weak magnetic fields. This significantly differs from the strong-field case where $T_1 \approx T_2$.

Radical with $S = 1/2$ ($I_1 = I_2 = 1/2$). To draw general conclusions about relaxation due to anisotropic hyperfine interaction, we will consider a radical containing two equivalent nuclei with the spins $I = 1/2$. The spin-Hamiltonian of this system has the form

$$\begin{aligned}\hat{H}_1(t) = {} & \left[\hat{S}_z\hat{I}_{1z} - (1/4)(\hat{S}_+\hat{I}_{1-} + \hat{S}_-\hat{I}_{1+})\right]\cdot F_0^{(1)}(t) + \\ & + (\hat{S}_+\hat{I}_{1z} + \hat{S}_z\hat{I}_{1+})\cdot F_1^{(1)}(t) + (\hat{S}_-\hat{I}_{1z} + \hat{S}_z\hat{I}_{1-})\cdot F_1^{(1)*}(t) + \\ & + (\hat{S}_+\hat{I}_{1+})\cdot F_2^{(1)}(t) + (\hat{S}_-\hat{I}_{1-})\cdot F_2^{(1)*}(t) + \\ & + \left[\hat{S}_z\hat{I}_{2z} - (1/4)(\hat{S}_+\hat{I}_{2-} + \hat{S}_-\hat{I}_{2+})\right]\cdot F_0^{(2)}(t) + \\ & + (\hat{S}_+\hat{I}_{2z} + \hat{S}_z\hat{I}_{2+})\cdot F_1^{(2)}(t) + (\hat{S}_-\hat{I}_{2z} + \hat{S}_z\hat{I}_{2-})\cdot F_1^{(2)*}(t) + \\ & + (\hat{S}_+\hat{I}_{2+})\cdot F_2^{(2)}(t) + (\hat{S}_-\hat{I}_{2-})\cdot F_2^{(2)*}(t), \end{aligned} \tag{17}$$

where the random functions F are given by expressions (11) in such a manner that $F_i^{(1)} = F(\theta_1, \varphi_1)$ and $F_i^{(2)} = F_i(\theta_2, \varphi_2)$. The angles θ_1 (θ_2) and φ_1 (φ_2) are the azimuthal and polar angles in the polar laboratory frame and the subscripts "1" and "2" denote the first and second nuclei, respectively. Additionally, one should take into account that

$$\overline{F_0^{(1)}(t)F_0^{(2)}(t)} = \frac{2}{5}q^2(3\cos^2\theta_0 - 1),$$

$$\begin{aligned}\overline{F_1^{(1)}(t)F_1^{(2)*}(t)} &= \overline{F_1^{(1)*}(t)F_1^{(2)}(t)} = \\ = \overline{F_2^{(1)}(t)F_2^{(2)*}(t)} &= \overline{F_2^{(1)*}(t)F_2^{(2)}(t)} = \\ &= \frac{3}{20}q^2[\cos(2\theta_0) + \cos\theta_0],\end{aligned} \tag{18}$$

where θ_0 is the angle between the radius vectors directed from the electron to each nucleus; all other average values are equal to zero ($\overline{F_i^{(1)}(t)F_j^{(2)*}(t)} = 0$). Thus, spin relaxation of the radical containing two nuclei additionally depends on the structure of this species through the parameter θ_0.

Expressions for the relaxation matrix in strong and zero magnetic fields were reported elsewhere.[19] Despite a large number of the spin states and relaxation transitions, general trends in the behavior of spin relaxation are very similar to the case of the radical containing one magnetic nucleus. In a zero magnetic field the system can occur only in the states characterized by three different energy values, namely, $E'_{1-4} = a/2$, $E'_{5,6} = -a$, and $E'_{7,8} = 0$ (see Fig. 1, *b*). According to calculations, the relaxation transitions between the states $|5'\rangle$, $|6'\rangle$ and $|7'\rangle$, $|8'\rangle$ at frequency $\omega = a$ are forbidden in zero magnetic field, whereas the other two transitions, namely, $|1'\rangle$—$|4'\rangle \leftrightarrow |5'\rangle$, $|6'\rangle$ ($\omega = (3/2)\cdot a$) and $|1'\rangle$—$|4'\rangle \leftrightarrow |7'\rangle$, $|8'\rangle$ ($\omega = a/2$) are allowed. The relaxation transition probabilities show a strong dependence on the magnetic field, as in the case considered above ($S = 1/2$, $I = 1/2$). In Figure 4 the relaxation rates of three transitions ($|1'\rangle \leftrightarrow |6'\rangle$, $|2'\rangle \leftrightarrow |5'\rangle$, and $|3'\rangle \leftrightarrow |4'\rangle$) corresponding to the EPR transitions in strong magnetic field are plotted *vs.* magnetic field. The probability of the $|1'\rangle \leftrightarrow |6'\rangle$ transition corresponding to the low-field EPR line $|\alpha_e\alpha_{1n}\alpha_{2n}\rangle \leftrightarrow |\beta_e\alpha_{1n}\alpha_{2n}\rangle$ at $\omega_e \gg a$, decreases by a factor of six on going to the magnetic field with $\omega_e \ll a$. On the contrary, the relaxation transition $|2'\rangle \leftrightarrow |5'\rangle$ is forbidden in a strong field, being allowed in a weak field. The results of calculations for a particular case $\theta_0 = 120°$ are shown in Fig. 4. However, it should be noted that only the absolute values of the relaxation rates depend on the angle θ_0, whereas the character of the magnetic field dependences remains unchanged.[19] Unlike the radical with $S = 1/2$ ($I = 1/2$), not only transitions between degenerate levels, but also transitions at frequencies $\omega = (3/2)\cdot a$ and $\omega = a/2$ are allowed in zero magnetic field.

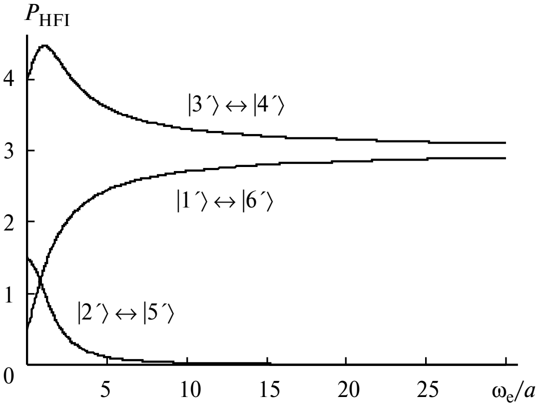

Fig. 4. Probabilities of relaxation transitions $|i\rangle \leftrightarrow |j\rangle$ induced by modulation of anisotropic hyperfine interaction (P_{HFI}) plotted *vs.* magnetic field (in units of ω_e/a) for a radical containing two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) at $\theta_0 = 120°$ and $(\Delta E_i')^2\tau_c^2 \ll 1$.[19]

A particular case $\theta_0 = 0$ corresponds to coincidence of the coordinates of both nuclei. Although this is impossible in practice, the results obtained for relaxation between the states $|1'\rangle$ and $|6'\rangle$ ($I_\Sigma = 1$) are applicable to the radical containing one nucleus ($I = 1$). The relaxation transition probabilities for the radical with $S = 1/2$ ($I = 1$) also strongly depend on the magnetic field, but the relaxation transitions at nonzero frequency $\omega = (3/2)\cdot a$ in zero magnetic field are allowed in contrast to the case of the radical with the spins $S = 1/2$ and $I = 1/2$.

Spin relaxation due to modulation of isotropic hyperfine interaction

Consider spin relaxation due to modulation of isotropic HFI constant. This mechanism is realized when the motions of a radical (*e.g.*, rotation of Me group about the C—C bond in ethyl radical or rotation of Me groups in *tert*-butyl radical) are accompanied by a change in its geometry, which leads to the time dependence of the HFI constants. Because the HFI constants of methyl protons are slightly different,[34] rotation of the Me group about the

C—C bond causes fluctuations of each isotropic HFI constant with time.

If the isotropic HFI constant of a radical varies stochastically, the corresponding Hamiltonian has the form

$$\hat{H}_{\mathrm{HFI}} = \bar{a}\hat{S}\hat{I} + \delta a(t)\hat{S}\hat{I}. \qquad (19)$$

In this case, efficient cross-relaxation transitions are induced (projection of the electron spin remains unchanged, $\Delta m = 0$).

Radical with $S = 1/2$ ($I = 1/2$). The relaxation rate ($1/T_{\mathrm{cr}}$) of a radical containing one magnetic nucleus ($I = 1/2$) in a strong magnetic field ($\omega_e \gg a$) can be calculated from a relationship[35]

$$\frac{1}{T_{\mathrm{cr}}} = \frac{1}{2}\cdot\frac{\overline{\delta a^2}\tau_c}{1 + \omega_e^2\tau_c^2}, \qquad (20)$$

where $\delta a^2 = [a(t) - \bar{a}]^2$. The matrix of spin relaxation due to modulation of isotropic hyperfine interaction in weak magnetic fields was calculated similarly to the case of relaxation due to modulation of anisotropic hyperfine interaction. The Hamiltonian of stochastically modulated isotropic hyperfine interaction in the basis of Eqs (6) can be written as

$$\hat{H}_{\delta a} = \delta a(t)\hat{S}\hat{I} = \\ = \frac{\delta a(t)}{4}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -(1-4C_1C_2) & 0 & 2(C_2^2 - C_1^2) \\ 0 & 0 & 1 & 0 \\ 0 & 2(C_2^2 - C_1^2) & 0 & -(1+4C_1C_2) \end{bmatrix}. \qquad (21)$$

The only relaxation transition $|2\rangle \leftrightarrow |4\rangle$ is allowed in both strong and weak magnetic fields. Its rate is given by

$$\frac{1}{T_{\mathrm{cr}}} = \frac{(C_1^2 - C_2^2)^2}{2}\cdot\frac{\overline{\delta a^2}\tau_c}{1 + (\omega_e^2 + a^2)\tau_c^2}. \qquad (22)$$

At $\omega_e \gg a$, expression (22) is exactly the same as relationship (20), but in a weak magnetic field ($\omega_e \ll a$) the relaxation rate $1/T_{\mathrm{cr}} \to 0$ because $C_1 \approx C_2$.

Thus, when relaxation due to modulation of isotropic hyperfine interaction in a weak magnetic field dominates, it should be correctly taken into account. Because in zero magnetic field one has $1/T_{\mathrm{cr}} = 0$, exact inclusion of relaxation affects calculations of the CIDNP and magnetic field effects in micelles analogously to the case of relaxation due to modulation of anisotropic hyperfine interaction. Additionally, because the EPR-transition $|2\rangle \leftrightarrow |4\rangle$ is allowed in weak magnetic fields provided that the radiofrequency field is applied parallel to external magnetic field, the time-resolved EPR kinetics detected using this transition should also be calculated using correctly included spin relaxation. It seems quite natural to expect that correctly included relaxation between the levels $|2\rangle$ and $|4\rangle$ will strongly influence the kinetics of the time-resolved EPR-transitions $|1\rangle \leftrightarrow |4\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ in weak magnetic field. In this case the kinetics will strongly depend on the spin-level population ratio in the radical.

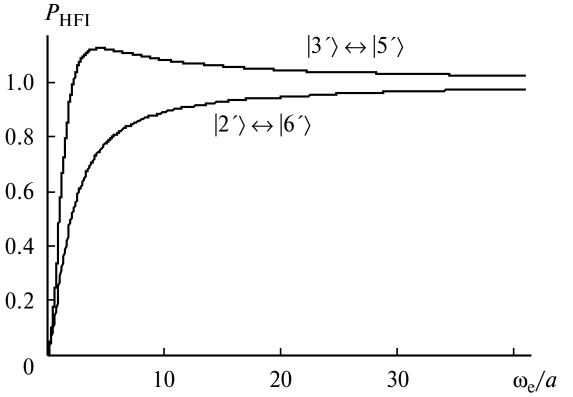

Fig. 5. Probabilities of relaxation transitions $|i\rangle \leftrightarrow |j\rangle$ induced by modulation of isotropic hyperfine interaction (P_{HFI}) plotted *vs.* magnetic field (in units of ω_e/a) for a radical containing two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) at $\delta a_1(t) = \delta a_2(t)$ and $(\Delta E_i')^2\tau_c^2 \ll 1$.[19]

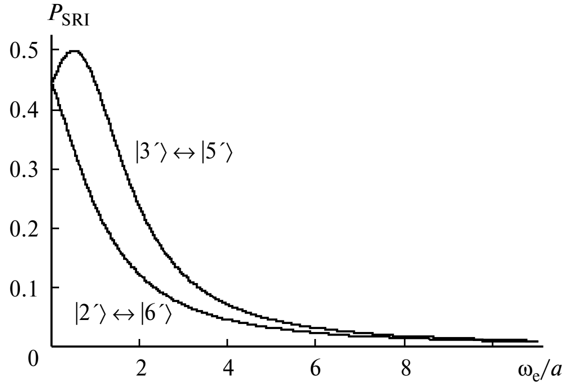

Fig. 6. Probabilities of relaxation transitions $|i\rangle \leftrightarrow |j\rangle$ induced by modulation of spin-rotational interaction (P_{SRI}) plotted *vs.* magnetic field (in units of ω_e/a) for a radical containing two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) at $(\Delta E_i')^2\tau_c^2 \ll 1$.[19]

Radical with $S = 1/2$ ($I_1 = I_2 = 1/2$). For a radical containing two equivalent HFI constants a the spin-Hamiltonian of a stochastically fluctuating isotropic hyperfine interaction has the form

$$\hat{H}_1(t) = \delta a_1(t)\hat{S}\hat{I}_1 + \delta a_2(t)\hat{S}\hat{I}_2 = \\ = \delta a_1(t)\hat{S}_z\hat{I}_{1z} + \frac{\delta a_1(t)}{2}(\hat{S}_+\hat{I}_{1-} + \hat{S}_-\hat{I}_{1+}) + \\ + \delta a_2(t)\hat{S}_z\hat{I}_{2z} + \frac{\delta a_2(t)}{2}(\hat{S}_+\hat{I}_{2-} + \hat{S}_-\hat{I}_{2+}). \qquad (23)$$

According to calculations, six relaxation transitions are allowed in both strong and weak magnetic fields. The terms $(\Delta E_i')^2\tau_c^2$ in expressions[19] for the relaxation transition rates were found to be erroneous. Here we report the corrected form of these relationships

$$
\begin{aligned}
\frac{1}{T_{\mathrm{cr}}^{|2'\rangle\leftrightarrow|6'\rangle}} &= \frac{\left[-\sqrt{2}(C_1')^2 + C_1'C_2' + \sqrt{2}(C_2')^2\right]^2 \overline{(\delta a_1 + \delta a_2)^2}\tau_{\mathrm{c}}}{8 + (18a^2 + 8a\omega_{\mathrm{e}} + 8\omega_{\mathrm{e}}^2)\tau_{\mathrm{c}}^2}, \\
\frac{1}{T_{\mathrm{cr}}^{|3'\rangle\leftrightarrow|5'\rangle}} &= \frac{\left[-\sqrt{2}(C_3')^2 + C_3'C_4' + \sqrt{2}(C_4')^2\right]^2 \overline{(\delta a_1 + \delta a_2)^2}\tau_{\mathrm{c}}}{8 + (18a^2 - 8a\omega_{\mathrm{e}} + 8\omega_{\mathrm{e}}^2)\tau_{\mathrm{c}}^2}, \\
\frac{1}{T_{\mathrm{cr}}^{|2'\rangle\leftrightarrow|7'\rangle}} &= \frac{(C_1' - \sqrt{2}C_2')^2 \overline{(\delta a_1 - \delta a_2)^2}\tau_{\mathrm{c}}}{8 + \left[5a^2 + 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2 - (a + 2\omega_{\mathrm{e}})\sqrt{9a^2 + 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2}\right]\tau_{\mathrm{c}}^2}, \\
\frac{1}{T_{\mathrm{cr}}^{|3'\rangle\leftrightarrow|8'\rangle}} &= \frac{(C_3' - \sqrt{2}C_4')^2 \overline{(\delta a_1 - \delta a_2)^2}\tau_{\mathrm{c}}}{8 + \left[5a^2 - 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2 - (a - 2\omega_{\mathrm{e}})\sqrt{9a^2 - 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2}\right]\tau_{\mathrm{c}}^2}, \\
\frac{1}{T_{\mathrm{cr}}^{|6'\rangle\leftrightarrow|7'\rangle}} &= \frac{(\sqrt{2}C_1' + C_2')^2 \overline{(\delta a_1 - \delta a_2)^2}\tau_{\mathrm{c}}}{8 + \left[5a^2 + 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2 + (a + 2\omega_{\mathrm{e}})\sqrt{9a^2 + 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2}\right]\tau_{\mathrm{c}}^2}, \\
\frac{1}{T_{\mathrm{cr}}^{|5'\rangle\leftrightarrow|8'\rangle}} &= \frac{(\sqrt{2}C_3' + C_4')^2 \overline{(\delta a_1 - \delta a_2)^2}\tau_{\mathrm{c}}}{8 + \left[5a^2 - 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2 + (a - 2\omega_{\mathrm{e}})\sqrt{9a^2 - 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2}\right]\tau_{\mathrm{c}}^2}.
\end{aligned}
\tag{24}
$$

The probabilities of two transitions, $|2'\rangle \leftrightarrow |6'\rangle$ and $|3'\rangle \leftrightarrow |5'\rangle$, are proportional to $\overline{(\delta a_1 + \delta a_2)^2}$, whereas those of the other four transitions are proportional to $\overline{(\delta a_1 - \delta a_2)^2}$. Therefore, spin relaxation strongly depends on the character of intra-radical motions that modulate isotropic hyperfine interaction. If both HFI constants are modulated synchronously ($\delta a_1(t) \equiv \delta a_2(t)$), only two transitions, $|2'\rangle \leftrightarrow |6'\rangle$ and $|3'\rangle \leftrightarrow |5'\rangle$, are allowed in both strong and weak magnetic fields. Asynchronous modulation of both HFI constants requires accurate calculations of the average values, $\overline{(\delta a_1 + \delta a_2)^2}$ and $\overline{(\delta a_1 - \delta a_2)^2}$. For instance, if $\delta a_1 = \delta a_0 \cdot \cos(wt)$ and $\delta a_2 = \delta a_0 \cdot \cos(wt + \psi)$, the average values are given by $\overline{(\delta a_1 + \delta a_2)^2} = \delta a_0^2(1 + \cos\psi)$ and $\overline{(\delta a_1 - \delta a_2)^2} = \delta a_0^2(1 - \cos\psi)$.

Using expressions (8) for the coefficients C_1'—C_4', one can show with ease that only two relaxation transitions with $\omega = a$, namely, $|6'\rangle \leftrightarrow |7'\rangle$ and $|5'\rangle \leftrightarrow |8'\rangle$, are allowed in zero magnetic field. Other possible transitions at frequencies $\omega = a/2$ and $\omega = (3/2) \cdot a$ are forbidden. Note that this result differs from that given above for the case of modulation of anisotropic hyperfine interaction. Therefore, studies of relaxation transitions in zero magnetic field can provide information on the contributions of the modulation of anisotropic and isotropic hyperfine interaction to the overall spin relaxation rate.

Assume that $\delta a_1(t) = \delta a_2(t) \equiv \delta a(t)$. Then, only two transitions, $|2'\rangle \leftrightarrow |6'\rangle$ and $|3'\rangle \leftrightarrow |5'\rangle$, are allowed in any magnetic fields. Figure 5 shows the probabilities of these relaxation transitions plotted *vs.* magnetic field at $(\omega_{\mathrm{e}}^2 + a^2)\tau_{\mathrm{c}}^2 \ll 1$. In zero field, both transition probabilities are zero as in the case of a radical containing one magnetic nucleus. Moreover, it is quite obvious that a similar situation will also be observed for radicals with any number of synchronously modulated equivalent HFI constants (all $\delta a_i(t)$ values are equal to one another). Indeed, the steady-state spin-Hamiltonian of such a radical in zero magnetic field has the form

$$\hat{H}_0 = a\sum_i \hat{S}\hat{I}_i. \tag{25}$$

Because the HFI constant a appears in Eq. (25) only as a common multiplier, the eigenfunctions (wave functions) of this Hamiltonian remain unchanged upon modulation of a. In other words, the perturbation has the diagonal form in the basis of the eigenfunctions of the steady-state Hamiltonian and therefore no relaxation transitions will be induced. Therefore, experimental studies of the spin relaxation due to modulation of isotropic hyperfine interaction in weak and zero magnetic fields can provide information on the character of intra-radical motions. For instance, the type of the motion responsible for relaxation in *tert*-butyl radical (inversion of carbon or rotation of Me groups[36,37]) has not been established so far.

Modulation is synchronous in the former and asynchronous in the latter case.

Summing up, note that in the case of synchronous modulation all conclusions drawn for radicals with more than one equivalent nuclei ($I = 1/2$) are also valid for a radical containing one magnetic nucleus and an arbitrary spin ($I > 1/2$). In particular, relationships (24) for the states $|1'\rangle$—$|6'\rangle$ ($I_\Sigma = 1$) are applicable to a radical with $S = 1/2$ ($I = 1$).

Spin relaxation due to spin-rotational interaction

Gas-phase studies of radicals showed that the magnetic moment of the unpaired electron interacts with the total angular momentum of the radical. In liquids, the angular momentum fluctuates because of collisions with other species, thus leading to spin relaxation. The main relaxation mechanism of small alkyl and acyl radicals (*e.g.*, $^{\bullet}CH_3$ and $HC(O)^{\bullet}$) in nonviscous fluids is spin-rotational relaxation.[38,39]

For most radicals the components of the tensor of spin-rotational interaction are unknown, but they can be estimated using the components of the *g*-tensor.[40] For instance, if the *g*-tensor is axially symmetric, the time of relaxation due to spin-rotational interaction in a strong magnetic field is given by

$$\frac{1}{T_1} \approx \frac{1}{12\pi r^3}\left(\Delta g_{\parallel}^2 + 2\Delta g_{\perp}^2\right)\frac{kT}{\eta}, \qquad (26)$$

where $\Delta g_i = g_i - 2.0023$ ($i = \parallel, \perp$), r is the radius of the radical, k is the Boltzmann constant, T is temperature, and η is the viscosity of the solution.

To consider spin-rotational relaxation in weak magnetic fields, we will carry out calculations similar to those of modulation of anisotropic and isotropic hyperfine interaction. It should be noted that collisions of radicals with the surrounding species cause modulation of the isotropic and anisotropic components of the spin-rotational interaction with the same correlation time. Therefore, it is sufficient to allow for isotropic spin-rotational interaction because the inclusion of anisotropy will only introduce minor corrections.

Radical with $S = 1/2$ ($I = 1/2$). The Hamiltonian of isotropic spin-rotational interaction written in the basis of Eqs (6) has the form

$$\hat{H} = C\hat{S}\hat{j}(t) =$$

$$= C \times \begin{bmatrix} \frac{\hat{j}_z}{2} & \frac{C_2\hat{j}_-}{2} & 0 & -\frac{C_1\hat{j}_-}{2} \\ \frac{C_2\hat{j}_+}{2} & \frac{(C_1^2 - C_2^2)\hat{j}_z}{2} & \frac{C_1\hat{j}_-}{2} & C_1C_2\hat{j}_z \\ 0 & \frac{C_1\hat{j}_+}{2} & -\frac{\hat{j}_z}{2} & \frac{C_2\hat{j}_+}{2} \\ -\frac{C_1\hat{j}_+}{2} & C_1C_2\hat{j}_z & \frac{C_2\hat{j}_-}{2} & \frac{(C_2^2 - C_1^2)\hat{j}_z}{2} \end{bmatrix}, \qquad (27)$$

where C is the isotropic spin-rotational coupling constant and $\hat{j}(t)$ is the angular momentum operator for the radical. The spectral density of spin-rotational interaction is given by expression (3). The correlation time of the angular momentum fluctuations is

$$\tau_j = I/(8\pi r^3\eta), \qquad (28)$$

where I is the isotropic momentum of inertia. Then one gets

$$\overline{\hat{j}_z^2} = \frac{1}{2}\overline{\hat{j}_+\hat{j}_-} = \frac{1}{2}\overline{\hat{j}_-\hat{j}_+} = I \cdot kT. \qquad (29)$$

Because the parameter τ_j is similar to the inverse frequencies of molecular collisions in liquids (10^{-13}—10^{-14} s^{-1}) and $\omega_e{}^2\tau_j{}^2$, $a^2\tau_j{}^2 \ll 1$ in magnetic fields 0—300 mT, the last-mentioned two quantities can be neglected if the HFI constants lie within a conventional range. Then one can calculate the elements of the relaxation matrix $R_{ij,kl}$ for zero magnetic field using expressions (4) and (27)—(29). The expressions for the matrix elements $R_{ij,kl}$ related to the probabilities of transitions between the spin levels of the radical are as follows:

$$\begin{aligned} P_{1\leftrightarrow 2} &= R_{11,22} = C^2C_2{}^2 \cdot IkT \cdot \tau_j = R_{33,44} = P_{3\leftrightarrow 4}, \\ P_{1\leftrightarrow 3} &= R_{11,33} = R_{33,11} = 0, \\ P_{1\leftrightarrow 4} &= R_{11,44} = C^2C_1{}^2 \cdot IkT \cdot \tau_j = R_{22,33} = P_{2\leftrightarrow 3}, \\ P_{2\leftrightarrow 4} &= R_{22,44} = 2C^2C_1{}^2C_2{}^2 \cdot IkT \cdot \tau_j. \end{aligned} \qquad (30)$$

The number of the allowed transitions is two ($|1\rangle \leftrightarrow |4\rangle$ and $|2\rangle \leftrightarrow |3\rangle$) in a strong and five ($|1\rangle \leftrightarrow |4\rangle$, $|2\rangle \leftrightarrow |3\rangle$, $|1\rangle \leftrightarrow |2\rangle$, $|3\rangle \leftrightarrow |4\rangle$ and $|2\rangle \leftrightarrow |4\rangle$) in a weak magnetic field.

For the spin levels $|1\rangle$ and $|3\rangle$ the sum of the transition probabilities is independent of magnetic field

$$P_{1\leftrightarrow 2} + P_{1\leftrightarrow 3} + P_{1\leftrightarrow 4} = P_{3\leftrightarrow 1} + P_{3\leftrightarrow 2} + P_{3\leftrightarrow 4} = C^2IkT\tau_j.$$

Therefore, in a weak magnetic field the overall rate of relaxation between each of these levels and other levels remains unchanged, being redistributed.

In zero magnetic field the levels $|1\rangle$—$|3\rangle$ are degenerate. From relationship (30) it follows that the total probability of the relaxation transitions $|1\rangle$—$|3\rangle \leftrightarrow |4\rangle$ in zero field is 1.5 times higher than the probability of the relaxation transition $|1\rangle \leftrightarrow |4\rangle$ in a strong field. This is due to the fact that yet another transition, $|2\rangle \leftrightarrow |4\rangle$, becomes allowed in a weak magnetic field. The probability of this transition in zero magnetic field equals the probability of each of the two transitions $|1\rangle \leftrightarrow |4\rangle$ and $|3\rangle \leftrightarrow |4\rangle$. Note that in strong magnetic fields the $|2\rangle \leftrightarrow |4\rangle$ transition is

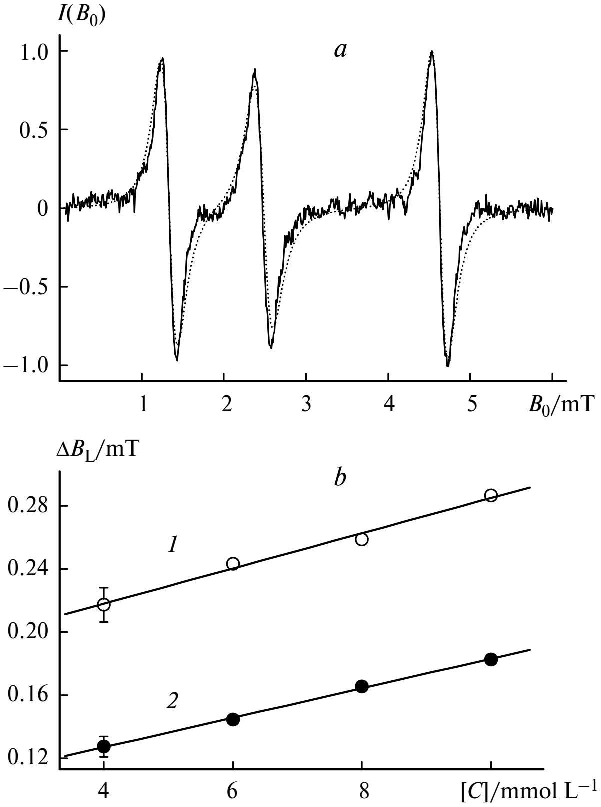

Fig. 7. *a*. Experimental (solid line) and simulated (dotted line) EPR spectra of radical TEMPO in a weak magnetic field (slow exchange; $[C] = 2$ mmol L^{-1}, $B_1 = 0.02$ mT). *b*. Half-width at half-height (ΔB_L) of the line corresponding to the $|3'\rangle \leftrightarrow |4'\rangle$ transition plotted *vs*. TEMPO concentration: experiment (open and solid circles) and simulation (lines) in a weak (94 MHz) (*1*) and strong (10 GHz) (*2*) magnetic field.[20] Here and in Fig. 8 B_0 is the external magnetic field strength and I is the signal intensity.

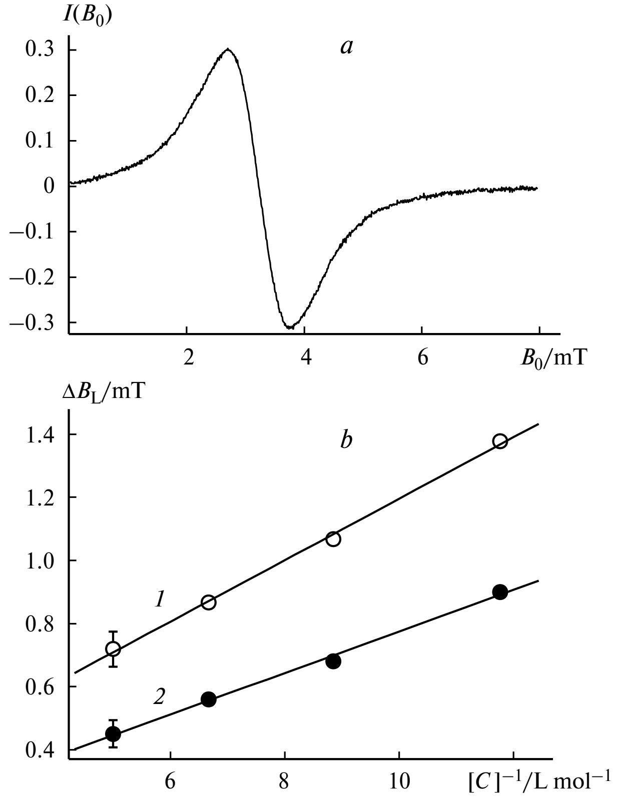

Fig. 8. *a*. Experimental and simulated EPR spectra of radical TEMPO in a weak magnetic field (fast exchange, $[C] = 150$ mmol L^{-1}, $B_1 = 0.02$ mT). *b*. Half-width at half-height (ΔB_L) of the exchange-narrowed line plotted *vs*. TEMPO concentration: experiment (open and solid circles) and simulation (lines) in a weak (94 MHz) (*1*) and strong (10 GHz) (*2*) magnetic field.[20]

forbidden. This should be kept in mind when calculating the CIDEP kinetics in perpendicular and parallel radiofrequency fields (especially in the latter case) and when calculating the absolute values of the CIDNP and magnetic field effects in micelles.

Radical with spin $S = 1/2$ ($I_1 = I_2 = 1/2$). If a radical contains one magnetic nucleus or two equivalent nuclei, the nuclear spins are not involved in spin-rotational interaction at all and calculations are reduced to treatment of the Hamiltonian $\hat{H}_1(t) = C\hat{S}\hat{j}(t)$ in the basis given by Eqs (8). The probabilities of the relaxation transitions between the spin states $|7'\rangle$ and $|8'\rangle$ in any magnetic field are $P_{7'\leftrightarrow 8'} = C^2 IkT\tau_j$, whereas other transitions involving these states are forbidden. The probabilities of the transitions between six other levels in the basis $|1',1'\rangle$, $|2',2'\rangle$, ..., $|6',6'\rangle$ are given by the matrix[19] $\hat{R}^{\rm sr}$

$$\hat{R}^{\rm sr} = \begin{bmatrix} -1 & (C_2')^2 & 0 & 0 & 0 & (C_1')^2 \\ (C_2')^2 & -1-2(C_1')^2(C_2')^2 & (C_1')^2(C_3')^2 & 0 & (C_1')^2(C_4')^2 & 2(C_1')^2(C_2')^2 \\ 0 & (C_1')^2(C_3')^2 & -1-2(C_3')^2(C_4')^2 & (C_4')^2 & 2(C_3')^2(C_4')^2 & (C_2')^2(C_3')^2 \\ 0 & 0 & (C_4')^2 & -1 & (C_3')^2 & 0 \\ 0 & (C_1')^2(C_4')^2 & 2(C_3')^2(C_4')^2 & (C_3')^2 & -1-2(C_3')^2(C_4')^2 & (C_2')^2(C_4')^2 \\ (C_1')^2 & 2(C_1')^2(C_2')^2 & (C_2')^2(C_3')^2 & 0 & (C_2')^2(C_4')^2 & -1-2(C_1')^2(C_2')^2 \end{bmatrix} C^2 IkT\tau_j. \quad (31)$$

Conclusions drawn upon analysis of the matrix (31) in the limiting cases of zero and strong magnetic fields are similar to those known for the radical containing one magnetic nucleus. In weak magnetic fields the $|2'\rangle \leftrightarrow |6'\rangle$ and $|3'\rangle \leftrightarrow |5'\rangle$ transitions become allowed, whereas the probabilities of other transitions are redistributed (Fig. 6).

Therefore, one can conclude that the rate of spin relaxation due to spin-rotational interaction increases in weak magnetic fields. A physical explanation for this phenomenon is as follows: the effect of the fluctuating spin-rotational interaction on the spin system is analogous to the effect of oscillating magnetic field described by the Hamiltonian $\hat{H}_1(t) = \hat{S}\hat{B}_1(t)$ ($\hat{B}_1(t)$ is the operator of the alternating magnetic field). It is well known that in strong magnetic fields ($\vec{B}_0$) the EPR-transitions are only allowed at $\vec{B}_1 \perp \vec{B}_0$, whereas in weak fields transitions at $\vec{B}_1 \| \vec{B}_0$ are also allowed.

Spin relaxation induced by electron spin exchange

Electron spin exchange (ESE) between radicals in liquids can contribute largely to the relaxation rate if the rate constant for radical recombination is no higher than the diffusion constant.[33,41] Usually, spin exchange causes broadening of c.w. EPR lines of stable radicals in solutions. As the concentration of radicals increases, the spectral components are averaged (this is called "exchange narrowing"). This is the case of fast exchange corresponding to the situation where the spin-exchange rate exceeds the Larmor frequency difference between the spectral components. Spin exchange at low radical concentrations is termed slow and only causes broadening of spectral lines. Since the concentration of radicals in the experimental studies on the magnetic and spin effects in weak magnetic fields can be high, the contribution of spin exchange to relaxation should be taken into account. In particular, the local concentration of radicals in the experiments on radiolysis and photolysis in the solutions characterized by high optical density can be rather high. Additionally, the ESE-induced line broadening in c.w. EPR spectra recorded in weak magnetic fields can be large similarly to the situation in strong magnetic fields. This gives an impetus to ESE studies in weak magnetic fields.

In terms of the theory of stochastic processes, spin exchange is a "collisional noise". Here, knowledge of the correlation function basic to the Redfield theory is insufficient. This theory is inapplicable even in the case of slow exchange, because collisions between radicals cause significant changes in their stationary states

$$\hat{H}_1(t) = J(t)\hat{S}_1\hat{S}_2 \gg \hat{H}_0,$$

where $J(t)$ is the exchange interaction constant. In this connection, treatment of ESE-induced relaxation requires not only calculations of the probabilities of relaxation transitions between stationary states, but also the inclusion of the changes in these states. Earlier,[20] ESE-induced relaxation in weak magnetic fields was theoretically treated by solving the Liouville equation. ESE-induced relaxation was calculated following a known approach.[42] In the binary approximation, the kinetic equation for the single-particle density matrix of radicals has the form[41,43]

$$\frac{\partial \rho_{\mathrm{A}}}{\partial t} = i\left(\hat{\hat{L}} + i\hat{\hat{R}}\right)\rho_{\mathrm{A}} - [C]\frac{v}{\tau_{\mathrm{p}}}\mathrm{Tr}_{\mathrm{A}'}\left(\hat{\hat{K}}^{\mathrm{AA}'}\rho_{\mathrm{A}}\cdot\rho_{\mathrm{A}'}\right), \tag{32}$$

where ρ_{A} is the density matrix of radical A; $\rho_{\mathrm{A}'}$ is the density matrix of the partner radical A′; $\hat{\hat{L}}$ is the Liouvillian describing the spin-state dynamics of the radicals between collisions; the term $\hat{\hat{R}}$ describes relaxation of the radical spin states; the Liouville matrix $\hat{\hat{K}}^{\mathrm{AA}'}$ describes the change in the radical spin states in the course of collisions; and $[C]$ is the concentration of radicals. For simplicity, the exchange interaction was considered constant in a narrow spatial region corresponding to rather large overlap between the orbitals of the unpaired electrons and equal to zero outside of this region. The volume of this region is denoted as v and the overall residence time of radicals in this region is denoted as τ_{p}.[41] The matrix $\hat{\hat{K}}^{\mathrm{AA}'}$ in the singlet-triplet (ST) basis of a pair of interacting radicals has only the following nonzero elements[41]:

$$\begin{aligned}(\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{ST_0,ST_0}} &= (\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{T_0S,T_0S}} = (\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{ST_+,ST_+}} = \\ &= (\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{T_+S,T_+S}} = (\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{ST_-,ST_-}} = (\hat{\hat{K}}^{\mathrm{AA}'})_{\mathrm{T_-S,T_-S}} = \\ &= iK_J\tau_{\mathrm{p}}/(1 + iK_J\tau_{\mathrm{p}}) \equiv p,\end{aligned} \tag{33}$$

where K_J is the exchange interaction constant expressed in frequency units and the parameter p characterizes the efficiency of spin exchange. Using a commonly accepted terminology, exchange is called strong at $K_J\tau_{\mathrm{p}} \gg 1$ and weak at $K_J\tau_{\mathrm{p}} \ll 1$.[41]

The convolution over the states of the partner radical A′ is given by

$$\begin{aligned}\mathrm{Tr}_{\mathrm{A}'}\left(\hat{\hat{K}}^{\mathrm{AA}'}\rho_{\mathrm{A}}\cdot\rho_{\mathrm{A}'}\right)_{nm} &= \sum_{n_pn_q} K^{\mathrm{AA}'}_{n_in_j,n_pn_q}(\rho_{\mathrm{A}}\cdot\rho_{\mathrm{A}'})_{n_pn_q} = \\ &= \sum_{lm}(\hat{\hat{R}}_{\mathrm{p}})_{nk,lm}(\rho_{lm}).\end{aligned} \tag{34}$$

In the text below we will consider the ESE-induced phase relaxation.

Radical with $S = 1/2$ ($I = 1/2$). The phase relaxation probabilities calculated for this radical in the case of strong exchange $(\hat{\hat{R}}_{\mathrm{p}})_{ij,ij} \equiv P^{\mathrm{ph}}_{i\leftrightarrow j}$ are given by:

$$
\begin{aligned}
&P^{\mathrm{ph}}_{1\leftrightarrow 2} = -C_2^2\,\frac{v[C]}{4\tau_{\mathrm{p}}}\,\mathrm{Re}p = P^{\mathrm{ph}}_{3\leftrightarrow 4},\\
&P^{\mathrm{ph}}_{1\leftrightarrow 3} = 0,\\
&P^{\mathrm{ph}}_{1\leftrightarrow 4} = -C_1^2\,\frac{v[C]}{4\tau_{\mathrm{p}}}\,\mathrm{Re}p = P^{\mathrm{ph}}_{2\leftrightarrow 3},\\
&P^{\mathrm{ph}}_{2\leftrightarrow 4} = 0.
\end{aligned}
\tag{35}
$$

As can be seen, the magnetic field dependence of the transition probabilities is expressed through the mixing coefficients C_i, being similar to the case of longitudinal relaxation due to spin-rotational interaction and calculated in the framework of Redfield´s theory (see Eq. (31)). The difference consists in the absence of the relaxation transition $|2\rangle \leftrightarrow |4\rangle$.

The EPR spectrum in the frequency domain was calculated as follows[20]:

$$
Q = -\omega_{\mathrm{e}}\omega_1[C][C_2\mathrm{Im}(\rho_{12} + \rho_{34}) + C_1\mathrm{Im}(\rho_{14} + \rho_{23})], \tag{36}
$$

where ω_1 is the frequency of the oscillating magnetic field and the density matrix elements can be found from the Liouville equation (32) with allowance for Eq. (34).

Radical with $S = 1/2$ ($I = 1$). In this case the phase relaxation probabilities under strong exchange can be calculated using the following expressions

$$
\begin{aligned}
&P^{\mathrm{ph}}_{1'\leftrightarrow 2'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_2')^2\mathrm{Re}p, \qquad P^{\mathrm{ph}}_{1'\leftrightarrow 6'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_1')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{2'\leftrightarrow 3'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_1')^2(C_3')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{2'\leftrightarrow 5'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_1')^2(C_4')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{3'\leftrightarrow 4'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_4')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{3'\leftrightarrow 6'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_2')^2(C_3')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{4'\leftrightarrow 5'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_3')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{5'\leftrightarrow 6'} = -\frac{v[C]}{3\tau_{\mathrm{p}}}(C_2')^2(C_4')^2\mathrm{Re}p,\\
&P^{\mathrm{ph}}_{2'\leftrightarrow 6'} = 0, \qquad P^{\mathrm{ph}}_{3'\leftrightarrow 5'} = 0.
\end{aligned}
\tag{37}
$$

Figure 7, *a* shows the experimental EPR spectrum of stable nitroxyl radical TEMPO in CCl_4 in weak magnetic fields. Measurements were carried out at a resonance frequency of 94 MHz, which allowed all three EPR transitions to be observed ($|1'\rangle \leftrightarrow |6'\rangle$ at 1.33 mT, $|2'\rangle \leftrightarrow |5'\rangle$ at 2.48 mT, and $|3'\rangle \leftrightarrow |4'\rangle$ at 4.63 mT). The line corresponding to the $|2'\rangle \leftrightarrow |5'\rangle$ transition is much broader (by 0.02 mT) than the lines corresponding to the $|1'\rangle \leftrightarrow |6'\rangle$ and $|3'\rangle \leftrightarrow |4'\rangle$ transitions.

An increase in the TEMPO concentration causes broadening of the EPR line due to ESE. The half-width of the EPR line is plotted *vs.* TEMPO concentration in Fig. 7, *b* (the case of slow exchange). For comparison, we also present here a similar plot for the case of strong magnetic field. The half-width at half-height of the Lorentzian line corresponding to the $|3'\rangle \leftrightarrow |4'\rangle$ transition is denoted as ΔB_{L}. According to relationships (37), in weak magnetic field the rate of phase relaxation due to ESE should be by a factor of $(C_4')^2$ lower than in strong magnetic field at the same concentration of radicals. The experimental concentration dependences have equal slopes due to the fact that the difference between the slopes caused by the ESE-induced relaxation is compensated by the effect of recording field-sweep EPR spectra in weak magnetic fields. This can be substantiated with ease analytically. For the $|3'\rangle \leftrightarrow |4'\rangle$ transition the coefficient of proportionality (κ) between the resonance frequency $\Delta E = E_3 - E_4$ and the magnetic field in frequency units $\omega_{\mathrm{e}} = \gamma B_0$ (γ is the magnetogyric ratio) is calculated using expressions (8)

$$
\kappa(\omega_{\mathrm{e}}) = \frac{\mathrm{d}\Delta E}{\mathrm{d}\omega_{\mathrm{e}}} = \frac{1}{2}\left(1 - \frac{a - 2\omega_{\mathrm{e}}}{\sqrt{9a^2 - 4a\omega_{\mathrm{e}} + 4\omega_{\mathrm{e}}^2}}\right) = (C_4')^2. \tag{38}
$$

Therefore, variation of the magnetic field causes a slower frequency change (by a factor of $(C_4')^2$) and the EPR line is broadened by a factor of $(C_4')^2$, which compensates the predicted line narrowing by a factor of $(C_4')^2$ due to the magnetic field dependence of the relaxation transition probability (see Eqs (37)). Thus, experimental data are in excellent agreement with the predicted magnetic field dependence of the relaxation rate. The exchange-narrowed EPR spectrum of radical TEMPO in weak magnetic field is shown in Fig. 8, *a*. In contrast to the case of strong magnetic field (where position of the narrowed line coincides with the position of the central line in the exchange-broadened spectrum) in weak field this line is shifted by 3.15 mT toward the strong magnetic field region relative to the central line (transition $|2'\rangle \leftrightarrow |5'\rangle$).

The concentration dependences of the half-widths at half-height of the exchange-narrowed lines in weak and strong magnetic fields are shown in Fig. 8, *b*. In the former case the slope is 1.5 times greater. As in the case of slow exchange, in weak fields the lines are broader than in strong fields at the same radical concentration. Simulation was carried out using the analytical expressions derived for the radical with $S = 1/2$. The HFI constant was chosen in such a manner that the second moment of the EPR spectrum be equal to the second moment of the EPR spectrum of TEMPO radical. According to calculations, the slopes of the concentration dependences in strong and weak (at a resonance frequency of 94 MHz) magnetic fields should differ by a factor of 1.34, which is in reasonable agreement with the experimental data.[20]

Note that as in the case of spin-rotational relaxation (see above) ESE in strong magnetic fields induces only the electron spin-flip transitions, but in weak magnetic fields relaxation becomes electron-nuclear in character. This salient feature of ESE-induced relaxation should be taken into account when analyzing the magnetic field dependences of the CIDNP in the reactions involving radical ions and stable nitroxyl radicals in weak magnetic fields,[44] because the effect of this feature on the kinetics of spin polarization and on the EPR spectra is mainly determined by the initial spin-level populations in radicals.[20]

* * *

Thus, we theoretically and experimentally showed that the spin relaxation rates of radicals in liquids show a strong dependence on the magnetic field. The behavior of radicals in weak magnetic fields (at most equal to the HFI constants of the radicals) is expected to show some features, *e.g.*, the appearance of new allowed relaxation transitions and the changes in the probabilities of the transitions allowed in strong fields. These conclusions were drawn by analyzing the main relaxation mechanisms of radicals in weak magnetic fields taking simple radicals containing one magnetic nucleus ($I = 1/2, 1$) and two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) as examples; however, general trends are also valid for any radicals.

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