Study of slow molecular motions by stable-radical EPR

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A review is given of theoretical papers devoted to the calculation of EPR spectra of stable radicals in the range of slow molecular motions not accessible to analysis by perturbation theory. Modulation of anisotropic magnetic interactions of the spin of an unpaired electron by random rotations of its carrier is assumed to be the principal relaxation mechanism in viscous media and at low concentrations of the radicals. Molecular reorientations are modeled by various random processes of the Markov type. A method is described for obtaining the basic relaxation equation for the spin density matrix which is known as the random path method or the method of the stochastic Liouville equation. A method is described for solving relaxation equations which is common for different models of rotation. Approximate methods for solving such equations are discussed. Results are given of the comparison of calculations with observed spectra which permit conclusions to be drawn concerning the nature and intensity of molecular motions.

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CONTENTS

1. INTRODUCTION

Electron paramagnetic resonance (EPR) is used to study the whole gamut of condensed media containing either intrinsic paramagnetic centers, or, more often, paramagnetic centers injected into the system from the outside as spin tags and probes. (Free paramagnetic centers are known as probes and centers covalently bound to molecules of the medium under study are called tags.)

The intensive development of the method during the past decade has resulted in large part from progress in the chemistry and physics of stable free radicals, which have come into wide-spread use as tags and probes. The shapes of the EPR spectra of radicals carry information not only on their electron-spin properties, but also on their motion. By measuring the rotational and translational mobilities of the radicals with the aid of EPR techniques, we can obtain inferences as to the structure and dynamics of liquids, organic and liquid crystals, polymeric systems, and the

like. The use of spin tags and probes in molecular biology makes it possible to obtain information on the structure, microrelief, and conformational dynamics of proteins, enzymes, membranes, and other biomolecules.

The fundamentals of a general theory of magnetic relaxation were developed by Bloch[1-3], Redfield[4], and others[5-8]. Freed and Fraenkel[6] were among the first to report investigations of the shapes of the EPR spectra of free-radicals. The monographs of Ref.[9-11] present a detailed exposition of the Bloch-Redfield theory. In this theory, the interaction of the spins with all other degrees of freedom of the system (spin-lattice interaction) is required as a weak perturbation. Calculation of the relaxation parameters by perturbation theory methods limits the application of the Bloch-Redfield equations to sufficiently rapid random motions of the spin carriers under the action of the thermal motion of surrounding molecules.

The comparatively recent papers[12-26], which devel-

oped methods for calculation of magnetic resonance spectra, place no limitations on the magnitude of the spin-lattice interaction. It was these advances in the theory that stimulated the rapid and productive development of the spin-probe and spin-tag methods in molecular biology and made it possible to interpret the EPR spectra of slowly rotating radicals in high-viscosity liquids, polymers, and biomolecular systems[27-32].

As we set forth below the principles of the new method as applied to the theory of EPR line shapes of stable radicals, we shall consider only situations in which the radical concentration in the medium is quite low (10^{17} cm^{-3}) and the interaction between the spins of different radicals can be neglected (magnetically dilute solutions). Thus, calculation of the EPR spectra is based on analysis of a single radical molecule in motion under the influence of its environment. Under these conditions, the basic relaxation mechanism is assumed to be modulation of the anisotropic magnetic interactions of the radical by its random rotations. If the random reorientation process is characterized by the correlation time τ of the rotations and the anisotropic part of the magnetic interactions of the radical is denoted by σ (frequency units), the condition for validity of the Bloch-Redfield theory[1-4] will be written as

$$\sigma\tau \ll 1. \tag{1.1}$$

It signifies that the characteristic frequency σ of the spin-lattice interaction must be much smaller than the frequency of reorientation $\nu = \tau^{-1}$ of the radical molecule.

Leaving aside the thoroughly understood range of rapid rotations, we shall include in the review only those theoretical studies that contain calculations and procedures for analysis of EPR spectra in the range of slow molecular rotations ($\sigma\tau \gtrsim 1$).

Since stable nitroxyl radicals (NR) are used in the overwhelming majority of studies, we shall present the theory in application to these radicals.

2. THE SPIN HAMILTONIAN

Progress in the use of nitroxyl radicals as spin tags and probes has been due to their unique properties: high stability and the possibility of varying their chemical structure in accordance with the particular objective with practically no change in their paramagnetic properties. The latter are determined by the paramagnetic fragment $>N-\cdot O$, which is common to all NR (Fig. 1a). It is essential that the stability of NR does not rest on delocalization of the unpaired electron over the bonds. The unpaired electron is concentrated
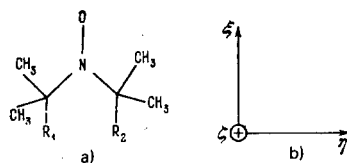

FIG. 1. a) Radical fragment of nitroxyl radical; b) system of principal axes of the g and A tensors. The ξ axis is perpendicular to the plane of the drawing.

on the $N-\cdot O$ group. The nucleus of the most abundant O^{16} isotope does not have a magnetic moment, i.e., there is no hyperfine interaction with the oxygen nucleus. Therefore the unpaired NR electron interacts effectively only with the N nucleus, and the weak hyperfine interaction with the protons is responsible for the unresolved hyperfine structure of the spectrum.

If we disregard the weak spin interactions with the molecules of the environment, which may influence the unresolved hyperfine structure of the spectrum, the radical in a magnetically dilute medium is an isolated spin system. In this case, the spin Hamiltonian is obtained by averaging the total Hamiltonian of the molecule over one of its orbital states (usually the ground state). The effectiveness of this approximation depends on how many times greater is the distance between orbital energy levels compared to the distance between spin sublevels. References[10,11,34] give more details as to the possibility of using the spin-Hamiltonian concept, and as to its calculation.

The spin Hamiltonian of a nitroxyl radical in an external magnetic field H has the form[11]

$$\mathscr{H} = \sum_{\alpha,\alpha'=x,y,z} (\beta H_\alpha g_{\alpha\alpha'} S_{\alpha'} + I_\alpha A_{\alpha\alpha'} S_{\alpha'} - \hbar\gamma_n H_\alpha I_{\alpha'} + \hbar\gamma h(t) S); \tag{2.1}$$

here $g_{\alpha\alpha'}$ and $A_{\alpha\alpha'}$ are the components of the Zeeman and hyperfine (HFI) interaction tensors, S and I are the electron and nuclear spin operators, β is the Bohr magneton, and γ_n and γ are the gyromagnetic ratios of the nucleus and electron, respectively.

The last term in the Hamiltonian describes the weak resultant interaction of the unpaired electron with the stochastic magnetic fields h(t) created by the surrounding medium (induced, for example, by nearby protons). The influence of h(t) on the unresolved hyperfine structure of the spectrum (HFS) will henceforth be taken into account by applying an imaginary increment to the EPR spectrum. Thus the last term in the Hamiltonian (2.1) can be dropped. Since the relaxation broadening of the hyperfine structure of the spectrum (see, for example, Ref.[35]) is much greater than the Zeeman nuclear frequency in the range of slow molecular motions ($\sigma\tau \gtrsim 1$), the third term in (2.1) can also be discarded.

It has been shown that the principal axes of the tensors g and A very nearly coincide for NR[36]. Then the Hamiltonian (2.1) without the omitted terms can be written as follows in a principal-axis coordinate system rigidly bound to the radical (see Fig. 1b):

$$\mathscr{H} = \beta(g_{\xi\xi}H_\xi S_\xi + g_{\eta\eta}H_\eta S_\eta + g_{\zeta\zeta}H_\zeta S_\zeta) + A_{\xi\xi}I_\xi S_\xi + A_{\eta\eta}I_\eta S_\eta + A_{\zeta\zeta}I_\zeta S_\zeta. \tag{2.2}$$

It is convenient to choose the z axis of the laboratory system in the direction of the constant external magnetic field H. Then in sufficiently strong fields (such that the condition $(g\beta H\tau/\hbar)^2 \gtrsim 1$ is satisfied) we may discard the terms of the Hamiltonian that are nonsecular in S_z, i.e., terms that do not commute with S_z.[10,37] As a result, the spin Hamiltonian assumes in the laboratory system the form

$$\mathscr{H} = (g_{zz}\beta H + A_{zx}I_x + A_{zy}I_y + A_{zz}I_z) S_z; \tag{2.3}$$

where g_{zz} and $A_{z\alpha}$ ($\alpha = x, y, z$) are the tensor compon-

ents in this system. The orientation of the system of principal axes of the magnetic-interaction tensors relative to the laboratory system is usually described by the Euler angles $\Omega = (\varphi, \theta, \psi)$. We find the dependence of g_{zz} and $A_{z\alpha}$ on these angles by carrying out the necessary transformations required by conversion to the new coordinate system. Introducing the operators

$$I_1^{\pm 1} = \mp \frac{1}{\sqrt{2}} (I_x \pm iI_y), \qquad (2.4)$$

we can represent the Hamiltonian (2.3) in the form

$$\mathcal{H}(\Omega) = \hbar S_z \left[a(\Omega) + a_0(\Omega) I_z - a_{-1}(\Omega) I_1^{+1} - a_{+1}(\Omega) I_1^{-1} \right], \qquad (2.5)$$

where the coefficients $a, a_0,$ and $a_{\pm 1}$, which are linearly related to the principal values of the interaction tensors, take the forms

$$a(\Omega) = \frac{g\beta H}{\hbar} = \frac{\beta H}{\hbar} \left\{ D_{0,0}^{(2)}(\Omega) \Delta g \right.$$
$$\left. + \sqrt{\frac{2}{3}} [D_{0,2}^{(2)}(\Omega) + D_{0,-2}^{(2)}(\Omega)] \Delta g_\perp \right\} + i\delta,$$
$$a_0(\Omega) = \frac{A}{\hbar} + D_{0,0}^{(2)}(\Omega) \frac{\Delta A}{\hbar} + \sqrt{\frac{2}{3}} [D_{0,2}^{(2)}(\Omega) + D_{0,-2}^{(2)}(\Omega)] \frac{\Delta A_\perp}{\hbar},$$
$$a_{\pm 1}(\Omega) = \frac{\sqrt{3}}{2} D_{\pm 1,0}^{(2)}(\Omega) \frac{\Delta A}{\hbar} + \frac{1}{\sqrt{2}} [D_{\pm 1,2}^{2}(\Omega) + D_{\pm 1,-2}^{(2)}(\Omega)] \frac{\Delta A_\perp}{\hbar}; \qquad \Bigg\} \quad (2.6)$$

here

$$g = \tfrac{1}{3}(g_{\xi\xi} + g_{\eta\eta} + g_{\zeta\zeta}), \quad \Delta g = g_{\zeta\zeta} - g, \quad \Delta g_\perp = \tfrac{1}{2}(g_{\xi\xi} - g_{\eta\eta}),$$
$$A = \tfrac{1}{3}(A_{\xi\xi} + A_{\eta\eta} + A_{\zeta\zeta}), \quad \Delta A = A_{\zeta\zeta} - A, \quad \Delta A_\perp = \tfrac{1}{2}(A_{\xi\xi} - A_{\eta\eta}), \qquad (2.7)$$

$D_{m,n}^{(l)}(\Omega)$ are generalized spherical functions and δ is the relaxation width, which is governed by the stochastic field $h(t)$.

The monograph of Ref. 38 gives a rather complete list of calculated and observed values of the hyperfine and Zeeman interaction tensor components for a number of nitroxyl radicals. Certain minor differences between the values of the magnetic-interaction constants for the various radicals are determined primarily by the electronic state and by the geometry of the paramagnetic fragment $>N-\cdot O$, which vary from radical to radical. Below we present the principal values of the magnetic interaction tensors of the di-tert-butylnitroxyl radical[6]:

$$\left. \begin{array}{ll} g_{\xi\xi} = 2.0088 \pm 0.0003, & A_{\xi\xi} = A_{\eta\eta} = 5.2 \pm 0.5 \text{ G}, \\ g_{\eta\eta} = 2.0061 \pm 0.0003, & A_{\zeta\zeta} = 31 \pm 0.5 \text{ G}. \\ g_{\zeta\zeta} = 2.0027 \pm 0.0003, & \end{array} \right\} \qquad (2.8)$$

The axial symmetry of the A-tensor for most NR[1)] greatly simplifies the angular dependence of the Hamiltonian (2.5).

It is seen from expressions (2.6) that the spin Hamiltonian and, consequently, the position of any energy level, depend on the orientation of the radical. Since the radical participates in the thermal motion of the molecules, its orientation, i.e., the angles Ω, vary randomly in time.

The shape of the resonance signal depends both on the

anisotropy of the magnetic interactions ($\Delta_g, \Delta g_\perp, \Delta_A, \Delta_{A_\perp}$) and on the intensity of the disordered rotations which the radical undergoes. As we noted above, the rate of these reorientations of the molecules is usually characterized by the correlation time τ of the rotational motions (whose value depends on the temperature of the medium). It follows from (2.5) and (2.6) that the anisotropy of the magnetic interaction of the unpaired electron is characterized by the following parameter, which is expressed in frequency units:

$$\sigma = \max \left\{ \frac{\Delta g \beta H}{\hbar}, \frac{\Delta g_\perp \beta H}{\hbar}, \frac{\Delta A}{\hbar}, \frac{\Delta A_\perp}{\hbar} \right\}. \qquad (2.9)$$

For NR in the three-centimeter wavelength band that is normally used (H = 3300 Oe), it amounts to $4.5 \cdot 10^8$ sec^{-1}. Therefore, the Bloch-Redfield condition (1.1) is not satisfied for these radicals at $\tau > 10^{-9}$ sec.

3. RELAXATION THEORY AND THE SHAPE OF THE PARAMAGNETIC RESONANCE LINE

a) Shape of EPR line. Definition

The coefficient of absorption $\mathcal{A}(\omega)$ of the energy of an alternating magnetic field of frequency ω and the shape of the resonance signal $\mathcal{J}(\omega)$ are related by $\mathcal{J}(\omega) = \mathcal{A}(\omega)/\omega^2$. In the approximation of linear response to a weak radio-frequency field, the shape of the EPR is expressed[9,37] in terms of the Fourier transform of the relaxation function $G_{xx}(t)$:

$$\mathcal{J}(\omega) = \frac{1}{2\pi} \text{Re} \int_{-\infty}^{+\infty} G_{xx}(t) e^{-i\omega t} dt. \qquad (3.1)$$

The relaxation function $G_{xx}(t)$ is the autocorrelation function of the transverse (relative to the constant magnetic field H) component $M_x(t)$ of the specimen's magnetic moment:

$$G_{xx}(t) = \frac{\text{Sp}\{M_x \langle M_x(t) \rangle\}}{\text{Sp}(M_x^2)}, \qquad (3.2)$$

where M_x is the operator for the x-component of the spin-system magnetic moment and the brackets $\langle \ldots \rangle$ indicate averaging over the molecular motion.

We note that the relaxation function (3.2) can be replaced in formula (3.1) by the approximate form

$$G_{xx}(t) \approx \frac{\text{Sp}\{S_x \langle S_x(t) \rangle\}}{\text{Sp}(S_x^2)}. \qquad (3.3)$$

In fact, the operator M_x has the form

$$M_x = \beta (g_{xx} S_x + g_{xy} S_y + g_{xz} S_z) \qquad (3.4)$$

in the laboratory system. The diagonal g-tensor element g_{xx} is of the order of g (2.7), while the off-diagonal elements are of the order of Δg. Therefore the second and third terms in (3.4) are smaller than the first by a factor $g/\Delta g \sim 10^2$ and can be dropped. It has been shown[40] that the off-diagonal elements make a significant contribution to $\langle M_x(t) \rangle$ only in the range of strong resonance-line narrowing ($g\beta H \tau/\hbar \ll 1$). Thus, we can use the expression

$$\mathcal{J}(\omega) = \frac{1}{\pi} \text{Re} \int_{-\infty}^{+\infty} \text{Sp}\{S_x \langle S_x(t) \rangle\} e^{-i\omega t} dt$$
$$= \frac{1}{2\pi} \text{Re} \int_{-\infty}^{+\infty} \text{Sp}\{S_- \langle S_+(t) \rangle + S_+ \langle S_-(t) \rangle\} e^{-i\omega t} dt, \qquad (3.5)$$

[1)]Libertini and Griffith[39] found improved values of the HFI- and g-tensor components of the di-tert-butylnitroxyl radical and showed that the A-tensor is not axially symmetric. Thus, neglecting $\Delta A_\perp$ in formulas (2.6), it is more correct to speak of the axially symmetric approximation.

where $S_\pm = S_x \pm i S_y$ can be used for the resonance-line shape $\mathcal{J}(\omega)$ over practically the entire range of correlation times except for the range of very rapid rotations ($\tau < 10^{-11}$ sec).

b) Relaxation equations

To calculate the spectrum $\mathcal{J}(\omega)$ (3.5) it is necessary to find the time dependence $\langle S_\pm(t) \rangle$. The Heisenberg equation for the operator $S_\pm(t)$ (and similarly for the spin density matrix) has the form

$$\frac{dS_\pm(t)}{dt} = \frac{i}{\hbar} [\mathcal{H}(\Omega(t)), S_\pm(t)], \qquad (3.6)$$

where the $\Omega(t)$ are random functions of time because of the random motion of the radical in the liquid. The unknown values of $\langle S_\pm(t) \rangle$ can be found by solving Eq. (3.6) for an arbitrary $\Omega(t)$ dependence and averaging the resulting solutions over the distribution of a random process that models the reorientations of the radical. But it is obvious that this is generally impossible. There is another way. It is based on derivation of equations for $S_\pm(t)$ (or the spin density matrix) that have already been averaged over the stochastic motion $\Omega(t)$. For this purpose, it is necessary to use, in addition to (3.6), a mathematical description of the random process chosen to model the reorientation of the radical.

1. The Bloch-Redfield equation. If the relaxation time of the spin system is much larger than the correlation time of the molecular motion, an equation for the averaged value of $S_\pm(t)$ can be obtained by introducing a "coarse-grained" time whose unit interval is differentially small for the variation of the spin variables and large enough so that all quantities can be averaged on it over the molecular motion. Then condition (1.1) is satisfied and equations for the spin density matrix are derived within the framework of the Bloch-Redfield theory (similarly, they could be obtained for an arbitrary spin operator of the spin system under study). The Redfield equation[4] has the form

$$\frac{d\rho_{\alpha\alpha'}}{dt} = -i[E, \rho]_{\alpha\alpha'} + R_{\alpha\alpha'\beta\beta'}\rho_{\beta\beta'}, \qquad (3.7)$$

where α and β are the indices of the spin states, $\hbar E$ is the part of the spin Hamiltonian that includes only the spin operators and the external field and does not depend on the molecular coordinates, i.e., the "lattice" coordinates [for the Hamiltonian (2.5), for example, this is $g\beta H S_z + A S_z I_z$], and $R_{\alpha\alpha'\beta\beta'}$ is the relaxation matrix, the elements of which do not depend on time, since we are concerned with weak alternating fields. In the simplest cases, this matrix is determined by the two relaxation times T_1 and T_2 that were introduced by Bloch[41] into the macroscopic equations. Equation (3.7), unlike (3.6), no longer contains the lattice variables in explicit form. Lattice information is present only in the elements of the relaxation matrix R, which is the Fourier transform of the correlation functions of the variables that enter into the spin-lattice interaction. By the definition that follows from the theory,[4] calculation of the matrix is based on use of perturbation theory for the spin-lattice interaction. In the Hamiltonian (2.5), this interaction is described by the part that depends on the orientation angles of the radical. In this case, inequality (1.1) is the condition for smallness
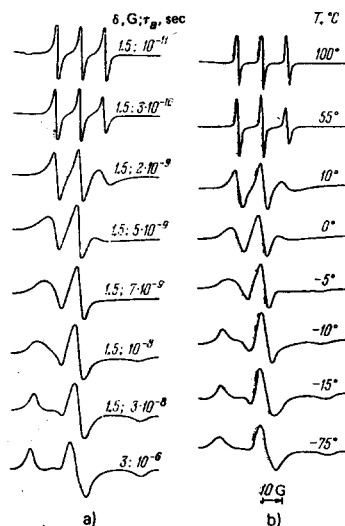

FIG. 2. Spectra of nitroxyl radical—(a) theoretical and (b) observed in glycerine at various temperatures.[35]

of this interaction. In the range of values of τ that satisfy this inequality (rapid rotations), the theoretical spectra obtained with Eq. (3.7) consist of well-resolved hyperfine-structure lines separated by a distance A, in agreement with the experimental facts[35].

2. Slow rotations. As we noted above, the range of slow rotations ($\sigma\tau \gtrsim 1$), where the spectrum becomes much more complicated (see Fig. 2), is of considerable interest. The most general derivation of the relaxation equations, which does not limit τ or state a specific form of the random process describing the reorientations of the radical, was presented in the original papers of Refs. 19–22 and in the collection of Ref. 42. We shall present an intuitive derivation of these equations for certain particular cases of random processes and then generalize the result to an arbitrary process of the Markov type[43].

We consider first the case in which the random process that models the motion of the radical reduces to the following. Let the radical be able to assume only a finite number of orientations $\Omega_1, \Omega_2, \ldots, \Omega_N$, and let it be for a certain time in some definite orientation Ω_k, after which it instantly changes its position, assuming another orientation Ω_j from the given discrete set. To describe this random process, it is necessary to specify two sets of quantities: firstly, the average lifetimes in each orientation, $\tau(\Omega_j)$, $j = 1, \ldots, N(\tau^{-1}(\Omega_j)$ has the meaning of the probability that the orientation Ω_j will change to any other orientation during a unit time), and, secondly, the probability of transition $p(\Omega_j, \Omega_k)$ from some orientation Ω_j to an orientation Ω_k, if it is known that a transition has taken place. It follows from the definition that

$$\sum_{k=1}^{N} p(\Omega_j, \Omega_k) = 1. \qquad (3.8)$$

For a stationary process, $\tau(\Omega_j)$ and $P(\Omega_j, \Omega_k)$ do not depend on time.

If we consider a time interval Δt so small that no more than one reorientation can take place during it, the ratio $\Delta t / \tau(\Omega_j)$ gives the dimensionless probability that the or-

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ientation Ω_j will change during time Δt. A condition for smallness of Δt is the inequality

$$\Delta t \ll \tau(\Omega_j), \quad j = 1,2,...,N. \tag{3.9}$$

Let the radical be in orientation Ω_k at time t and let the value of the Hamiltonian that corresponds to this orientation be $\mathcal{H}(\Omega_k)$. We use $S_+(\Omega_k, t)$ to denote the operator $S_+(t)$ of the radical in position Ω_k. On the basis of Eq. (3.6), we now find the changes of $S_+(\Omega_k, t)$ during a time Δt small enough to satisfy condition (3.9) and the inequality

$$\Delta t \omega_{mn}(\Omega_k) \ll 1, \tag{3.10}$$

where ω_{mn} is any of the allowed frequencies of the Hamiltonian $\mathcal{H}(\Omega_k)$. If the radical, having had orientation Ω_k at time t, retains it throughout the time interval Δt, the equation

$$\frac{dS_+(\Omega_k, t)}{dt} = \frac{i}{\hbar}[\mathcal{H}(\Omega_k), S_+(\Omega_k, t)] \tag{3.11}$$

and condition (3.10) indicate that the value of $S_+(\Omega_k, t)$ at time $t + \Delta t$ equals

$$S_+(\Omega_k, t+\Delta t) = \left\{S_+(\Omega_k, t) + \frac{i}{\hbar}[\mathcal{H}(\Omega_k), S_+(\Omega_k, t)]\Delta t\right\}\left(1 - \frac{\Delta t}{\tau(\Omega_k)}\right). \tag{3.12a}$$

If at time t the radical was in some other orientation Ω_j, it will change to orientation Ω_k during Δt with a probability $p(\Omega_j\Omega_k)\Delta t/\tau(\Omega_j)$. As a result of the transition of the radical to orientation Ω_k from any other orientation Ω_j with the corresponding value of the spin operator $S_+(\Omega_j, t)$ there arises another possibility for variation of $S_+(\Omega_j, t)$ in time:

$$S_+(\Omega_k, t+\Delta t) = \sum_{j \neq k} \frac{p(\Omega_j\Omega_k)}{\tau(\Omega_j)} S_+(\Omega_j, t)\Delta t. \tag{3.12b}$$

Summing (3.12a) and (3.12b) and retaining only terms of the first order in Δt, we find the total change of $S_+(\Omega_k, t)$ during the time Δt:

$$S_+(\Omega_k, t+\Delta t) - S_+(\Omega_k, t)$$
$$= \left\{\frac{i}{\hbar}[\mathcal{H}(\Omega_k), S_+(\Omega_k, t)] - \frac{S_+(\Omega_k, t)}{\tau(\Omega_k)} + \sum_{j \neq k} \frac{p(\Omega_j\Omega_k)}{\tau(\Omega_j)} S_+(\Omega_j, t)\right\}\Delta t. \tag{3.13}$$

Dividing both sides of this equation by Δt and letting $\Delta t \to 0$, we finally obtain the following system of equations for $S_+(\Omega_k, t)$[2]:

$$\frac{dS_+(\Omega_k, t)}{dt} = \frac{i}{\hbar}[\mathcal{H}(\Omega_k), S_+(\Omega_k, t)] - \frac{S_+(\Omega_k, t)}{\tau(\Omega_k)} + \sum_{j \neq k} \frac{p(\Omega_j\Omega_k)}{\tau(\Omega_j)} S_+(\Omega_j, t),$$
$$k = 1, 2, ..., N. \tag{3.14}$$

The initial conditions for $S_+(\Omega_k, t)$ are determined by the probability $\mathcal{P}_k$ of finding the radical in orientation Ω_k at time $t = 0$. They will obviously have the form

$$S_+(\Omega_k, 0) = \mathcal{P}_k S_+. \tag{3.15}$$

The averaged value $\langle S_+(t)\rangle$ over the given random process is found as follows:

$$\langle S_+(t)\rangle = \sum_{k=1}^{N} S_+(\Omega_k, t). \tag{3.16}$$

An equation similar to (3.14) for the density matrix was derived by Johnson,[45] who used it to take chemical exchange into account in solving some nuclear magnetic resonance (NMR) problems[46].

From (3.14) we can pass to an equation that pertains to the more general case of continuous distribution of the possible orientations. Letting $N \to \infty$, we introduce the quantities defined by the following relations:

$$\lim_{\Delta\Omega \to 0} \frac{\sum_i p(\Omega'\Omega_i)}{\Delta\Omega} = f(\Omega'\Omega), \tag{3.17}$$

where $\sum_i p(\Omega'\Omega_i)$ is the sum of the probabilities of transition from Ω' to orientations Ω_i that fall in the range $\Omega, \Omega + \Delta\Omega$, and, similarly,

$$\lim_{\Delta\Omega \to 0} \frac{\sum_i S_+(\Omega_i, t)}{\Delta\Omega} = \bar{S}_+(\Omega, t). \tag{3.18}$$

The function $f(\Omega'\Omega)$ has the meaning of the transition probability density, and the behavior of the radical is now described by the following model: for a certain average time $\tau(\Omega')$, the radical "lives" in a state with orientation Ω' and then with probability $f(\Omega'\Omega)/\tau(\Omega')$ abruptly changes to a new orientation Ω. As a result of this limit transition we obtain an integrodifferential equation for $\bar{S}_+(\Omega, t)$:

$$\frac{d\bar{S}_+(\Omega, t)}{dt} = \frac{i}{\hbar}[\mathcal{H}(\Omega), \bar{S}_+(\Omega, t)] - \frac{\bar{S}_+(\Omega, t)}{\tau(\Omega)} + \int \frac{f(\Omega'\Omega)}{\tau(\Omega')} \bar{S}_+(\Omega', t)d\Omega'. \tag{3.19}$$

The initial condition for (3.19) follows from (3.16) and contains, instead of the probability $\mathcal{P}_k$ the probability density $\mathcal{P}(\Omega) = \lim_{\nabla\Omega \to 0}(\sum_i \mathcal{P}_i/\Delta\Omega)$ as follows:

$$\bar{S}_+(\Omega, 0) = \mathcal{P}(\Omega) S_+, \tag{3.20}$$

and, finally, the average value $\langle S_+(t)\rangle$ over the reorientation process equals

$$\langle S_+(t)\rangle = \int \bar{S}_+(\Omega, t)d\Omega. \tag{3.21}$$

We note that the equations for the spin density matrix that are derived in this way differ from (3.14) and (3.19) only in the sign of the commutator.

3) *Rotational diffusion.* The random process described at the end of the preceding section also includes continuous rotational diffusion as a particular case. In this case, $f(\Omega'\Omega)$ resembles a δ function centered near Ω, and Eq. (3.19) reduces to a differential equation of the Fokker-Planck type (see, for example, Ref. 47).

Let us make certain simplifying assumptions. First, we assume that $\tau(\Omega)$ does not depend on Ω: $\tau(\Omega) = \tau$. Secondly, we assume that the transition probability density $f(\Omega'\Omega)$ depends only on the rotation angle ε that translates the orientation Ω' to Ω (and does not depend on Ω' and Ω): $f(\Omega'\Omega) = f(\varepsilon)$. By definition, the absolute value $|\varepsilon|$ equals the rotation angle, and the direction of ε coincides with that of the axis of rotation. Now the integral term in Eq. (3.19) can be represented in the form

$$\frac{1}{\tau} \int f(\varepsilon)\bar{S}_+(\Omega', t)d^3\varepsilon. \tag{3.22}$$

Here Ω' should be understood to represent only the or-

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[2] This derivation of the equation is a generalization of Kubo's derivation.[44]

ientations that give the orientation Ω after the rotation ε. The random process becomes a diffusion process under two assumptions regarding $f(\varepsilon)$:[48,49] 1) $f(\varepsilon) = f(-\varepsilon)$ and 2) all moments of $f(\varepsilon)$ higher than the second can be neglected.

Let us assume that $\bar{S}_+(\Omega, t)$ as a function of Ω can be expanded in a Taylor series; then on transition from Ω' to Ω it is transformed in accordance with the formula[50]

$$\bar{S}_+(\Omega', t) = \exp(i\varepsilon\vec{\mathscr{J}})\bar{S}_+(\Omega, t), \tag{3.23}$$

where the $\mathscr{J}_\alpha(\alpha = x, y, z)$ are the operators of infinitesimally small rotations and coincide with the angular-momentum operators ($\hbar = 1$). Substituting (3.23) into (3.19) after modifying the latter in accordance with (3.22), we find

$$\frac{d\bar{S}_+(\Omega, t)}{dt} = \frac{i}{\hbar}[\mathscr{H}(\Omega), \bar{S}_+(\Omega, t)] - \frac{\bar{S}_+(\Omega, t)}{\tau} + \frac{1}{\tau}\int f(\varepsilon)\exp(i\varepsilon\vec{\mathscr{J}})\bar{S}_+(\Omega, t)\, d^3\varepsilon. \tag{3.24}$$

Expanding $\exp(i\varepsilon\vec{\mathscr{J}})$ in powers of ε_α and retaining series terms up to and including the second powers, we obtain

$$\frac{\partial\bar{S}_+(\Omega, t)}{\partial t} = \frac{i}{\hbar}[\mathscr{H}(\Omega), \bar{S}_+(\Omega, t)] - \mathscr{J}_\alpha D_{\alpha\beta}\mathscr{J}_\beta\bar{S}_+(\Omega, t), \tag{3.25}$$

where

$$D_{\alpha\beta} = \frac{1}{2\tau}\int d^3\varepsilon\,\varepsilon_\alpha\varepsilon_\beta f(\varepsilon). \tag{3.26}$$

The aggregate of the $D_{\alpha\beta}$ is the radical's rotational-diffusion tensor, and the last term in (3.25) takes into account the influence of the rotational diffusion on the behavior of the spin system. The quantity $S_+(\Omega, t)$ has the meaning of the spin operator averaged over the rotational-diffusion process. However, this is not a complete averaging, since this quantity retains the dependence on the values Ω of the spin orientation at time t. According to (3.21), we obtain the fully averaged value of the spin operator $\langle S_+(t)\rangle$ by integrating $\bar{S}_+(\Omega, t)$ over all orientations Ω.

In a case that occurs often, the rotational-diffusion tensor is spherically symmetric, $D_{\alpha\beta} = D\delta_{\alpha\beta}$, and Eq. (3.25) assumes the form

$$\frac{\partial\bar{S}_+(\Omega, t)}{\partial t} = \frac{i}{\hbar}[\mathscr{H}(\Omega), \bar{S}_+(\Omega, t)] + D\nabla_\Omega^2\bar{S}_+(\Omega, t), \tag{3.27}$$

where ∇_Ω^2 is the Laplace operator. In general form, Eq. (3.25) describes the spin relaxation of a radical in anisotropic rotation. Anisotropy of rotation arises as a result of nonsphericity of the molecule[51,52] or because of anisotropy of the medium[53]. In the most general case, the anisotropic diffusion describes the rotation of a nonspherical molecule in an anisotropic medium.

c) Formulation of a general method for derivation of relaxation equations

The relaxation equations (3.14), (3.19), and (3.25) derived above are conveniently represented in the general form

$$\frac{d\bar{S}_+(\Omega, t)}{dt} = \frac{i}{\hbar}[\mathscr{H}(\Omega), \bar{S}_+(\Omega, t)] - L_\Omega\bar{S}_+(\Omega, t). \tag{3.28}$$

The last term in the equation, which contains the operator L_Ω, takes into account the influence of lattice-coordinate motion on the spin system. The specific form of this operator is determined by the type of random process that models the lattice motion. Namely,

$$L_\Omega = \left\{\frac{1}{\tau(\Omega)} - \int\frac{f(\Omega'\Omega)}{\tau(\Omega')}\dots d\Omega'\right\}, \tag{3.29a}$$

if the radical can assume all orientations from a continuous set and change its orientation through an arbitrary angle during an infinitesimally short time;

$$L_\Omega = \mathscr{J}_\alpha D_{\alpha\beta}\mathscr{J}_\beta \tag{3.29b}$$

in the case of rotational diffusion; and, finally,

$$L_\Omega = \{L_{jk}\},\quad L_{jk} = \begin{cases} -P(\Omega_j\Omega_k)/\tau(\Omega_j) & \text{when } j \neq k, \\ 1/\tau(\Omega_k) & \text{when } j = k, \end{cases} \tag{3.29c}$$

if the orientations that the radical can assume form a set of discrete values.

We note that Eq. (3.28) differs from the original equation (3.6) in that its Hamiltonian does not depend on the time. It is easily shown that the operator L_Ω determines the time variation of the probability density $\mathscr{P}(\Omega, t)$ that the radical will have orientation Ω at time t:

$$\frac{d\mathscr{P}(\Omega, t)}{dt} = -L_\Omega\mathscr{P}(\Omega, t). \tag{3.30}$$

The correspondence shown here between Eq. (3.30) for the probability density and Eq. (3.28) can be generalized to the case of an arbitrary Markov process,[43] and the method for derivation of the relaxation equations can be formulated as follows.

If the distribution function of the random Markov process that describes the molecular motion is described by an equation that can be written in the form (3.30), the relaxation equation for the incompletely averaged spin operator $\bar{S}_+(\Omega, t)$ has the form (3.28) or, similarly, the equation for the partial density matrix $\rho(\Omega, t)$[3] of the spin system can be written in the form

$$\frac{\partial\rho(\Omega, t)}{\partial t} = -\frac{i}{\hbar}[\mathscr{H}(\Omega), \rho(\Omega, t)] - L_\Omega\rho(\Omega, t). \tag{3.31}$$

The method developed is based on two assumptions. The first and strongest is that we ignore the effect of the spin system on the dynamics of the lattice. Secondly, in studying the influence of the lattice on the spin system, we assume that its dynamics is described with the aid of classical mechanics, since the motion of its coordinates is described with the aid of the random-path concept.

It follows from the first assumption that the quantum of energy $\hbar\omega$ transferred from the spin system to the lattice must be small, $\hbar\omega \ll kT$.[4] In fact, since we are discussing a situation in which the characteristic relaxation times of the spin and lattice coordinates are comparable, it is difficult to imagine how a sufficiently

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[3] The value $\langle\rho(t)\rangle$, which is fully averaged over the molecular motion, is related to $\rho(\Omega, t)$ by $\langle\rho(t)\rangle = \int\rho(\Omega, t)\, d\Omega$.

[4] This inequality is practically always satisfied under NMR and EPR conditions. For example, the quantum energy does not exceed 1 °K under ordinary EPR experimental conditions ($H \sim 10^3$ G).

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large quantum $\hbar\omega \gtrsim kT$ would not disturb (at least locally) the state of the lattice, and how this, in turn, would not affect the spin system. However, the final answer to the question as to how necessary the condition $\hbar\omega \ll kT$ is in order to be able to neglect the effect of the spin-system on the lattice can evidently be obtained only from a microscopic analysis. The paper by Bukhbinder, Kessel' and Khazanovich,[54] in which an equation similar to (3.31) was derived from a microscopic analysis of the lattice degrees of freedom, is interesting from this standpoint. This equation was derived on the assumptions that the condition $\hbar\omega \ll kT$ is satisfied, quasiclassical description of the "slow" lattice coordinates is admissable, and the correlation times of the velocities of the slow motions are small enough so that a coordinate description of the lattice motion is admissible. This demonstrated the sufficiency of $\hbar\omega \ll kT$ for derivation of Eq. (3.31), although the necessity of this condition was not proven.

The method discussed here for description of relaxation processes in spin systems bound to the lattice is based on the concept of integration over the paths (the Wiener integral[55]). Actually, a paramagnetic particle (radical, ion, molecule with magnetic nuclei) is acted upon not only by the external field, but also by the internal magnetic fields created by the molecular surrounding and by intermolecular interaction. The magnetic interaction depends both on the orientation of the particular magnetic-moment carrier in the external magnetic field and on its position relative to the surrounding molecules. Therefore the internal fields depend on the configurational coordinates of the paramagnetic particle, and, as a result of its motion, the particle's magnetic moment becomes a functional of its path. But since we observe the total magnetic moment of all molecules in an experiment, its evolution is determined by the entire set of molecular paths. Assuming statistical motion of the particle in the liquid, we choose an appropriate random process as a model of its motion. Averaging over the realizations of the random process is equivalent to integrating over the random paths.

Therefore the spin-relaxation description procedure based on Eqs. (3.31) might be called the random-path method. This method is sometimes referred to in the literature as the method of the stochastic Liouville equation. This name reflects the fact that the ordinary Liouville operator in Eq. (3.31) for the spin density matrix, the operator that describes fully the time variation of all coordinates and momenta of the lattice, is replaced by an operator that describes the stochastic nature of the magnetic molecule's motion. Therefore an approximate description of the molecular motion is used in this method, but its influence on the spin variables of the particle is taken into account exactly.

4. USE OF THE RANDOM-PATH METHOD IN CALCULATING THE EPR SPECTRA OF STABLE RADICALS

Use of the basic equation (3.31) for analysis of EPR spectra is most effective in the range of slow molecu-

lar motions ($\sigma\tau \gtrsim 1$), which is inaccessible to theoretical analysis on the basis of the Bloch-Redfield equations.

It is in this range that the shape of the EPR spectra is most "sensitive" to variation of the parameter τ, which characterizes the rate of the molecular motion. This was confirmed by the very first calculations of spectra that were performed by various authors[16-18,33,56,57] by the random-path method. The resulting theoretical spectra of stable radicals[33,56-59] and triplet molecules (ions)[18] duplicate the basic features of the experimentally observed lines and correctly reflect the changes in the experimental spectra with temperature as the parameter τ is varied (see, for example, Fig. 2). By comparing calculated and experimental spectra, we can estimate the mobility of the radicals in the temperature range in which τ varies in the range 10^{-9}–10^{-7} sec.

The form and methods of solution of the relaxation equations (3.29) and (3.31) are determined by the form of the operator L_Ω, which describes the variation of the coordinates responsible for relaxation. However, the Bloch-Redfield equations imply that in the range of rapid rotations the relaxational widths of the Lorentz spectral components depend only on the parameter of the model that characterizes the intensity of the rotations and not on the specifics of the reorientation process. It has been shown[20-22,24,25] that the shape of the calculated EPR lines begins to depend noticeably on the model of radical motion in the range $\sigma\tau \sim 1$. Therefore detailed comparison of the calculated with the experimental spectra and analysis of the results of comparison over the entire range of variation of the observed lines with temperature could, in principle, provide the answer to the question as to which radical-motion model can be used to best advantage in a given medium. The studies of Refs.[26,58,59] were devoted to the solution of this problem.

Before turning to an exposition of the principal content of these studies and of the methods developed for solving the relaxation equations, let us consider some models of random radical motions which after comparison with experimental data were discussed in the papers cited above as being competitive.

a) Some radical-reorientation models

The three models that will be discussed under this heading describe random rotations of a spherically symmetric molecule in an isotropic medium.

The Debye rotational diffusion model (A) assumes continuous variation of the variables Ω. The relaxation equation (3.27) with the operator $D\Delta_\Omega^2$ corresponds to this model.

The simplest variant of the model in which the orientations change abruptly was proposed by Korst.[22] This is the model of uncorrelated jumps (B), which assumes that the molecule has some fixed orientation Ω' during an average time τ_a; it then changes it instantaneously by a (jump) to a new orientation Ω, with jumps through various angles being equiprobable, i.e., there is no correlation between the two successive

orientation values Ω' and Ω. The relaxation equation corresponding to this model is derived from the general form (3.19) by putting $\tau(\Omega) = \tau_a$ (the molecule exists for the same time on the average in any given orientation) and $f(\Omega'\Omega) = 1/8\pi^2$ (the model assumes any orientation with equal probability irrespective of the preceding orientation):

$$\frac{d\overline{S}_+(\Omega, t)}{dt} = \frac{i}{\hbar} [\mathscr{H}(\Omega), \overline{S}_+(\Omega, t)] - \frac{S_+(\Omega, t)}{\tau_c} + \frac{1}{8\pi^2} \langle S_+(t)\rangle. \qquad (4.1)$$

The model that has come to be known as the free-diffusion model (C)[26] assumes that the molecule rotates freely (executes inertial motion) during the average time between two successive orientation changes by jumps. A mathematical description of this model will be discussed somewhat later.

Below we shall set forth a general approach to the solution of the relaxation equations. It is based on expansion of the solution in eigenfunctions of the operator L_Ω.

The eigenfunctions of the random-rotation operator [see, for example, (3.29a) with $\tau(\Omega) = \tau$] are generalized spherical functions $D_{m,n}^{(l)}(\Omega)$[49,60]. This means that

$$L_\Omega D_{m,n}^{(l)}(\Omega) = E_{l, m, n} D_{m,n}^{(l)}(\Omega), \qquad (4.2)$$

where $E_{l, m, n}$ are eigenvalues of the operator L_Ω. If the rotation is isotropic, the values of $E_{l, m, n}$ depend only on the index l: $E_{l, m, n} = E_l$.

The eigenvalues of the operator $D\nabla_\Omega^2$ [model (A)] are determined by the formula

$$E_l^D = l(l+1)D. \qquad (4.2a)$$

It is easily verified that the operator L_Ω^{jp} of the uncorrelated-jump model (see (4.1))

$$L_\Omega^{jp} = \frac{1}{\tau_a}\left(1 - \frac{1}{8\pi^2}\int \dots d\Omega\right) \qquad (4.3)$$

has eigenvalues of the form

$$E_l^{jp} = \tau_a^{-1}(1 - \delta_{l0}). \qquad (4.2b)$$

These molecular-reorientation models (A and B) are Markov-type processes. If we treat the changes in the position of the particle in diffusion phenomena or Brownian motion as a Markov process, this means that we do not take into account the inertia of the particle and it is sufficient to introduce only angular coordinates to describe its random rotations. Model C includes in the analysis inertial motion of the particle between two successive collisions with surrounding molecules. This model cannot be described in terms of a Markov process in coordinate space. This situation can be corrected by going over to Markov processes in the phase space of the particle. Use of the Fokker-Planck equation in the space of angular velocities and orientation coordinates[61] is an example of this approach to the description of rotational diffusion in EPR problems.

Goldman et al.,[58] who used the free-diffusion model (C) in calculating EPR spectra, specified this model formally by a set of eigenvalues:

$$E_l^{f.d.} = \frac{l(l+1)D}{\sqrt{1 + l(l+1)D\tau_a}}. \qquad (4.2c)$$

This mathematical formulation of the model is based on a rough estimation of the linewidth $\Delta\omega_l \approx E_l$,[62] which is defined by the Fourier transform of the correlation function of the Legendre polynominals $P_l[\cos\theta(t)]$. In calculating $\Delta\omega_l$, Goldman et al.[58] proceeded from the model discussed by Sack,[63] which takes particle inertia into account in a rough approximation. Later, Bruno and Freed[64] analyzed these approximations and showed on a simple example of a spectrum without hyperfine structure, calculated in the approximation of model (4.2c), that this approximation results, fortunately in an insignificant deviation from the spectra stemming from the model of Fixman,[61] which takes inertial effects into account correctly.

b) Methods of solving the relaxation equations

1) *The adiabatic approximation.* Several authors[16-18] have used the adiabatic approximation in solving the relaxation equations. Let us briefly describe this method of solution as it applies to the situation described by the Hamiltonian (2.5).

We represent the Hamiltonian (2.5) in the form

$$\mathscr{H}(\Omega) = S_z \mathscr{H}_I(\Omega), \qquad (4.4)$$

where

$$\mathscr{H}_I(\Omega) = \hbar [a(\Omega) + a_0(\Omega)I_z - a_{-1}(\Omega)I_1^+ - a_{+1}(\Omega)I_1^{-1}]. \qquad (4.5)$$

Let $\varepsilon_j(\Omega)$ be the eigenvalues of the Hamiltonian $\mathscr{H}_I(\Omega)$ (j assumes $2I+1$ values). Instead of the Hamiltonian (4.4), we substitute Hamiltonians of the form

$$\mathscr{H}_j(\Omega) = \hbar S^z \omega_j(\Omega),$$

into Eq. (3.29), with $\omega_j(\Omega) = \varepsilon_j(\Omega)/\hbar$. We obtain the equations

$$\frac{d\overline{S}_+^{(j)}(\Omega, t)}{dt} = [i\omega_j(\Omega) - L_\Omega]\overline{S}_+^{(j)}(\Omega, t), \qquad j = 1, 2, \dots, (2I+1). \qquad (4.6)$$

Now instead of the system of coupled equations that arises from (3.28) when the Hamiltonian (4.4) is used, we solve a system $2I+1$ independent equations (4.6). We then find the unknown $\overline{S}_+(\Omega, t)$ as the sum of the partial values $\overline{S}_+^{(j)}(\Omega, t)$:

$$\overline{S}_+(\Omega, t) = \sum_j S_+^{(j)}(\Omega, t). \qquad (4.7)$$

This substitution is legitimate only for rather slow molecular motions, $\sigma\tau \gg 1$, when the characteristic frequencies of variation $\omega_j(\Omega)$ in the variation of Ω are much smaller than the difference $\omega_j - \omega_k$. Therefore the error introduced by the adiabatic approximation becomes smaller the slower is the motion of the molecules. In the limiting case of completely "frozen" motions, the solution (4.7) is the exact solution of system (4.6). The physical content of the adiabatic approximation consists of the fact that the transitions between sublevels of the hyperfine interaction that are induced by the molecular motion can be neglected.

2) *General method for solution of relaxation equations.* The operators S_+ and S_- appear in expression (3.5) for the line shape. The only nonzero matrix elements $(+|S_+|-)$ of the operator S_+ corresponds to the electron spin transition $-1/2 \to 1/2$. Similarly, the element $(-|S_-|+)$ corresponds to the electron-spin transition from the state $1/2$ to the state $-1/2$.

Since only terms secular in S_z have been left in the spin Hamiltonian (2.5), the relaxation equations for the operator functions $\overline{S}_+(\Omega, t)$ and $\overline{S}_-(\Omega, t)$ are independent. However, the matrix elements $\overline{S}_+(\Omega, t)$ (and similarly for $\overline{S}_-(\Omega, t)$) that correspond to various initial and final nuclear-spin states are related to one another, since the Hamiltonian (2.5) contains terms with the operators $I_1^{\pm 1}$. The number of spin states with fixed electron-spin projections and different nuclear-spin projections is $2I+1$. Therefore the number of matrix elements $[m_I' + |\overline{S}_+(\Omega, t)| m_I -]$ of the operator $\overline{S}_+(\Omega, t)$ that correspond to the electron-spin transition $-1/2 \to 1/2$ and differ in the initial m_I and final m_I' spin states of the nucleus is $(2I+1)^2$. This number determines the dimension of the system of coupled equations for the matrix elements $\overline{S}_+(\Omega, t)$ that is obtained from the operator equation (3.28). In the simplest situation, in which the nuclear spin is $1/2$ (nitroxyl radical with the rare isotope $N^{15}{}^{59}$), Eq. (3.28) becomes a system of four equations. We shall set forth the method of solving the relaxation equations with this radical as an example.

We introduce the following notation for the matrix elements of the electron-spin transition $|-) \to (+|$, which differ in the nucleus indices ($m_I = \pm 1/2$):

$$u_+ = \left(\tfrac{1}{2}, \ + | \overline{S}_+(\Omega, t) | \tfrac{1}{2}, \ -\right),$$
$$u_- = \left(-\tfrac{1}{2}, \ + | \overline{S}_+(\Omega, t) | -\tfrac{1}{2}, \ -\right),$$
$$v^{(1)} = \tfrac{1}{2}(u_+ + u_-), \qquad v^{(2)} = \tfrac{1}{2}(u_+ - u_-),$$
$$v^{(3)} = \left(-\tfrac{1}{2}, \ + | \overline{S}_+(\Omega, t) | \tfrac{1}{2}, \ -\right),$$
$$v^{(4)} = \left(\tfrac{1}{2}, \ + | \overline{S}_+(\Omega, t) | -\tfrac{1}{2}, \ -\right).$$

$$(4.8)$$

We write the system of equations for the $v^{(i)}$ ($i = 1, 2, 3, 4$) obtained from the operator equation (3.28) in matrix form:

$$\frac{dv(\Omega, t)}{dt} = [i\mathcal{L}(\Omega) - L_\Omega] v(\Omega, t); \qquad (4.9)$$

here the matrix $\hat{\mathcal{L}}(\Omega)$ has the form

$$\hat{\mathcal{L}}(\Omega) = \begin{pmatrix} a & a_0/2 & -a_{-1}/2 & -a_{+1}/2 \\ a_0/2 & a & 0 & 0 \\ a_{+1}/2 & 0 & a & 0 \\ a_{-1}/2 & 0 & 0 & a \end{pmatrix}, \qquad (4.10)$$

and the components of the vector $v(\Omega, t)$ are composed of the matrix elements $v^{(1)}$, $v^{(2)}$, $v^{(3)}$, and $v^{(4)}$:

$$v(\Omega, t) = \begin{pmatrix} v^{(1)}(\Omega, t) \\ v^{(2)}(\Omega, t) \\ v^{(3)}(\Omega, t) \\ v^{(4)}(\Omega, t) \end{pmatrix}, \qquad v(\Omega, 0) = \frac{1}{8\pi^2}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \qquad (4.11)$$

The initial conditions for $v(\Omega, t)$ follow from the definition (4.8) and formula (3.20).

Applying the Laplace transformation

$$q(\Omega, \omega) = \frac{1}{2\pi} \int_0^\infty v(\Omega, t) e^{-i\omega t} dt, \qquad (4.12)$$

to Eq. (4.9), we find

$$i\omega q(\Omega, \omega) = [i\hat{\mathcal{L}}(\Omega) + L_\Omega] q(\Omega, \omega) + \frac{1}{2\pi} v(\Omega, 0). \qquad (4.13)$$

We note that $Sp\{S_-\langle S_+(t)\rangle\}$ in formula (3.5) can be expressed as follows in terms of the matrix elements (4.8):

$$\text{Sp}\{S_-\langle S_+(t)\rangle\} = \int (- | S_- | +) v^{(1)}(\Omega, t) \, d\Omega = \int v^{(1)}(\Omega, t) \, d\Omega.$$

Therefore the shape $\mathscr{F}(\omega)$ (3.5) of the resonance line is expressed in terms of the component $q^{(1)}(\Omega, \omega)$ of the vector $q(\Omega, \omega)$:

$$\mathscr{J}(\omega) = \text{Re} \int [q^{(1)}(\Omega, \omega) + q^{(1)}(\Omega, -\omega)] \, d\Omega. \qquad (4.14)$$

The elements of the matrix $\hat{\mathcal{L}}(\Omega)$ [see 4.10) and (2.6)] are expressed in terms of the generalized spherical functions $D^{(2)}_{m,n}(\Omega)$. It is therefore natural to seek the solution of (4.13) in the form of an expansion in terms of the complete set of orthogonal functions $D^{(l)}_{m,n}(\Omega)$, which are eigenfunctions of the operator L_Ω:

$$q(\Omega, \omega) = \sum_{l, m, n} C_{l, m, n}(\omega) D^{(l)}_{m, n}(\Omega). \qquad (4.15)$$

Substituting (4.15) into Eq. (4.13) and applying relation (4.3) and the orthogonality property

$$\int D^{(l)}_{m, n}(\Omega) D^{(l')*}_{m', n'}(\Omega) \, d\Omega = \frac{8\pi^2}{2l+1} \delta_{ll'} \cdot \delta_{mm'} \cdot \delta_{nn'}, \qquad (4.16)$$

we obtain

$$\frac{i}{2l+1}(\omega - iE_l) C_{l, m, n} - \sum_{l_1 m_1 n_1} \int D^{(l)*}_{m, n}(\Omega) D^{(l_1)}_{m_1, n_1}(\Omega) \mathcal{L}(\Omega) C_{l_1, m_1, n_1}$$
$$= -\frac{i}{16\pi^3} \delta_{l, 0}. \qquad (4.17)$$

Evaluating the integrals with the aid of the relation

$$\int D^{(l_1)}_{m_1, n_1}(\Omega) D^{(l_2)}_{m_2, n_2}(\Omega) D^{(l_3)}_{m_3, n_3}(\Omega) \, d\Omega = 8\pi^2 \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} \qquad (4.18)$$

(the expressions in parentheses are $3j$ symbols[65]), we obtain an infinite chain of algebraic equations for the coefficients $C^{(i)}_{l, m, n}$ in the expansion (4.15), where i labels the components of the vector $C_{l, m, n}$.

Only the coefficient $C^{(1)}_{0, 0, 0}$ appears in the expression for the line shape $\mathscr{J}(\omega)$ (4.14), as is easily verified by integrating the series (4.15) over the angles. Since, in the approximation of axial symmetry of the HFI tensor, the elements of the matrix $\hat{\mathcal{L}}(\Omega)$ [see (2.6)] contain only the functions $D^{(2)}_{m, n}(\Omega)$ with $m = 0, \pm 1$, only the coefficients $C^{(i)}_{l, m, n}$ with $m = 0, \pm 1$ turn out to be coupled to $C^{(1)}_{0, 0, 0}$ by the algebraic system (4.17). Therefore the coefficients of the series (4.15) have the structure

$$C_{l, m, n}(\omega) = \begin{pmatrix} C^{(1)}_{l, n}(\omega) \, \delta_{m, 0} \\ C^{(2)}_{l, n}(\omega) \, \delta_{m, 0} \\ C^{(3)}_{l, n}(\omega) \, \delta_{m, 1} \\ C^{(4)}_{l, n}(\omega) \, \delta_{m, -1} \end{pmatrix}. \qquad (4.19)$$

The infinite chain of algebraic equations (4.17) for the coefficients (4.19) is usually solved by numerical methods with the aid of computer.[5] The rate of convergence of the series (4.15) and, consequently, the dimension of the finite equation system that approximates the infinite system, depend on E_l. At a given intensity, the series converges more rapidly for the Debye model

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[5] It is not necessary to seek the solution of Eq. (4.13) in the form of the expansion (4.15) for the uncorrelated-jump model. It is much simpler to find the solution of the integral equation derived from (4.13) with L_Ω^H in the form (4.3). Owing to the simple form of the integral operator (4.3), the equation is reduced to a system of four algebraic equations for the $q^{(i)}(\omega)$ ($i = 1, 2, 3, 4$).[22,59]

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(4.2a) and convergence deteriorates with decreasing parameters $1/\tau_a$ and D regardless of the model.

The method set forth above (which is the same for the various models) for solving relaxation equations is applicable in principle to a spin system of any number of states. The system of algebraic equations for the coefficients in the expansion (4.15) was written out in detail in the paper of Ref.[58] for a radical in which the spin of a nucleus interacting with an electron equals 1. Figure 2 shows experimental and theoretical spectra of such a radical as obtained for the uncorrelated-jump model.[35] Examples of spectra calculated for other rotation models will be given in later sections.

c) Characteristic parameters of spectra as functions of correlation time of rotations

To compare experimental and calculated EPR spectra, it is helpful to find a theoretical relation between some spectral parameters and the model parameter characterizing the rate of rotation (calibration curves).

As we noted above, the rate of reorientation of a particle is usually characterized by the rotation correlation time τ (see, for example, Ref. 49). The average τ_a spent by the radical in a state with a fixed orientation in the jump model agrees by definition with the correlation time τ that figures in Redfield's theory[4]. In the continuous-diffusion model, there is no such direct correspondence between the model parameter and correlation time τ. In the limit of very rapid rotations, when the main contribution to the width of the Lorentz lines comes from the eigenvalue E_l^D with $l=2$, the quantity $\tau_D = 1/6D$ appears in the expression for the line shape in the same way as τ. For this reason, it can be expressed as a parameter characterizing the intensity of rotations in the continuous-diffusion model, and in a formulation without regard to model it is also customary to define the rotation correlation time by the formula

$$\tau = E_2^{-1}. \tag{4.20}$$

The spectral parameters sensitive to variation of τ that have been used in various studies are related in one way or another to the shift of the outer extremums of the derivative of an absorption line $d\mathfrak{I}(\omega)/d\omega$ (see Fig. 2). For example, Kuznetsov et al.[66] introduce the parameter

$$K = \frac{H_{+1}(\tau) - H_{+1}(\tau \to 0)}{H_{+1}(\tau \to \infty) - H_{+1}(\tau \to 0)} \cdot 100. \tag{4.21}$$

The quantity $H_{+1}(H_{-1})$ defines the position (in gauss) of the outermost extremum, which corresponds to $m_I = 1$ ($m_I = -1$). The strength of the constant magnetic field H is varied in experiments at a fixed alternating-field frequency. Therefore the extremum with $m_I = 1$ lies in lower fields ($H_{+1} < H_{-1}$). In the range $3 \cdot 10^{-9} \lesssim \tau \lesssim 10^{-8}$ sec, the high-field extremums ($m = -1$) of EPR spectra are indistinct (see Fig. 2), so that the shift of this extremum is measured less accurately in experiments. The low-field ($m_I = 1$) extremum is sharper throughout the entire range of τ. The normalized shift of this extremum from its position in the limit of very rapid rotations ($\tau \to 0$) (4.21) has been used[66] as a spec-
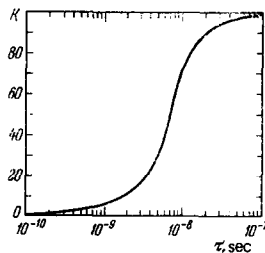

FIG. 3. Spectral parameter K vs. rotation correlation time.[66]

tral parameter that is convenient for measurements. Figure 3 shows a $K(\tau)$ relation calculated for the uncorrelated-jump model (4.3).[66]

The distance $2A'_{tt}$ between the outermost extremums of the absorption-line derivative $d\mathfrak{I}(\omega)/d\omega$ varies for a nitroxyl radical (with N^{14}) from $2A$ for very rapid rotations to $2A_{tt}$ for completely "frozen" rotations. Therefore $2A'_{tt}$, which equals the "peak-to-peak amplitude" of the spectrum and varies monotonically with τ, can also be taken as a characteristic spectral parameter for construction of the calibration curve. Thus, Freed et al.[67] introduced the dimensionless quantity

$$S = \frac{A'_{tt}}{A_{tt}} = \frac{H_{-1}(\tau) - H_{+1}(\tau)}{H_{-1}(\tau \to \infty) - H_{+1}(\tau \to \infty)} \tag{4.22}$$

and proposed that the theoretical $S(\tau)$ relation be used to mark experimental spectra with the parameter τ. $S(\tau)$ was calculated in the approximation of axially symmetric HFI and Zeeman-interaction tensors. The possibility of using this approximation to compute the $S(\tau)$ calibration curve was based on the argument that the anisotropic part of the magnetic interactions affects for the most part the shape of the central component ($m = 0$) and has little influence on the outer extremums of the absorption-line derivative.

McCalley, Shimshick, and McConnell[68] used $\Delta H_{\pm1}(\tau)$— the shifts of the outer extremums with respect to their positions for completely "frozen" rotations—as calibration parameters:

$$\Delta H_{\pm1}(\tau) = H_{\pm1}(\tau \to \infty) - H_{\pm1}(\tau). \tag{4.23}$$

The solid curves in Fig. 4 represent these parameters as functions of τ for a Brownian rotational-diffusion model. McCalley et al. used the adiabatic approximation in solving the relaxation equations.
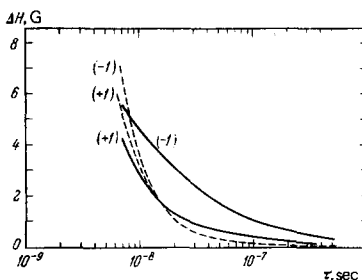
The dashed curves in the same figure represent the

FIG. 4. Shifts $\Delta H_{\pm1}$ of outer extremums of nitroxyl-radical spectrum vs. correlation time τ in the range of slow isotropic rotations. The dashed curves represent jumpwise Brownian rotation,[66] and the solid curves diffusional rotation.[68]

$\Delta H_{*1}(\tau)$ relations found by Kuznetsov *et al.*[66] for the uncorrelated orientation-jump model.

Figures 3 and 4 show that the calibration parameters remain practically constant as τ varies in the range $\tau \gtrsim 10^{-7}$ sec. The $S(\tau)$ relation is also of a similar nature. This makes it difficult to estimate the intensity of radical rotation from the observed spectra in this range. Accordingly, Mason and Freed[69] proposed using the parameters $W_i(i=\pm 1)$, which are equal to the ratios of the widths (at half-height) of the outer extremums to their values as $\tau \to \infty$. However, these parameters depend strongly on the magnitude of the unresolved HFS. In the view of these authors, use of the series of relations between $(W_i - 1)$ and τ that they computed for various values of δ would broaden the range of measurement of τ to $5 \cdot 10^{-6}$ sec.

Huang and Kivelson[70] proposed an original method for selection of calibration parameters. It is based on the formalism developed in Ref. 13 for solving the basic relaxation equation, whence it follows that the function $\mathcal{J}(\omega)$ can be represented in the form

$$\mathcal{J}(\omega) = \sum_j \frac{A_j T_j}{1 + (\omega - \omega_j - \sigma_j)^2 T_j} + \frac{B_j T_j^2 (\omega - \omega_j - \sigma_j)}{1 + (\omega - \omega_j - \sigma_j)^2 T_j} ; \qquad (4.24)$$

here $i(\omega - \omega_j - \sigma_j) + (1/T_j)$ are the eigenvalues of the operator defined by the right-hand side of Eq. (3.27), and the amplitudes A_j and B_j are expressed in terms of the eigenfunctions of the same operator. A theoretical investigation was carried through for the case in which there is no hyperfine interaction and the line shape is governed by the anisotropy of the axially symmetric g-factor. It was found that the line shape of the highest-intensity spectral component is accurately described by the first term of the sum in (4.24). Thus, the shape of the "principal" line (or at least its extremum part, excluding the wings) can be described by the formula

$$\mathcal{J}_0(\omega) = \frac{\mathcal{A}_0 T_0}{1 + (\omega - \omega_0 - \sigma_0)^2 T_0} + \frac{B_0 T_0^2 (\omega - \omega_0 - \sigma_0)}{1 + (\omega - \omega_0 - \sigma_0)^2 T_0} . \qquad (4.25)$$

Therefore the "principal" line of the spectrum is described as a Lorentz line (first term) with the addition of a dispersion-type term (the authors refer to this combination as a generalized Lorentz line). The half-width T_0^{-1} and shift σ_0 of the "principal" line and its asymmetry parameter $B_0/\mathcal{A}_0$ are convenient calibration parameters. They vary appreciably with variation of $\tau_D = 1/6D$ all the way up to $\tau_D \sim 10^{-7}$ sec. This choice has merit in the lucid physical interpretation of the parameters, which are related naturally to the structure of the solution. However, the experimental verification of the proposed method can be accepted as being only qualitative, since the parameters of the radical chosen by the authors of this paper did not conform adequately to the theoretical model.

d) Influence of nature of radical-reorientation process on shape of EPR spectra

1. *Isotropic-rotation models. Comparison with experiment.* Goldman, Bruno, Polnaszek, and Freed[58]

investigated the nature of the motion of the PADS[6] radical in various media (water-glycerine mixture, ice, and deuterated ice). Since the shape of the observed lines of the radical in ice varies with increasing temperature from the characteristic shape for "frozen" rotations to the shape corresponding to rotation at maximum speed, Goldman *et al.*[58] conclude that PADS rotates quite rapidly in cavities formed in the ice.

The hyperfine splitting of the spectrum of the inorganic PADS radical is governed, as in the case of the nitroxyl radicals, by the interaction between the spin of the unpaired electron and the spin of the nitrogen nucleus. However, PADS does not contain hydrogen atoms, and therefore the amount of unresolved HFS of this radical is much smaller than for most nitroxyl radicals. For the same reason, it is smaller in deuterated ice (D_2O) than in ordinary ice, and varies from 0.2 G in the range of rapid rotations to 1.1–1.5 G in the absence of rotation. The decrease of the contribution of the residual width δ to the relaxational linewidths enables us to determine both the values of the g- and A-tensor components and the nature of the radical's rotation with greater accuracy. In fact, the increase in the amount of unresolved HFS results in smoothing out subtle details of the spectrum and thereby lowers the "sensitivity" of the spectrum to the nature of this rotation.

Spectra of the PADS radical were calculated for two random-rotation models—continuous (A) and free (C) diffusion. The authors found the free-diffusion model preferable on the basis of comparison of curves found by the above method with experimental spectra[7] observed at various temperatures of the media studied. Curves 1 in Figs. 5 and 6 demonstrate the results of superposition of the spectrum observed at $T = -60\,°C$ in deuterated ice on the theoretical spectra of models A (Fig. 5) and C (Fig. 6). We note that the deviation of the theoretical from the observed spectrum in the ranges from -20 to -10 G and from 15 to 25 G is significantly smaller in the case of model C as compared to model A.

Nitroxyl radicals with the rare isotope N^{15} in a water-glycerine mixture were chosen by Antsiferova *et al.*[59] as objects for experimental and theoretical study of the influence of the model on the shape of the spectra. In the rapid-rotation range this system was first studied by Stryukov and Rozantsev.[71] They showed that the conditions for rotational isotropy are satisfied in the water-glycerine mixture for these radicals. Antsiferova *et al.*[59] proposed that a model of a spherical radical rotating in an isotropic medium could also be used in the range of slow rotations. The difference between the theoretical spectra of the two models—continuous diffusion (A) and uncorrelated jumps (B)—was

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[6]PADS is potassium nitroxyldisulfonate, an inorganic nitroxyl radical often known as Fremy's salt.

[7]We do not discuss methods and criteria for selection of the theoretical spectrum most appropriate to the experimental spectrum, instead referring the reader to the original papers cited here and below.[58,59]
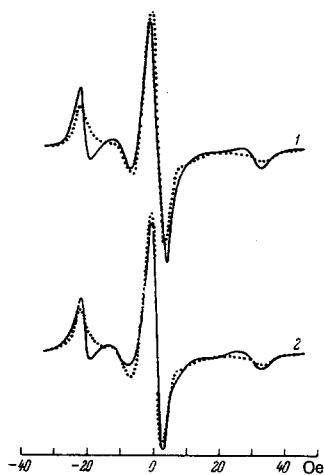
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FIG. 5. Comparison of experimental and theoretical spectra.[58] The dotted curves represent the experimental spectrum of the PADS radical in deuterated ice at $T = -60\,°C$, and the solid curves the theoretical spectra of the models: Diffusional isotropic rotation $(1)(\bar\tau = 6\sqrt{2/3}(\beta gH/\hbar)(E_2^0)^{-1} = 15)$ and axially symmetric diffusional rotation with an anisotropy factor $N = 3$ $(2)(\bar\tau_{\bar D} = 6\sqrt{2/3}(\beta gH/\hbar)\tau_{\bar D} = 15)$.

investigated under these hypotheses as a function of the hyperfine-interaction tensor parameters. The principal values of the g-tensor agree for the two structurally identical radicals with N^{14} and N^{15}, since they are determined by the spin-orbit interaction of the unpaired electron, while the values of the A-tensor components disagree because of the large difference between the gyromagnetic ratios of the N^{14} and N^{15} nuclei[72]. Spectra of models (A) and (B) were calculated for two sets of magnetic-interaction constants corresponding to the radicals with N^{14} and N^{15}. It was found that the line shapes of these two models differ more strongly in the case of the radical with N^{15}. This is because the values of the hyperfine interaction tensor components of the N^{15} radical are approximately 1.5 times[71] larger than the corresponding A-tensor com-
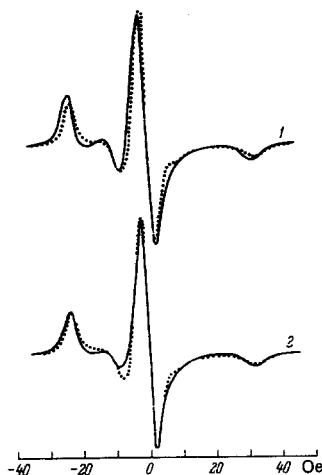
ponents of the structurally identical radical with N^{14}. These facts played a certain role in the selection by Antsiferova et al.[59] of the radical with N^{15} for studying the influence of the nature of its rotation on the shape of the spectrum.

Antsiferova et al.[59] presented a whole series of theoretical spectra for models A and B that had been calculated for various values of the parameters τ_{av} and τ_D. The amount of unresolved hyperfine structure δ was also varied in the calculations. It was assumed that δ varies monotonically with $\tau_{av}(\tau_D)$ from 1.5 to 4 G. Estimation of the limiting values of this quantity was based on analysis of experimental spectra for very rapid and completely "frozen" rotations. The calculated spectra were compared with experiment over the entire range of temperature variation of the observed lines. In the range $\tau_{av} = \tau_D \lesssim 3 \cdot 10^{-9}$ sec, the spectra of the two models considered are the same and agree well with experiment. Noticeable differences in the line shapes of models A and B appear at $\tau_a = \tau_D \geqslant 5 \cdot 10^{-9}$ sec. These differences increase as the mobility of the radical decreases. The uncorrelated-jump model gives a rather good description of experiment over the entire range of variation of the radical mobility with temperature. As an example, Fig. 7a presents experimental spectra for comparison with the theoretical spectra of model B. The existing differences in certain details of the spectra can be explained by the lack of precision in specifying the radical's parameters and by the assumptions on which the model is based (equal probability of jumps through any angle, isotropy of δ). However, the observed difference between the spectra of model A and the experimental spectra (Fig. 7b) is more substantive and cannot be explained by similar causes. Accordingly, Antsiferova et al.[59] find it possible to conclude that the uncorrelated-jump model gives a more adequate description of the motion of this radical in the viscous medium studied. In any event, we can definitely, say that a realistic model should contain jumps through finite angles.
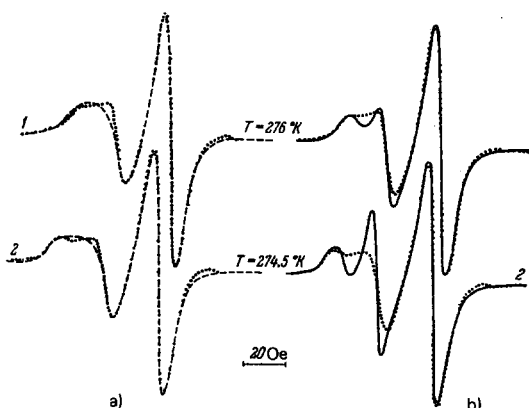

FIG. 6. Comparison of experimental and theoretical spectra.[58] Dotted curves: same as Fig. 5; the solid curves represent theoretical spectra of the models: isotropic free diffusion $(1)(\bar\tau = 6\sqrt{2/3}(\beta gH/\hbar)(E_2^{\cdot d})^{-1} = 10)$ and anisotropic free diffusion with an anisotropy factor $N = 3$ $(2)(\bar\tau_{\bar D} = 6\sqrt{2/3}(\beta gH/\hbar)\tau_{\bar D} = 10)$.

FIG. 7. Comparison of experimental and theoretical spectra.[59] The dotted curves represent the spectra of a nitroxyl radical with the isotope N^{15} in glycerine; the dashed curves in Fig. a) represent the theoretical spectra of the uncorrelated-jump model with $\tau_a = 7 \cdot 10^{-9}$ sec (1) and $\tau_a = 8 \cdot 10^{-9}$ sec (2); the solid curves in Fig. b) are the theoretical diffusional-rotation spectra with $\tau_D = 6 \cdot 10^{-9}$ sec (1) and $\tau_D = 7.5 \cdot 10^{-9}$ sec (2).

2. Anisotropic-rotation models. Comparison with experiment.

Goldman et al.[58] attribute the not quite satisfactory agreement between the theoretical and experimental data (for example, the disagreement between the amplitudes of the extremums to possible effects of the nonsphericity of the radical on the nature of its rotations, and, consequently, to deficiencies of the isotropic-rotation models A and C that were considered.

Anisotropic diffusion is described by the operator (3.29b) with the diffusion tensor $D_{\alpha\beta}$, whose principal values differ from one another in the general case. Let $x'y'z'$ be a system of diffusion-tensor axes that is bound to the radical, and let D_1, D_2 and D_3 be the principal values of the tensor that correspond to these axes.

Generally speaking, this system does not coincide with the $\xi\eta\zeta$ principal-axes system of the radical's magnetic-interaction tensors. In the axially symmetric diffusion model, we have $D_1 = D_2 \neq D_3$. Freed et al.[58] chose such a model as a probable model for the rotation of PADS. They concluded from spatial-symmetry features of this radical that the $x'y'z'$ axes coincide with the $\xi\eta\zeta$ axes, but left open the choice of the equivalence of the preferred axis of rotation z' to one of the axes ξ, η, ζ. Experimental spectra of the rapidly rotating PADS radical in ice and in a water-glycerine mixture were analyzed. It was shown on the basis of Redfield's theory[4] and Freed and Fraenkel's papers[6,8] that the best agreement between experiment and theory results when it is assumed that the z' axis coincides with the η axis. The value of the rotational-anisotropy parameter $N = D_3/D_1$ was determined and found to be equal to 2.9 ± 1 according to the data for PADS in ice and 4.7 ± 1 for PADS in the glycerine-water mixture.

The influence of the rotational-anisotropy factor on the shape of the theoretical spectra was investigated in the slow-motion range for two models—axially symmetric Browian diffusion (D) and anisotropic free diffusion (E). The diffusion operator of model D agrees up to a factor with the symmetrical-top Hamiltonian operator (see, for example, Ref. 65) and takes on the form

$$L_\Omega = -D_1 \nabla_\Omega^2 - (D_3 - D_1)\frac{\partial^2}{\partial\psi^2}.$$
(4.26)

The eigenvalues of this operator are

$$E_{l,n}^{\text{a.d.}} = D_1 l(l+1) + (D_3 - D_1) n^2.$$
(4.27)

Since the isotropic free-diffusion model was specified formally by Goldman et al.[58] by a series of eigenvalues $E_l^{\text{f.d.}}$ (4.2c), they introduced rotational anisotropy in this model by a simple generalization of formula (4.2c): namely:

$$E_{l,n}^{\text{a.f.d.}} = \frac{D_1 l(l+1) + (D_3 - D_1) n^2}{\sqrt{1 + \overline{D}\tau_a l(l+1)}};$$
(4.28)

here $\overline{D} = \sqrt{D_1 D_3}$. ($\overline{D}\tau_a$ was assumed equal to 1 in the calculations.)

The quantity $\tau_D = 6B_2\overline{D})^{-1}$ was used as a parameter with the meaning of the correlation time of the anisotropic rotations. Here B_l—the model parameter—

equals 1 for Brownian diffusion and $B_l = [1 + l(l+1)]^{-1/2}$ for free diffusion.

The results of comparison of the pair of theoretical spectra for models D and E with the observed spectrum of PADS in deuterated ice ($T = -60\,°C$) are represented by curves 2 in Figs. 5 and 6, respectively. As in the isotropic case ($N = 1$ curves 1 in Figs. 5 and 6), the spectrum of the free-diffusion model (see curve 2 in Fig. 6) gives a much closer approximation to the experimental spectrum than the spectra corresponding to Brownian diffusion. There are also certain improvements in the agreement between the spectrum calculated with $N = 3$ and the experimental spectrum (see curve 2 in Fig. 6) as compared to the isotropic case (see curve 1 in Fig. 6). This applies to the spectral range from -10 to -20 G and also to a decrease in the amplitudes of the hyperfine-splitting outermost extremums and in the width of the central component. The paper also includes spectra calculated with $N = 6$. Although these spectra give improvements in certain details as compared with $N = 3$, the agreement with the experimental spectrum cannot be regarded as satisfactory on the whole. On this basis, Goldman et al.[58] conclude that the best agreement between theory and experiment is obtained with the anisotropy parameter $N = 3$ in the free-diffusion model.

Kuznetsov and Radsig[73] studied the variation with temperature of the EPR-spectrum shapes of peroxide radicals (ROO$^•$) obtained on irradiation of polymers in the presence of oxygen. These are radicals without hyperfine interaction and with a g-tensor that as an approximation can be assumed to be axially symmetric with the symmetry axis directed along the $0—0^•$ axis. The EPR spectra of radicals of "terminal" and "middle" types were investigated in polytetrafluoroethylene (PTFET and PTFEM). It has been established earlier[74] that the EPR line shape of the PTFEM radical is governed in the range of rapid rotations by the rotation of the polymer chain around its long axis, and that the angle between the axis of rotation and the symmetry axis of the g-tensor is close to $\pi/2$. Comparison with the theoretical slow-rotation spectra (in the anisotropic uncorrelated-jump model) showed that the nature of this radical's motion does not change as the temperature is lowered. It was established on comparison of theory with the observed EPR lines of the PTFET radical that this radical also rotates around a single axis that forms an angle $\pi/4$ with the symmetry axis of the g-tensor.

Mason, Polnaszek, and Freed[75] interpreted the EPR spectra of spin-tagged polybenzyl glutamate in a dimethylformamide solution. Experimental data on electron resonance in this system were published by Wee and Miller[76] (the nitroxyl radical was used as the tag). Analysis of the data showed that the tag radical rotates rapidly about the line of the chemical bond, while the actual macromolecule to which it is attached reorients slowly in the isotropic liquid. Mason et al.[75] proposed a simplified model for this motion, using an axially symmetric diffusion tensor such that $D_{\parallel}(D_3)$ pertains to the motion around the line of the bond, while $D_{\perp}(D_1)$

takes all other rotations into account. Thus the problem of calculating the spectra is formally equivalent to the problem solved by Goldman et al.[58] A continuous-diffusion model was used to describe rotation around these axes. Specific calculations were made for the fixed value $\tau_{D_\perp} = (6D_\perp)^{-1} = 5 \cdot 10^{-8}$ sec and various values of $\tau_{D_\parallel} = (6D_\parallel)^{-1}$ from $6 \cdot 10^{-11}$ to $5 \cdot 10^{-8}$ sec. Here the anisotropy parameter N (in the terminology of Ref. 58) varied from 1 to $8.66 \cdot 10^2$. It was found that agreement with experiment is good when the spectra are calculated on the basis of this significantly simplified interpretation of the complex motion of the tag radical.

A general theory of relaxation for the case in which the lattice has "rapid" and "slow" parameters was developed by Bukhbinder et al[54]. Spectra of an anisotropically rotating radical were calculated on the basis of this theory for the same model that was proposed by Mason et al.[75]. The anisotropy parameter was varied in the range from 1 to 100.

The motion of a radical in a liquid crystal is one example of anisotropic rotations governed by the anisotropy of the medium. Bruno, Polnaszek, and Freed[77] calculated EPR spectra in the range of slow rotations of a radical in such media.

3. Nature of the rotations of the radical as a function of its relative dimensions. Arguments advanced by Frenkel'[78] indicate that the manner in which a particle rotates in a liquid depends on its relative dimensions. If the size of the molecule under study is large enough compared to the dimensions of the solvent molecule, the continuous rotational diffusion model can be used. As the size of the molecule of interest becomes smaller, there is an increasing probability of jumpwise reorientation through large angles. Therefore the model of jumpwise changes in orientation is more likely for particles in a surrounding of molecules of comparable or larger size. The results of the investigations described in subsection d) of this section do not contradict this reasoning. For spin-tagged oxyhemoglobin in aqueous solutions, whose relative dimensions are large, the experimental spectra agreed closely with the theoretical spectra calculated using the Debye rotational-diffusion model[68].

Experimental studies of the nature of the reorientation process as a function of radical size were undertaken by Kuznetsov et al.[79].

As Fig. 4 shows, the value of ΔH_{+1} depends weakly on the rotation model, while the plots of ΔH_{-1} against τ for the jump and diffusion models differ noticeably. Therefore, $R = \Delta H_{-1}/\Delta H_{+1}$ plotted against ΔH_{+1} can serve as a model characteristic that is helpful in interpretation of experimental data. The region of variation of the theoretical $R(\Delta H_{+1})$ is shaded in Fig. 8 from an upper boundary that represents the shape of this function for the diffusion model to a lower curve that corresponds to the uncorrelated-jump model. Experimental $R(\Delta H_{+1})$ curves were plotted[79] for six radicals of different sizes and molecular weights in n-butanol (their characteristics are given in Table I). These curves lie in the shaded region and are closer to the lower boundary the larger
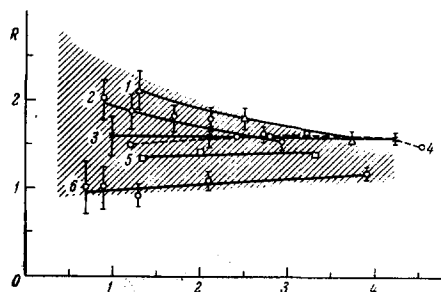

FIG. 8. Plots of the parameter R against ΔH_{+1} for a number of nitroxyl radicals in n-butanol.[79]

are the relative dimensions of the radical. These results can be regarded as a confirmation of concepts of Frenkel'.

e) Temperature dependence of rotation correlation time

Comparison of the experimental spectra of a radical in a medium at various temperatures with the theoretical spectra yields the dependence of τ on temperature. This relation is found in the rapid rotation range by measuring the widths and amplitudes of individual hyperfine components of the observed lines and calculating τ from analytic formulas derived on the basis of Redfield's theory (see, for example, Ref. 66). Calibration curves are used to construct this relation in the slow rotation range. Correspondence is established between a given value of τ and a temperature from the agreement of the calibration parameter values measured on the observed and theoretical spectra[66]. Figure 9 shows plots of τ against reciprocal temperature as obtained by this method[58,59] from data for a water-glycerine mixture. The relation between $\log \tau$ and $1/T$ is linear throughout the entire temperature range studied. This means that $\tau(T)$ can be described by a formula of the Arrhenius type: $\tau(T) = \tau_0 \exp(E_a/kT)$, where E_a is the activation energy of reorientation. According to Ref. 66, its value is 12 ± 0.5 kcal/mole. Goldman et al.[58] and Antsiferova et al.[59] obtained values in this range for the activation energies in the same medium (water-glycerine mixture): $E_a = 13 \pm 0.2$ kcal/mole and $E_a \approx 11$ kcal/mole. Certain differences in the E_a result from the fact that the height of the activation barrier depends on the viscosity of the medium, and the percentage compositions of the water-glycerine mixture were not the same in the various experiments.

5. NONLINEAR-RESPONSE METHOD

The EPR spectra discussed in the preceding sections were recorded with a weak radio-frequency field that

TABLE I.

Radical	M	V_0	d	Radical	M	V_0	d
1	376	7	3	4	267	4	2.2
2	303	6.5	1.8	5	182	2.5	1.2
3	289	6	2	6	166	2	1.3

M is the molecular weight and V_0 the molecular-volume ratio of the radical and n-butanol; $d = 2l_1/(l_2+l_3)$, where l_1 is the linear dimension of the radical along its longest axis and l_2 and l_3 are its linear dimensions along the other two axes.
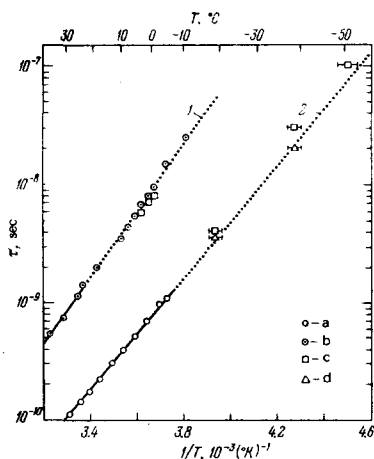
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FIG. 9. Rotation correlation time (logarithmic scale) vs. $1/T$. 1) For nitroxyl radical with isotope N^{15} in glycerine;[59] 2) for PADS radical in the same medium;[58] a) Redfield theory;[4] b) uncorrelated-jump model; c) continuous diffusional rotation; d) free diffusion.

did not disturb the equilibrium distribution in the spin system. This makes it possible to construct a spin-system relaxation theory in an approximation linear in the radio-frequency field, which leads eventually to expression (3.1) for the shape of the EPR line. The methods that have been developed for calculation of the spectra place no limits on the mobility parameter τ of the spin carrier. However, EPR study of molecular mobility under conditions far from saturation is limited to the temperature range corresponding to $\tau \lesssim 10^{-7}$ sec, since the shape of the line undergoes practically no change with increasing τ at rotation correlation times $\tau \gtrsim 10^{-7}$ sec.

Hyde and Dalton[80] and Goldman, Bruno, and Freed[81] showed that EPR spectra obtained at saturation, i.e., on application of a comparatively strong radio-frequency field, are "sensitive" to temperature changes in the range of very slow molecular motions ($\tau \gtrsim 10^{-7}$ sec). The linear-response approximation is not suitable in this case. Therefore, the description of the spin system must take exact account of the time dependence of the applied field and the Hamiltonian $\mathscr{H}(\Omega)$ (2.5) in the equation for the density matrix (3.31) must be replaced by a Hamiltonian of the form

$$\mathscr{H} = \mathscr{H}(\Omega) + \hbar \varepsilon(t); \qquad (5.1)$$

here $\varepsilon(t)$ takes into account the interaction between the spin system and the external alternating fields and can be written in the form

$$\varepsilon(t) = d_1(S_+e^{-i\omega t} + S_-e^{i\omega t}) + (d_sS_z + d_s'I_z)(e^{i\omega_s t} + e^{-i\omega_s t}), \qquad (5.2)$$

where

$$d_1 = \frac{g\beta}{2\hbar}H_1, \quad d_s = \frac{g\beta}{2\hbar}H_s, \quad d_s' = -\frac{\gamma_n}{2}H_s,$$

H_1 is the amplitude of the applied radio-frequency field of frequency ω, and H_s is the amplitude of modulation of the constant field H with frequency ω_s. The state of the spin system becomes essentially nonequilibrium at saturation. Accordingly, it is especially important to consider transfer of spin-system energy to the lattice. To take account of this transfer, the equations for the

diagonal elements of the spin density matrix acquire a term that determines the relaxation of these elements at the rate T_{1e}^{-1} (T_{1e} is the spin-lattice relaxation time for the electron spin, which is usually estimated from independent experiments).

In this case, the solution of the spin density matrix equation can be sought in series form:

$$\rho = \rho_0 + \sum_{k=-\infty}^{+\infty} \sum_{l,\,m,\,n} C_{m,\,n}^{(l)}(k)\,D_{m,\,n}^{(l)}(\Omega)\exp\left[i\left(\omega+k\omega_s\right)t\right], \qquad (5.3)$$

where ρ_0 is the equilibrium spin density matrix and the coefficients $C_{m,n}^{(l)}(k)$ form a matrix in the space of spin variables whose components are related by an infinite chain of equations similar to (4.17).

Three types of experiments involving saturation effects have been discussed in the literature[80-87] as methods for studying molecular motions with correlation times exceeding 10^{-7} sec. Simplest among these is the stationary-saturation method, which uses a moderately saturating field (a field such that the signal has an amplitude sufficient for observation). EPR spectra observed in the stationary-saturation regime were investigated in comparison with the theoretical spectra[81]. It was noted that the shape of the spectra changes appreciably with changes in the strength of the radio-frequency field. Accordingly, it was proposed that the spectra be compared with respect to the parameters $H_{\max}(+1)/H_{\max}(0)$ and $H_{\max}(+1)/H_{\max}(-1)$, where $H_{\max}(m_I)$ is the value of the radio-frequency field at which the component m_I($m_I = 0, \pm 1$) of the hyperfine structure of the spectrum has its largest value. Comparison of the theoretical and experimental values of these ratios enables us to plot τ against temperature in the range of large correlation times from 10^{-7} to 10^{-4} sec. Calculations made for the Debye and free rotational-diffusion models have shown that EPR spectra in the saturation regime are "insensitive" to the type of molecular motion.

Another experimental approach to the investigation of very slow motions is the stationary electron-electron double resonance (ELDOR) method[82-84].

In ELDOR, two resonant radio-frequency fields act on the specimen. One of them is a saturating field with frequency ω_p, and the other is a weaker "tracking" field of frequency ω. The relative decrease of the EPR signal is recorded as a function of the frequency difference: $(\omega_p - \omega)/2\pi = \Delta\nu$. As for calculations of this effect, a term $d_p(S_+e^{-i\omega_p t} + S_-e^{i\omega_p t})$, which describes the interaction of the electron spin with the saturating microwave field, must be added to expression (5.2) for $\varepsilon(t)$, and the expression $d_1(S_+e^{-i\omega t} + S_-e^{i\omega t})$ must be understood as its interaction with the weak "tracking" field. Theoretical relationships for the ELDOR signal as a function of the frequency difference $\Delta\nu$ were obtained[84] for τ_a of $3 \cdot 10^{-6}$, 10^{-6}, $1.2 \cdot 10^{-5}$, and $3 \cdot 10^{-5}$ sec. A jump model with a fixed angle step was chosen as the radical-reorientation model. The results of calculations made for two values of the unit orientation jumps (0.5 and 0.15 radian) differ appreciably. This encourages the belief that it may be possible to choose a model that permits optimum simulation of the ob-

served ELDOR spectra and estimation of rotation correlation times all the way up to $\tau = 10^{-5}$ sec.

Study of still slower motions with correlation times of up to 10^{-3} sec was made possible by the use of rapid passage through resonance under saturation conditions[80,85-88]. Portis[88] was the first to observe spectra under conditions of rapid EPR passage. The shape and intensity of the EPR signal depend strongly on the adiabaticity[8)] of the passage, as well as on the relation between the time of passage across resonance and the times of longitudinal T_1 and transverse T_2 relaxation[41]. The conditions for adiabatically fast passage through resonance are the inequalities[9]

$$\frac{1}{T_1}, \ \frac{1}{T_2} \ll \frac{1}{H_1}\left|\frac{dH}{dt}\right| \ll |\gamma H_1|.$$

Use of the fast-passage method to investigate low molecular motions has the following physical basis. Because of the anisotropy of the radical's magnetic interactions, passage through resonance conditions is brought about not only by the change in the external field, but also because of the rotational motions of the radicals themselves. Therefore the velocity of rotation determines the nature of the passage across resonance, and this has a significant effect on the observed rapid-passage signal.

Hyde and Dalton[80] observed the spectra of tanol in sec-butylbenzene at various temperatures. The rotation correlation time corresponding to these temperatures, which was estimated from the Debye-Stokes formula[89'] varied in the range from 10^{-7} to 10^{-4} sec. The conditions for experimental observation of the signal were determined by the inequalities

$$\frac{H_1}{H_s} < \omega_s T_{1e} < 1, \quad \Delta H > H_s,$$

where ΔH is the total width of the resonance line. The spectrum was recorded by phase detection at the modulation frequency. It was shown that the first harmonic of the dispersion signal, which is phase-shifted $90°$ from the modulating field, is most "sensitive" to variation of τ in the slow-rotation range.

The dependence of the observed dispersion signal on the intensity of the radical's rotation was confirmed by the theoretical calculations of Thomas and McConnell[85], who modeled the experimental conditions of Ref. 80. They used the adiabatic approximation in solving the initial equations and chose Debye diffusion as the molecular-rotation model.

It was shown that the line shapes of the first dispersion-signal harmonic, with the $90°$ phase shift from the modulation field, and of the second absorption-signal harmonic, which has the same shift, change noticeably as τ varies in the range from 10^{-7} to 10^{-3} sec. The amplitudes of these signals are quite high, amounting to 50% of the amplitude of the ordinary absorption signal for the anomalous dispersion and 25% for the anomalous absorption.

[8)]In adiabatic passage, the projection of the magnetization vector on the direction of the effective field remains constant in a coordinate frame that rotates at the frequency ω.
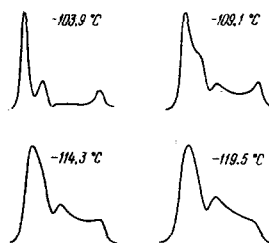
FIG. 10. Observed[86] anomalous dispersion spectra of TANONE nitroxyl radical with isotope N^{15} in sec-butylbenzene at various temperatures.

Dalton et al.[86] observed the spectra of the TANONE nitroxyl radical with the isotope N^{15} in sec-butylbenzene under conditions of adiabatically rapid passage through resonance. The resulting spectra were compared to theoretical spectra calculated with Eq. (3.31) for the density matrix, using the Debye diffusion model, the Hamiltonian (5.2), and the expansion (5.3). Figures 10 and 11 show the experimental and theoretical anomalous dispersion spectra given in that paper. The latter change shape noticeably as the parameter τ varies all the way up to $\tau = 10^{-3}$ sec. The agreement of the calculated and experimental curves can be regarded as quite satisfactory. Certain differences in the centers of the spectra are attributed by Dalton et al. to the approximation of axial symmetry of the g-tensor that was used to simplify the calculations. The cited paper also presents rapid-passage spectra that demonstrate the clear dependence of their shape on the power of the radio-frequency field.

The reliability of quantitative molecular-motion characteristics obtained by EPR methods that involve saturation effects depends in an essential manner on the precision of measurement of the spin-lattice relaxation time T_{1e}. In fact, the radio-frequency field energy acquired by the spin system is transferred to the lattice at a rate T_{1e}^{-1}. Rotation of the radical drives the spin system out of saturation at an average rate τ^{-1}. Therefore the range of variation of the saturation spectra that is critical with respect to the rate of molecular rotation is the range of τ comparable in magnitude to T_{1e}

Further progress in investigation of slow rotations by EPR techniques depends in principle on improvement of experimental procedures, since methods for theoretical calculation of spectra on the basis of relaxation equations of the type (3.31) are suitable for molecular motions that are arbitrarily slow. Moreover, certain theoretical studies are ahead of experiment. For ex-
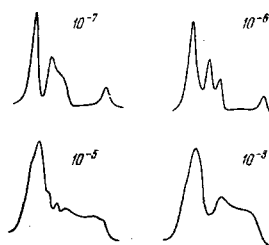

FIG. 11. Theoretical anomalous dispersion spectra for various values of the correlation time τ, sec.[86]

ample, Freed[90] and Smigel and Dalton[91] considered the possibilities of nonstationary EPR methods in investigation of slow molecular rotations. They give a theoretical treatment of the "recovery," with time, of the spectrum that forms on pulsed saturation of the specimen to the usual spectrum without saturation as a function of the relation between the times of rotational correlation τ, spin-lattice relaxation T_{1e}, and the saturating pulse duration T_p. Smigel and Dalton[91] also investigated the influence of the molecular-reorientation model on the details of "recovery" of line shape.

It should be noted in conclusion that nonmarkovian random processes have recently been examined as molecular-rotation models. The spectrum of a deuterated nitroxyl radical was investigated in various deuterated solvents over a broad temperature range[92]. It was concluded on the basis of a very subtle analysis similar to that in Refs. 58, 67 that it is advantageous to take into account the fluctuating moments of forces exerted on the radical by its surroundings. If it is assumed that the correlation time of these fluctuations is non-zero, the Fokker-Planck-type diffusion equation that describes the rotation of the radical will contain an integral operator that takes the aftereffect into account. In this case, derivation of an equation similar to (3.1) for the density matrix of the spin system is a special problem.

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Note in proof. It will be well to mention the recently published monograph,[93] which contains a large set of theoretical EPR spectra that correspond to situations frequently encountered in experimental practice.

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