

More about Spin-Spin Dipole-Dipole Interactions Contributions to the Shapes of Nitroxide EPR Spectra in Solution

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More about Spin-Spin Dipole-Dipole Interactions Contributions to the Shapes of Nitroxide EPR Spectra in Solution

M.M. Bakirov, I.T. Khairutdinov, R.B. Zaripov, K.M. Salikhov

Abstract

In this work, experimental data were obtained confirming unusual contribution of dipole-dipole interaction between unpaired electron of the radical and its own ^{15}N nucleus (DD_1) to EPR resonance line shapes in solutions of ^{15}N -Tempol radicals. One might expect that the random modulation of DD_1 by rotational diffusion leads to spectral diffusion of the resonance frequencies: DD_1 randomly flips the orientation of the nitrogen nuclear spin, causing the electron spin to randomly change frequencies and jump from one hyperfine component to another. Spectral diffusion is expected. This is an expected process in the case of the interaction of a nuclear spin with the lattice or with electrons in other radicals, or in the case of spin diffusion within the nuclear spin system. In this case, the electron spin facilitates flipping of the nuclear spin, and resonant frequency of that electron changes. As Marsh demonstrated, the elementary process is not limited merely to the nuclear spin flip. In addition to the frequency shift, spin coherence of unpaired electron acquires an extra phase of π . It should be noted that a similar effect was previously predicted by Salikhov and experimentally confirmed in studies by Bales and colleagues regarding paramagnetic relaxation associated with the dipole-dipole interaction of unpaired electrons in dilute solutions of nitroxide radicals (DD_2). In this work, we present experimental data demonstrating negative interference between contributions of DD_1 and DD_2 paramagnetic relaxation mechanisms, on the one hand, and paramagnetic relaxation caused by spin exchange during random bimolecular collisions of radicals, on the other. Spin exchange leads to spectral diffusion without π -phase jumps of spin coherence.

1. Introduction

Dipole-dipole interaction plays a significant role in the dynamics and paramagnetic relaxation of unpaired electron spins in paramagnetic species and magnetic nuclei in many cases [1]. This article focuses on the dipole-dipole (DD) interaction contribution to the paramagnetic relaxation of unpaired electrons of stable nitroxide radicals in dilute and low viscosity solutions. This topic includes the interaction between electrons of different radicals (DD_2) and the interaction of an unpaired electron with the magnetic nucleus of the radical, i.e. anisotropic hyperfine interaction (DD_1). In the case of a nitroxyl radical, it is the nitrogen nuclear spin.

It should be noted that one obtain information on the paramagnetic relaxation kinetics of unpaired radical electrons using Electron Paramagnetic Resonance (EPR) methods. This involves the analysis of the lineshape of continuous wave EPR spectra and/or the decay kinetics of observed signals in pulsed EPR methods [2, 3].

Interest in the study of the paramagnetic relaxation of unpaired electron spins in nitroxide radicals solutions stems from the fact that stable radicals are frequently used as spin probes to measure the frequency of bimolecular collisions in complex biological systems and porous structures [2, 4, 5]. One of the effective mechanisms of paramagnetic relaxation of probe spins in such systems is the bimolecular process of spin exchange. Spin exchange involves a change in the spin state of a radical's unpaired electron, driven by Heisenberg spin exchange (HSE) interaction during random collisions between two radicals. Spin exchange causes both the relaxation of the spin precession phase (decoherence of each individual spin) and spin coherence transfer from the collision partner (a "transfer" of quantum coherence occurs).

The coherence transfer process contributions are HSE and DD_2 . Both interactions contribute simultaneously to paramagnetic relaxation. Therefore, the determination of HSE contribution to paramagnetic relaxation for the purpose of calculating the bimolecular collision frequency requires confirmation of concentration-dependent DD_2 contribution to the shape of the observed EPR spectra.

In the widely accepted and applied paradigm set forth in all textbooks, for example in [1, Equation (VIII.89)] it is asserted that DD_2 leads only to the relaxation of the spin precession phase (i.e., to the decoherence of each individual spin). It is assumed that DD_2 does not produce the transfer of quantum coherence from an interaction partner (like in classical mechanics, would amount to abandoning Newton's third law).

Over the 80 years of EPR spectroscopy's development, fundamental changes have occurred in theoretical description of electron spin paramagnetic relaxation in liquids. These changes and the emergence of a new paradigm of spin exchange, that are described in detail in works [4, 6–15]. The theory of paramagnetic spin relaxation in liquids and gases was revised by K.M. Salikhov in [3]. It has been shown (see [3], Chapter 4) that DD_2 actually induces not only spin decoherence but also the transfer of quantum coherence from the interaction partner (!). It turns out that the two mechanisms of paramagnetic spin relaxation, that are HSE and DD_2 , both contribute to the decoherence of each individual spin and to coherence transfer from the interaction partner (the coherence "recoil effect" during the interaction). The spin decoherence effect and the quantum coherence recoil effect are described in the kinetic equations for the transverse component of spin magnetization by corresponding coefficients. One might think that the total contribution of these two mechanisms to paramagnetic relaxation would be described simply by the sum of the pairs of

corresponding coefficients. However, the result of the theory turned out to be completely unexpected. Indeed, in the case of spin decoherence, these mechanisms “interfere” constructively and the decoherence rate coefficients for unpaired electron spins resulting from these two mechanisms are additive. And in the case spin coherence transfer these two electron spin relaxation mechanisms “interfere” destructively. The spin coherence transfer rate coefficients due to HSE and DD₂ are subtracted! This result can be interpreted as follows: as a result of dipole-dipole interaction, the transfer of spin coherence from the interaction partner occurs with a phase shift of π . For spin $\frac{1}{2}$, coherence is determined by the off-diagonal matrix element of the density matrix, that is ρ_{12} . Dipole-dipole interaction leads that spin will acquire quantum coherence from its interaction partner with a phase shift of $\exp(i\pi) \rho_{12}$. It should be particular noted that coherence transfer from an interaction partner caused by HSE during random bimolecular collisions of paramagnetic particles occurs without altering the phase of the collision partner's quantum coherence [2, 4]. The specific manifestations of DD₂ to the shape of EPR spectra were analyzed in [6].

For illustration let's consider radicals whose EPR spectrum exhibits two resonance lines, A and B, that due to hyperfine interaction with a single magnetic nucleus with spin $I = 1/2$. Let $\{C_A, C_B\}$ and $\{M_A^-, M_B^-\}$ denote the concentrations and transverse magnetizations of electron spins in the respective radical sub-ensembles with nuclear spin projections of $+1/2$ (A) and $-1/2$ (B). In this case, $C_A = C_B = C/2$, where C is the radical concentration in the solution. For nitroxide radicals, HSE can be considered equivalent; that is, the various elementary processes of decoherence (W_{sd}) and coherence transfer (V_{sct}) can be described by a single spin-exchange rate constant, K_{ex} [4, 8].

For the model of a radical with a single magnetic nucleus of spin $I=1/2$ the kinetics of paramagnetic relaxation of transverse magnetization induced by HSE and DD₂ are described by equations [9]:

$$\begin{aligned} \frac{\partial M_A^-}{\partial t} &= -W_{sd} M_A^- + V_{sct} M_B^- \\ \frac{\partial M_B^-}{\partial t} &= V_{sct} M_A^- - W_{sd} M_B^- \end{aligned} \quad (1)$$

where

$$\begin{aligned} W_{sd} &= \frac{1}{2} K_{ex} C + K_{dd,sd} C \\ V_{sct} &= \frac{1}{2} K_{ex} C - K_{dd,sct} C \end{aligned} \quad (2)$$

here $K_{dd,sd}$ и $K_{dd,sct}$ – spin dephasing and spin coherence transfer DD₂ rate constants, respectively.

Equations (1,2) show that the two interaction contributions to spin dephasing (decoherence) are additive (W_{sd}), whereas the contributions to spin coherence transfer (coherence relay) are subtractive (V_{sct}). The term $K_{dd,sct}C$ is omitted in the common paradigm underlying methods for determining the rate of bimolecular collisions between molecules. These methods include EPR spectroscopy and the spin probe method.

It should be noted that spin exchange can be viewed as an example of spectral diffusion: during the brief interval of a bimolecular collision, the HSE causes a virtually instantaneous change in the electron spin precession frequency. Following the frequency change, the spin continues its precession, starting with the phase it possessed at the moment of the sudden jump in the precession frequency [3, 4].

Here, we wish to draw attention to another mechanism of paramagnetic relaxation of the unpaired electron spin of a radical. This mechanism is not associated with interaction between radicals and therefore does not depend on spin concentration. It arises from the dipole-dipole interaction (DD_1) between the electron spin and the nuclear spin of the same radical. However, it also contributes to coherence transfer from one transition between two electron spin states to another transition between two quantum states of the same radical. Thus, spectral diffusion of the electron spin appears, that caused by random changes in the orientation of the nuclear spin.

Isotropic hyperfine interaction (HFI) splits the EPR spectrum into components corresponding to a specific projection of the nuclear spin. For example, in the case of a ^{15}N nitroxide radical there are two EPR lines. Under typical EPR experimental conditions, the difference between the Zeeman frequencies of electron spins and radical nuclear spins is large compared to the magnitude of the isotropic hyperfine interaction constant A (expressed in frequency units). Therefore, HFI term in the spin Hamiltonian can be written in the following form:

$$H_{HFI} = AS_zI_z, \quad (3)$$

here S_z и I_z – operators of the z-projections of electron and nuclear spin, A – isotropic HFI constant.

Random nuclear spin flips cause the resonance frequency of the unpaired electron spin transition to change randomly by an amount A . As a result, we obtain a mechanism of spectral diffusion induced by random changes in the nuclear spin projection. Such a mechanism of spectral diffusion was considered in the works [16, 17]. It is currently widely held that, in this situation, the relaxation of the transverse magnetization of electron spins can be described using

the spectral diffusion model, driven by random fluctuations in the projection of the nuclear spin onto the quantization axis. Any spectral diffusion implies the occurrence of coherence transfer; therefore, a concentration-independent term equal to $\frac{1}{2T_{1n}}$ is added to the total coherence transfer rate (2). Parameter T_{1n} is the nuclear spin-lattice relaxation time. This relaxation mechanism will contribute to the kinetic equations in the same way as the spin-exchange contribution.

However, prof. D. Marsh [18] showed that the aforementioned arguments are inapplicable if random changes in the nuclear spin orientation (nuclear spin-lattice relaxation) are caused by the dipole-dipole interaction between the unpaired electron of the radical and that nuclear spin. At the same time, the isotropic hyperfine interaction with this nucleus changes the precession frequency of the electron spin. It was shown in [18] that, in this situation, the dipole-dipole interaction DD_1 between the unpaired electron spin and the nucleus manifests itself analogously to the interaction DD_2 between radicals during random bimolecular collisions [3, 4, 6-9]. DD_1 contributes to the transfer of coherence from one hyperfine component of the EPR spectrum to another—that is, to the transfer of coherence from one transition between two electron spin states to another transition. As noted above, the process involved is not usual spectral diffusion. Upon a random nuclear spin flip, the electron spin not only changes its precession frequency but also acquires a phase shift of π .

As a result, one find that the electron spin coherence transfer is composed of the following spin interactions contributions:

- exchange interaction during random bimolecular collisions of radicals (HSE);
- dipole-dipole interaction of unpaired electron spins of all radicals, modulated by the translational diffusion of the radicals (DD_2);
- anisotropic dipole-dipole hyperfine interaction of the unpaired electron with the magnetic nucleus (DD_1), modulated by the rotational diffusion of radicals, which causes a shift in the electron spin resonance frequency due to the isotropic (contact) hyperfine interaction;

Taking into account Marsh's theory [18], total expected relaxation rates of transverse magnetization components (spin dephasing) and coherence transfer rates for unpaired electron spins (see (2)) must be supplemented by an additional term that is independent of the radical concentration:

$$W_{sd} = \frac{1}{T_2} + \frac{1}{2}K_{ex}C + K_{dd,sd}C + W_{HFI}$$

$$V_{sct} = \frac{1}{2}K_{ex}C - K_{dd,sct}C - V_{HFI}. \quad (4)$$

Terms W_{HFI} and V_{HFI} in (4) were derived in [18] and it is presented below. A $\frac{1}{T_2}$ has been added phenomenologically to the decoherence rate W_{sd} in (4). This member accounts other spin interactions contributions of kinetics of paramagnetic relaxation. We have explicitly singled out only those relaxation mechanisms that result in spin coherence transfer.

2. Aim of this work

There are currently several studies in the literature presenting data that confirm the stated tenets of the new spin exchange paradigm [12–15, 19–24]. However, we have the impression that these provisions have not yet found widespread application within the scientific community. The aim of this work is to obtain new experimental evidence of the “negative interference” of quantum coherence transfer between radicals, caused by HSE and DD₂.

At a certain temperature and/or radical concentration, quantum coherence transfer may be absent as a result of the destructive interference of various contributions. In this case, the spectral lines should not have a dispersion contribution. The EPR spectrum will exhibit resonances at frequencies $\omega_e + \frac{A}{2}$ and $\omega_e - \frac{A}{2}$, without any shifts! However, resonance line broadening due to spin exchange and dipole-dipole interactions will be observed.

In this work, experimental data of DD₁ contribution to spin coherence transfer in solutions of TEMPOL-¹⁵N radicals were obtained. A comparison of the obtained results with Marsh’s theory [18] is also presented. EPR spectra analysis was done using kinetic equations formulated within a new Spin Exchange paradigm, incorporating terms that describe DD₁ contribution in a solution of the TEMPOL-¹⁵N radical. The protocol for determining spin exchange rate between spin probes was also modified to account for DD₁ contribution to paramagnetic relaxation of electron spins. This method allows determination of bimolecular collision frequency of molecules in biological media. Experimentally found DD₁ contribution to spin coherence transfer rate is in qualitative agreement with theoretical estimation of dipole-dipole HFI contribution with ¹⁵N, modulated by rotational diffusion of TEMPOL-¹⁵N radicals.

3. Theoretical estimation of kinetic parameters of paramagnetic relaxation

The parameters characterizing mechanisms of paramagnetic spin relaxation in the cases cited above are discussed in detail in [11, 12]. Here, we present approximate equations that allow for estimation of these parameters for nitroxide radicals under typical EPR experimental conditions. In any real situation, the kinetic equations differ slightly, since the number and values

of these parameters depend on the number of components in the EPR spectrum. We present these parameters for simple radical model, which contains a single magnetic nucleus with spin $I=1/2$.

Spin exchange rate constant during random collisions of two radicals is given by Smoluchowski formula [2]

$$K_{ex} = 4\pi r_{ex} D_{12} = 8\pi r_{ex} D. \quad (5)$$

In equation (5) parameter D_{12} – mutual diffusion coefficient of two colliding radicals, D – radical translational diffusion coefficient, where $D_{12}=2D$. Parameter r_{ex} is effective HSE radius. Since exchange integral is sufficiently large, the collision radius is equal to the sum of van der Waals radii r_0 of the two radicals. Upon collision at this radius, spin exchange occurs with a probability of 1/2. So, for estimates we will use $r_{ex}=(1/2)r_0$ and

$$K_{ex} = 4\pi r_0 D. \quad (6)$$

In non-viscous system EPR experiments, the resonance frequencies of unpaired electron spins, ω_e , satisfy the condition $\omega_e \tau_D > 1$; consequently, approximate formulas can be used for estimation (see [4], (3.30, 3.31)).

In this approximation, corresponding kinetic coefficients in equations (1, 2, 4) are given by (7) [4].

$$\begin{aligned} V_{dd, sd} &= 7 K_{dd} C, \\ V_{dd, sct} &= 4 K_{dd} C, \\ K_{dd} &= \frac{2\pi \gamma_e^4 \hbar^2 \tau_D}{75 r_0^3} = \frac{\pi \gamma_e^4 \hbar^2}{75 r_0 D}, \\ \tau_D &= \frac{r_0^2}{2D}, \end{aligned} \quad (7)$$

γ_e – electron gyromagnetic ratio.

In this case, W_{HFI} contribution to decoherence rate of electron spins in the m -th hyperfine component ($m = 1/2, -1/2$) is given by expression [18]

$$W_{HFI} = \frac{\gamma_e^2 \gamma_n^2 \hbar^2 \left(4J^0(0) + J^0(\omega_e - \omega_n) + 18J^1(\omega_e + Am) + 9J^1\left(\omega_n + \frac{A}{2}\right) + 9J^1\left(\omega_n - \frac{A}{2}\right) + 9J^2(\omega_e + \omega_n) \right)}{32}, \quad (8)$$

here $J^x(\omega)$ – spectral densities of the correlation function of the relative positions of the unpaired electron spin and the magnetic nucleus spin [1, (VIII.104)]; ω_e and ω_n are Zeeman frequencies of electron and nuclear spins, respectively.

It can be expected that the condition is satisfied $\omega_e \tau_D > 1$. Taking into account also that $\omega_e \gg \omega_n$, equation (8) can be written in the form:

$$W_{HFI} = \frac{9\gamma_e^2 \gamma_n^2 \hbar^2 \left(\frac{4}{9} J^0(0) + J^1\left(\omega_n + \frac{A}{2}\right) + J^1\left(\omega_n - \frac{A}{2}\right) \right)}{32}. \quad (9)$$

If the viscosity is sufficiently low and the condition is satisfied $\left(\omega_n + \frac{A}{2}\right) \tau_r < 1$, we obtain an estimate

$$W_{HFI} = \frac{7}{20} \gamma_e^2 \gamma_n^2 \hbar^2 \frac{\tau_r}{b^6}, \quad (10)$$

here b denotes the effective distance between the unpaired electron spin and the nuclear spin. The characteristic rotational relaxation time τ_r of a molecule with a van der Waals radius $r_0/2$ in a medium with viscosity η is equal

$$\tau_r = \frac{\pi \eta r_0^3}{6kT}. \quad (11)$$

DD₁ contribution to spin-correlation transfer rate between the two HFI components corresponding to nuclear spin orientations $m=1/2$ и $-1/2$ is equal to [18]

$$V_{HFI} = \frac{9}{32} \gamma_e^2 \gamma_n^2 \hbar^2 \left(J^{(1)}\left(\omega_n + \frac{a}{2}\right) + J^{(1)}\left(\omega_n - \frac{a}{2}\right) \right). \quad (12)$$

If the viscosity is small enough and the condition $(\omega_n \pm a/2)\tau_r < 1$ is satisfied, we obtain the estimate

$$V_{HFI} = \frac{3}{20} \gamma_e^2 \gamma_n^2 \hbar^2 \frac{\tau_r}{b^6}. \quad (13)$$

Within the framework of the continuum model, the viscosity coefficient in (11,14) can be expressed in terms of the radical translational diffusion coefficient D using the Stokes formula $\eta = kT/(3\pi r_0 D)$. As a result, we get

$$\tau_r = \frac{r_0^2}{18D}. \quad (14)$$

The rotational diffusion time τ_r (11) was obtained under the assumption that the molecule rotates in a continuous medium. Of course, on the scale of a molecule's size, the medium is far from continuous. Therefore, (11) can provide an order-of-magnitude estimate of the rotational diffusion time. By substituting (14) into (13), the total contribution of all three spin coherence transfer mechanisms we have considered in non-viscous media can be expressed in a form where the temperature dependence is determined solely by the translational diffusion coefficient

$$V_{sct} = \frac{1}{2}(K_{ex} - K_{dd})C - V_{HFI} \approx 2\pi r_0 DC - \frac{2\pi \gamma_e^4 \hbar^2 C}{75 r_0 D} - \frac{1}{120} \gamma_e^2 \gamma_n^2 \hbar^2 \frac{r_0^2}{b^6 D}. \quad (15)$$

It should be noted that total coherence transfer rate can vanish upon changes in temperature and radical concentration.

For illustration, let us choose a ^{15}N nitroxide radical with a van der Waals diameter of $r_0 = 6 \times 10^{-8}$ cm and the distance between electron and nuclear spins is $b = 0.5 \times 10^{-8}$ cm. Nuclear spin ^{15}N gyromagnetic ratio $\gamma_n = -0.27 \times 10^4$ (sec G) $^{-1}$, and for electron $\gamma_e = 1.76 \times 10^7$ (sec G) $^{-1}$. Let us assume that the concentration of spins $C = 10$ mM. Substituting these numerical values into (15), one determines the value the radical diffusion coefficient must take for the various mechanisms of spin coherence transfer to cancel each other out, such that the total rate of spin coherence transfer (15) becomes zero. We obtain $D = 1.5 \times 10^{-6}$ cm ^{2} /s.

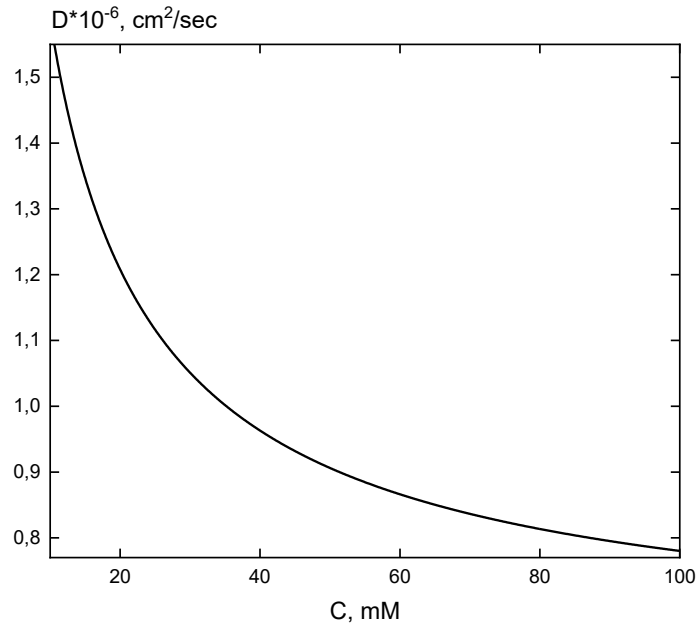


Fig. 1 Dependence of diffusion coefficient under the condition $V_{sct}=0$.

Figure 1 shows the radical diffusion coefficient calculated from (15); this coefficient is required so that, at a given radical concentration C , a condition is established under which the contributions from different spin coherence transfer mechanisms completely cancel each other out $V_{sct}=0$ (1, 4, 15). Figure 1 clearly demonstrates that, as the radical concentration increases, the radical diffusion coefficient must be lowered. This means the temperature must be reduced to achieve such compensation. This can also be achieved by replacing a low-viscosity solvent with a more viscous one.

4. Experiment and analysis

Solutions of the nitroxide radical [15N]-4-hydroxy-2,2,6,6-tetramethylpiperidine-d17-1-oxyl (Tempol-¹⁵ND), purchased from CDN isotopes, in 60 wt% aqueous glycerol solutions were studied. They were prepared gravimetrically from stock solutions with concentrations from 0.1 to 178 mM. The samples were placed in 50- μ l pipettes (Sigma) and sealed at both ends with a flame. The steady-state EPR measurements were carried out on an EMX spectrometer (Bruker) at a temperature from 258 to 333 K using a nitrogen-flow standard Oxford temperature unit. Experimental parameters are: field sweep 100 G, field resolution 0.1 G, modulation amplitude 0.1 G, modulation frequency 100 kHz, and microwave power 0.2 mW.

In this work we used deuterated sample without hyperfine structure from protons.

The EPR spectral line shape of a nitroxide radical with a ¹⁵N nucleus consists of two asymmetric lines. The description of the line shape using Lorentzian absorption and Lorentzian dispersion lines is suitable in our case [13]. Under these circumstances, the mixed shape of one resonance line can be approximated in the following form:

$$J(H) = V_{Abs} \frac{8\xi}{(3+\xi^2)^2} \mp V_{Disp} \frac{3(3-\xi^2)}{(3+\xi^2)^2}, \quad (16)$$

$$\xi = 2 \frac{H-H_0}{\Delta H_{pp}^0}$$

where H is the swept magnetic field and H_0 is the resonance field of one of the two nitrogen hyperfine lines due to ¹⁵N nitroxides in gauss units.

The Figure 2 shows the experimental spectrum of 19 mM Tempol-¹⁵ND at room temperature. Using equation (16), spectral components A and B were presented as decomposed into a sum of Lorentzian absorption and dispersion derivatives. In our work, we used the parameters of Lorentzian linewidth (H_{pp}^{Lor}), resonant fields ($H \pm A_{eff}/2$), and amplitudes of absorption (V_{abs}) and dispersion (V_{disp}).

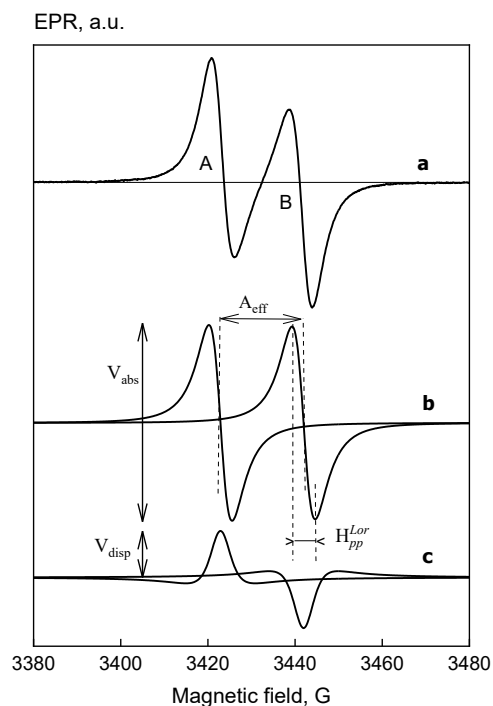


Fig. 2 The decomposition of the total spectrum of 19 mM Tempol- ^{15}ND (a) into absorption (b) and dispersion (c) components of two resonance lines.

The spin exchange rate can be determined from concentration dependence of the EPR spectrum shape analysis. A widely used method is to analyze the concentration broadening of resonance lines. However, concentration broadening arises not only from HSE, but also from DD presenting the problem of separating the HSE and DD contributions.

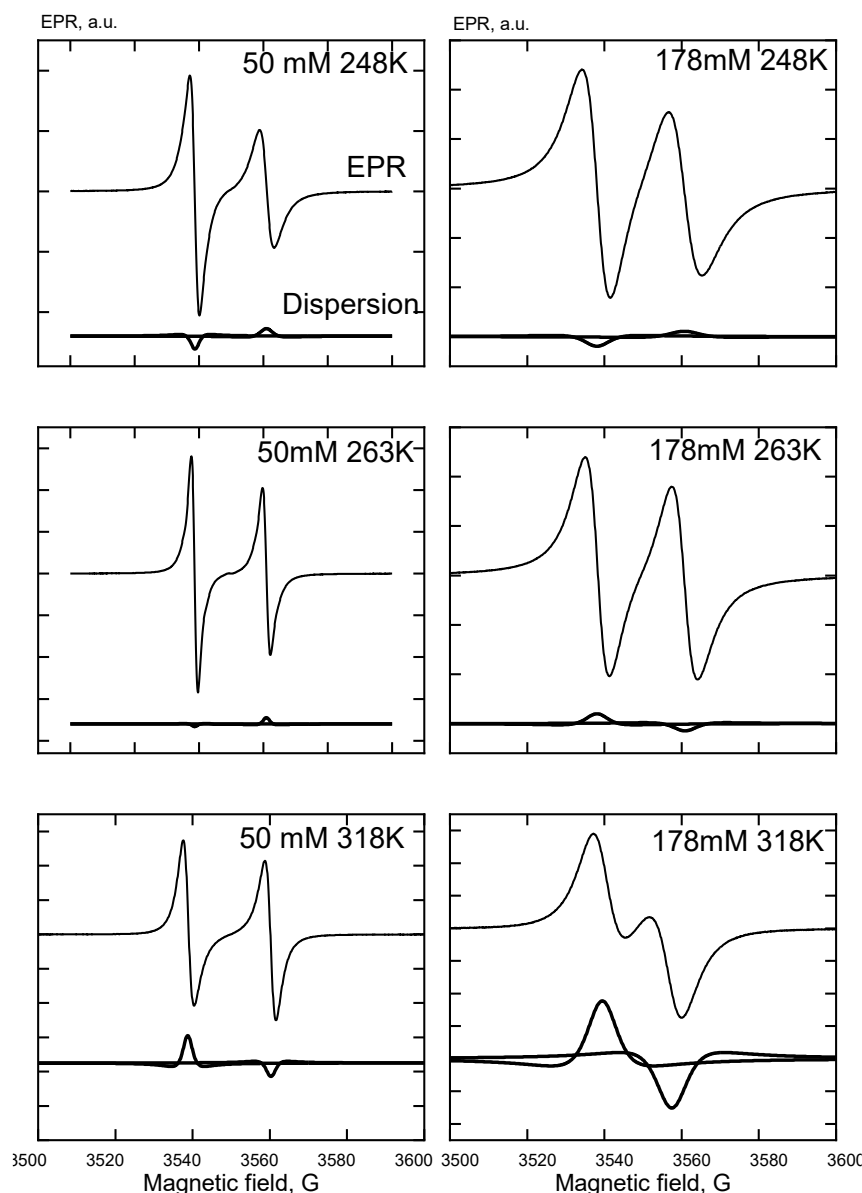


Fig.3 The total EPR spectra of Tempol ^{15}ND observed in experiment (thin curves) and the dispersion parts of individual resonance lines (thick curves) for 50 mM and 178 mM at different temperatures

Figure 3 shows EPR spectra of Tempol- ^{15}ND at concentrations of 50 and 178 mM at different temperatures. There are two spectral components from two modes of the collective motion of subensembles of radicals, in which the spins of the nitrogen ^{15}N nucleus have a projection of $+1/2$ or $-1/2$. Each mode represents a line of mixed form: absorption and dispersion contributions. In this work, particular attention is paid to the dispersion. On the Figure 3 the dispersions of the individual components are shown as a thick line below the full spectrum. It can be seen that the dispersion changes sign as the temperature increases. This is due to the fact that the spin exchange contribution begins to dominate the DD_2 contribution as the temperature

increases (see eq. 4 for V_{sct}). Rate constants K_{ex} and K_{dd} depend on temperature. Kinetic rates are related to observed parameters in spectrum in following way [8, 12]:

$$\begin{aligned} W_{sd} &= \frac{\sqrt{3}}{2} H_{pp}^{Lor}, \\ V_{sct} &= \frac{4}{3\sqrt{3}} \frac{V_{Disp}}{V_{pp}} \frac{A_{eff}}{2}. \end{aligned} \quad (17)$$

In order to determine spin exchange rates, protocol formulated in [4,7,8,9,11] is taken as a basis:

- The EPR spectrum is represented as a sum of resonant lines, each of which has a mixed shape, that is, it contains the contributions of absorption and dispersion (see (16));
- By varying the parameters A_{eff} , H_{pp}^{Lor} and the ratio of the contributions of dispersion and absorption $\frac{V_{Disp}}{V_{pp}}$, the test shape of the spectrum calculated according to equation (16) is maximally adjusted to the shape of the spectrum observed in the experiment;

The shape of EPR spectra was analyzed in detail in [9] for a situation where only spin exchange was considered (see (1)). However, we wrote equations (4) in a form in which the solution to the problem taking into HSE, DD_2 , and DD_1 can be immediately written from the results of work [9], if one makes substitutions: the spin decoherence rate $\frac{1}{2}K_{ex}C$ is replaced by $W_{sd} = \frac{1}{2}K_{ex}C + \frac{7}{4}K_{dd}C + W_{HFI}$ and the spin coherence transfer rate $\frac{1}{2}K_{ex}C$ is replaced by $V_{sct} = \frac{1}{2}(K_{ex}C - K_{dd}C - 2V_{HFI})$.

As a result we get:

$$\begin{aligned} H_{pp}^{Lor} &= \frac{2}{\sqrt{3}} \left(\frac{1}{\gamma T_2} + \frac{1}{2}K_{ex}C + \frac{7}{4}K_{dd}C + W_{HFI} \right); \\ \frac{4}{3\sqrt{3}} A_{eff} \frac{V_{Disp}}{V_{pp}} &= (K_{ex}C - K_{dd}C - 2V_{HFI}). \end{aligned} \quad (18)$$

Resonance line broadening H_{pp}^{Lor} on concentration slope determines $\frac{2}{\sqrt{3}} \left(\frac{1}{2}K_{ex} + \frac{7}{4}K_{dd} \right)$, and from $A_{eff} \frac{V_{Disp}}{V_{pp}}$ slope on concentration, $\frac{3\sqrt{3}}{4} (K_{ex} - K_{dd})$ is determined. Using these relations, we determine kinetic parameters K_{ex}, K_{dd} . Having obtained K_{ex} and K_{dd} the values from the concentration dependence (18), we can determine V_{HFI} from (15).

This protocol was used to analyze radical concentration and temperature dependences of dispersion contribution to EPR lines. In case of HSE dominance (see sign of the low field dispersion line at 318 K in Fig.3), dispersion contribution must have a plus sign. In case of

dominance of DD₂ (see sign of the low field dispersion line at 248 K in Fig.3), dispersion sign is negative.

Change in the sign of the dispersion contribution to the shape of the resonance line serves as confirmation of the correctness of the theory, which predicted the contribution of the DD₁ interaction. The dispersion contribution $V_{\text{disp}}/V_{\text{pp}}$ observed in the experiment is directly related to the rate of spin coherence transfer. The Figure 4 shows the temperature dependence of the dispersion contribution $V_{\text{disp}}/V_{\text{pp}}$ of both spectral components. One can observe that the sign of dispersion contribution changes to the opposite as the temperature changes from 248 K to 318 K. As the radical concentration increases, the intersection point shifts in an approximately linear manner to a lower temperature (Fig.4f).

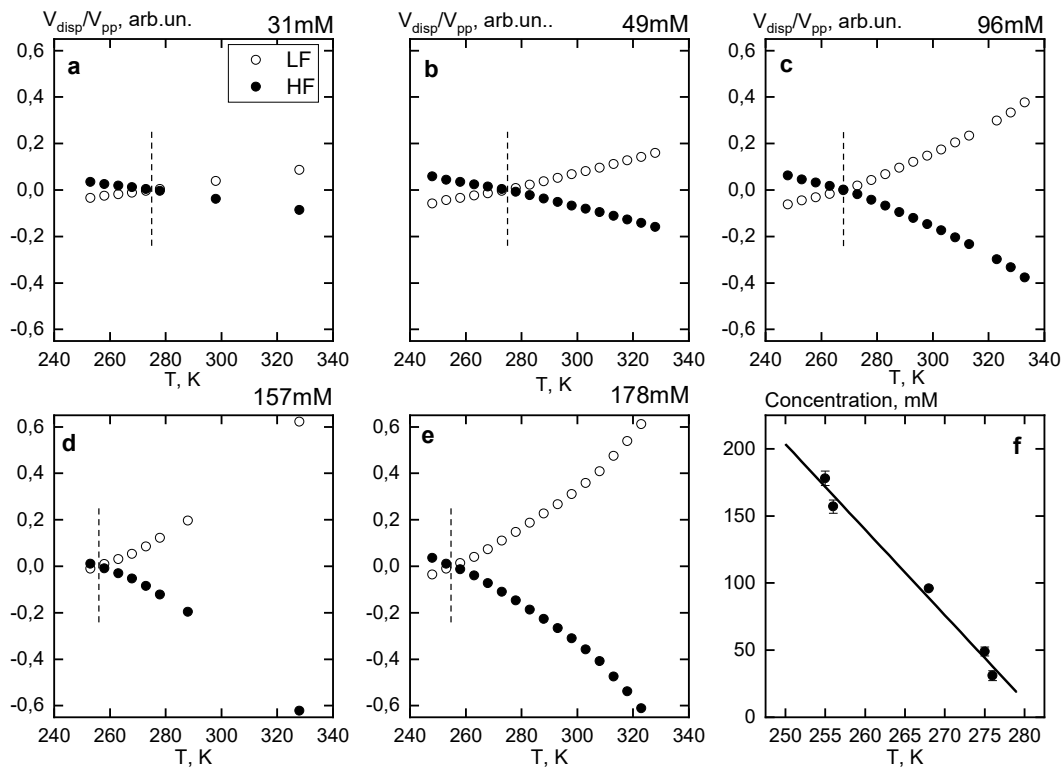


Fig. 4 Dependencies of dispersion component (a - e) for low field (LF) and high field (HF) component for at different temperatures. Figure f is black line – temperature dependence of concentration at which $V_{\text{disp}}/V_{\text{pp}}$ contribution passes through zero

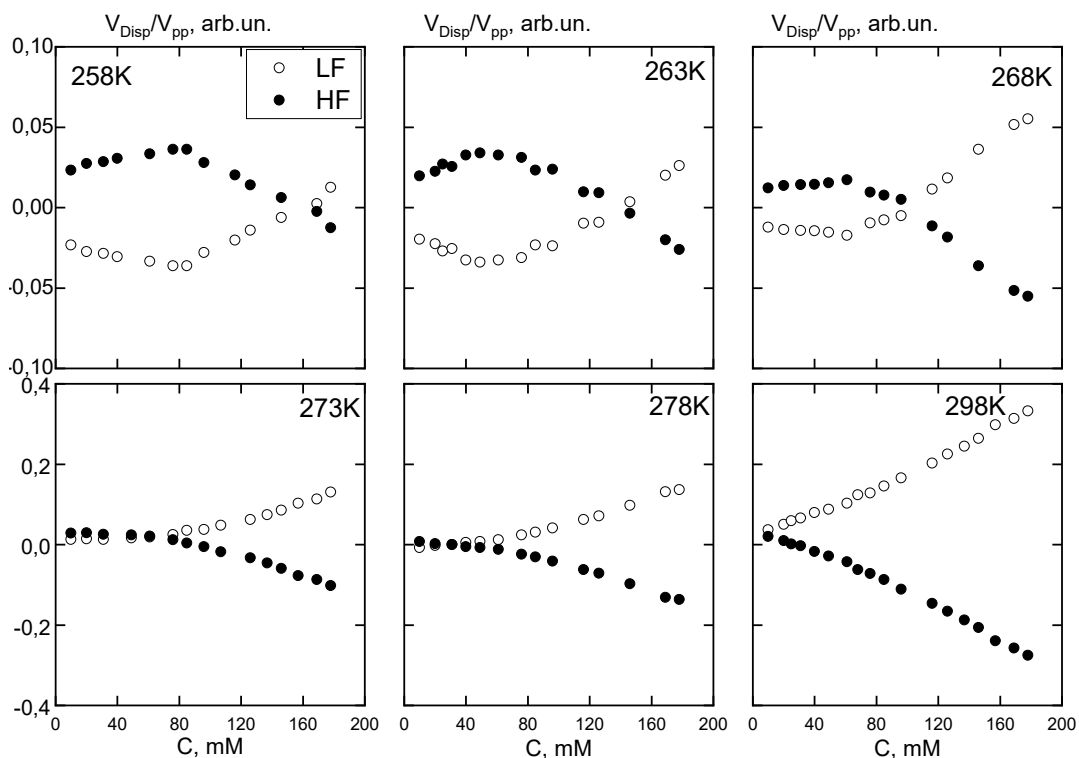


Fig. 5 Concentration dependencies of dispersion component for low field and high field component at different temperatures

An analysis of the experimental dependences of the dispersion contribution $V_{\text{disp}}/V_{\text{pp}}$ on the concentration (Fig.5) was carried out. It is evident that there is a dispersion contribution at concentrations of about zero. This demonstrates the presence of a concentration-independent coherence transfer contribution to V_{sct} (see eq.15). From the slopes of this lines, the values of K_{ex} and K_{dd} were found (Fig.6). It is worth noting that rate constants K_{ex} and K_{dd} were determined at fairly high concentrations above 80 mM. This is due to the fact that the terms $K_{\text{ex}}C$, $K_{\text{dd}}C$ of the type dominate over the others at such concentrations.

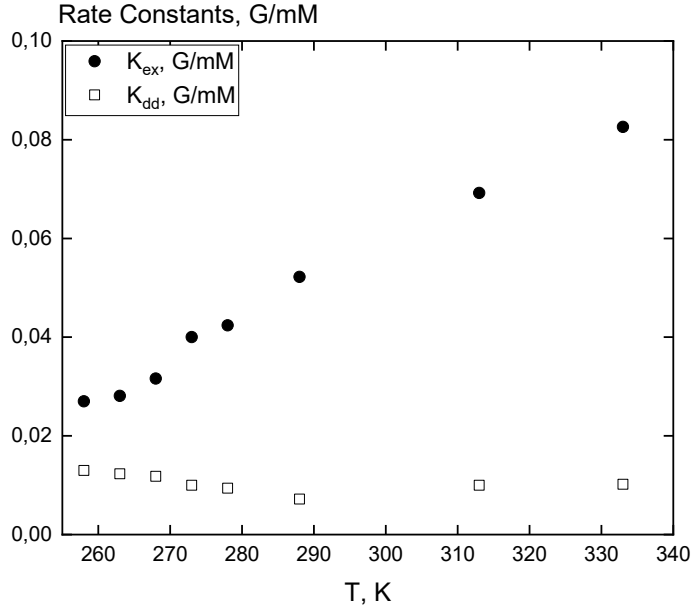


Fig.6 Temperature dependence of rate constants of HSE and DD₂ interactions

At high temperatures, contribution of DD₂ interaction to spin coherence transfer rate is expected to be much less than the contribution of exchange interaction. This is confirmed by Fig.6.

The contribution of the dipole-dipole hyperfine interaction of an unpaired electron with the magnetic nitrogen nucleus to the coherence transfer between electron spin transitions which belong to different hyperfine components of ¹⁵N was found by Marsh [18]. Estimation of DD₁ contribution of hyperfine interaction to the transfer of spin coherence are close to the contribution to the broadening of the nitrogen components of the spectrum. Once the kinetic rate constants are determined, it becomes possible to find a contribution V_{HFI} that is independent on concentration. This is done using (15) under condition $V_{scf}=0$. This corresponds to the case of zero dispersion contribution, i.e. this is the intersection point of the dispersion contributions of the low- and high-field components of the spectrum. The results are shown in the Fig.7.

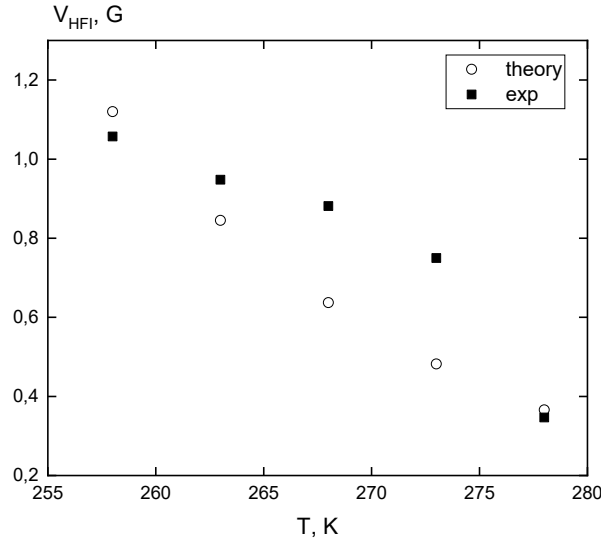


Fig. 7 Dependence V_{HFI} (15) on T . Comparison with experimental data found from spectra with zero dispersion contribution. Calculation parameters: $r_0=6 \cdot 10^{-8}$ cm, $b=0.5 \cdot 10^{-8}$ cm.

The theoretical dependence V_{HFI} was calculated using (13) and (14). Figure 7 shows that theoretical [18] and experimental dependencies are in qualitative agreement.

5. Conclusion

In this work, we have summarized current data regarding the contribution of dipole-dipole interaction to electron spin coherence transfer in non-viscous media. Our interest in this specific process stems from the fact that the dipole-dipole interaction between radicals manifests alongside with the Heisenberg exchange interaction during bimolecular radical collisions in dilute solutions. Measuring spin-exchange rate constants is widely used in molecular biology and chemistry as one of the best methods for determining the frequency of bimolecular collisions. Consequently, the realization that dipole-dipole interaction interferes destructively with the Heisenberg exchange interaction in coherence transfer between different transitions of electron spins became a key factor for correct determination of the rate of bimolecular collisions in complex media as polymer solutions, systems of molecular biology [4]. Accounting for spin coherence transfer driven by dipole-dipole interaction between radicals has significantly altered the protocol for determining spin-exchange rate constants and molecular bimolecular collision frequencies.

However, the results of our work may have much broader applications. Using a specific example, we have theoretically and experimentally demonstrated the fundamentally important role played by so-called non-secular terms in the theory of paramagnetic relaxation of paramagnetic species in liquids and gases (see [1], (VIII.36)).

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