Motional and exchange narrowing of NMR spectra in a reference frame rotating at the magic angle
V. E. Zobov and K.M. A. Popov
L. V. Kirenskii Institute of Physics, Russian Academy of Sciences, Siberian Branch, 660036 Krasnoyarsk, Russia; Krasnoyarsk State University, 660002 Krasnoyarsk, Russia.

The influence of the isotropic exchange interaction and slow atomic and molecular motions in a solid on the free-induction decays of the nuclear spins in a rotating reference frame with radio-frequency narrowing of the NMR lines by magic-angle spinning is considered. The Anderson–Weiss approach [P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953); P. W. Anderson, J. Phys. Soc. Jpn. 9, 316 (1954)] is employed. It is shown that under conditions such that the contribution of a two-spin interaction to the precession frequency can be described by a Gaussian random process, the contribution of a three-spin effective interaction is described by two independent Gaussian random processes, one of which is taken quadratically. A Gaussian–Gaussian process is used to describe the exchange narrowing, and a Gaussian–Markovian process is used to describe the fluctuations of the local field at the selected spin due to the mobile spins, while the variation of the precession frequency of the subject spin as it moves is assigned by a purely discontinuous Markov process. Relations which replace the Anderson–Weiss equations are derived. The dependence of the transverse relaxation time in the rotating frame on the exchange integral or the mean frequency of atomic motions in three motion models is calculated. Differences between these dependences in systems with two- and three-spin interactions, as well as in the different motion models, are revealed. The theoretical temperature dependence of the transverse relaxation time in solid benzene is qualitatively consistent with the experimental dependence [A. E. Mefedov and V. A. Atsarkin, Phys. Status Solidi A 93, K21 (1986)]. © 1995 American Institute of Physics.

1. INTRODUCTION

In the modern techniques of high-resolution nuclear magnetic resonance (NMR) in solids the dipole–dipole interaction, which is a primary factor in shaping broad absorption lines in conventional NMR, is eliminated by a strong radio-frequency (rf) field. Under the new conditions the line shape or its Fourier transform, i.e., the free-induction decay (FID), is now determined by the weaker effective interaction obtained after averaging the processes occurring during the rapid oscillations caused by the action of the strong rf field. The Hamiltonian of the effective interaction differs significantly from the original dipolar interaction. This is true of the Hamiltonian of the three-spin interaction when a continuous rf field is applied with magic angle spinning\(^1\) and of the Hamiltonian of the four-spin interaction for the WHH-4 multiple-pulse narrowing sequence.\(^2\) The main features of FID's in a rotating frame in the case of a three-spin interaction were discussed in Refs. 4–7 for systems of stationary atoms (in a rigid lattice). The influence of the fluctuations of the spin precession frequency caused by the motion of the atoms and molecules in a solid or by an isotropic exchange interaction on such FID's was investigated in the present study.

Information on the internal mobility is valuable for solid state physics on both the scientific and practical levels. NMR has proven itself as one of the most informative methods for studying it. In the modern techniques of high-resolution NMR in solids\(^1\) the possibility of manipulating a many-particle effective Hamiltonian provides a chance to significantly expand its possibilities when the fine-scale characteristics of slow atomic and molecular motions are studied. However, the theory needed to extract this information is still not available. In Ref. 8 we theoretically demonstrated the possibility of further motional narrowing of a high-resolution NMR line in a solid. This conclusion was confirmed by Atsarkin and Khazanovich,\(^9\) but was questioned by other investigators.\(^10\) The debate was continued in Ref. 11, in which such cascade narrowing of a line in the NMR signal of solid benzene by an rf field under magic-angle-spinning conditions and then by molecular motions was observed.

In solid benzene each spin has many neighbors; therefore, the theoretical results obtained for a rotating two-spin system in Ref. 9 cannot be used. In Ref. 8 equations were derived for the WHH-4 multiple-pulse sequence in fairly rapid motion. In this paper a simple theoretical model, which is a generalization of the familiar Anderson–Weiss model\(^12\) to the case of three-spin interactions, is proposed for the purpose of covering the entire range of motions down to a rigid lattice in the dense spin system of a solid. That model is based on the replacement of the real motion of a magnetic moment resulting from its interaction with many spins in its environment by its precession in a fluctuating one-component local magnetic field, whose time dependence is treated as a random process. A Gaussian–Gaussian process was chosen to describe the narrowing of an absorption line by an exchange interaction, while a Gaussian–Markovian or Markov process was chosen for motional narrowing.
Finally, the statistical properties of the new Gaussian contribution to the precession frequency is considered in Appendix B. The temperature dependence of the NMR line shape in the rotating frame was determined from the second and third moments of the NMR line shape in the rotating frame. Instead of such phenomenological use of the Anderson–Weiss model, the present paper treats this model on a microscopic level, which makes it possible to obtain all the necessary parameters and functions in a consistent manner.

The Anderson–Weiss approach was recently applied in Refs. 6 and 7 to a system with a three-spin effective interaction in a rigid lattice to explain the long-time exponential tails of FID's in a rotating frame. A Markovian random process was selected. It was theorized in Ref. 6 that the value of the precession frequency varies abruptly, while in Ref. 7 this variation was described as a continuous diffusion process. A phenomenological use of the Anderson-Weiss model, the present paper treats this model on a microscopic level, which makes it possible to obtain all the necessary parameters and functions in a consistent manner.

In the second section of this paper it is shown that in the case of a three-spin effective interaction and an exchange interaction the variation of the precession frequency with time is described in the Anderson–Weiss approximation by two independent Gaussian random processes, one of which is taken quadratically. Equations which replace the Anderson–Weiss equations in such systems are derived. The dependence of the spin temporal correlation functions on the parameters of the fluctuating field is studied. In the third section the precession frequency is represented by a Markovian random process, which describes the random motions of atoms and molecules. The dependence of the characteristic time of FID in the rotating frame (\( T_{2e} \)) on the frequency of motion is calculated for three models. The theoretical temperature dependence of \( T_{2e} \) is compared with experiment. Finally, the statistical properties of the new Gaussian contribution to the precession frequency is considered in Appendix A, and the exponential function of the quadratic Gaussian noise is averaged with a correlation function of arbitrary form in Appendix B.

2. EXCHANGE NARROWING

Let us consider a system of spins in a strong constant magnetic field \( H_0 \) and a strong rf field with an amplitude \( H_1 \) and a frequency \( \omega_0 \), which is close to the Larmor precession frequency \( \omega_0 \). In a frame rotating with a frequency \( \omega_0 \) about the field \( H_0 \), an effective field of strength \( \omega_0 \) (in frequency units), which forms an angle \( \theta \) with the field \( H_0 \), acts on the spins:

\[
\omega = \sqrt{H_1^2 + (\omega - \omega_0)^2}, \quad \theta = \arctan \left( \frac{\gamma H_1}{\omega - \omega_0} \right). 
\]

The angle \( \theta \) and, thus, the form of the effective Hamiltonian can be varied by varying the amplitude and frequency of the rf field. The greatest narrowing of an NMR line in the rotating frame is achieved at the magic value of the angle \( \theta \):

\[
\theta = \arccos \left( \frac{1}{\sqrt{3}} \right) = 54.7^\circ, 
\]

at which the dipolar interaction is completely averaged by the strong rf field, and the interaction of the spins \( S^* \) is described by the effective Hamiltonian:

\[
\mathcal{H}_{\text{eff}} = \frac{3}{8 \omega_0} \sum_{ij} b_{ij} S_i^j + \frac{1}{4 \omega_0} \sum_{ij} \{4b_{ij} \mu_0 S_i^j S_i^j S_i^j - 3S_i^j S_i^j + S_i^j S_i^j \} \{ 4b_{ij} \mu_0 - b_{ij} \}, 
\]

where \( b_{ij} = \gamma^2 H_1^2 (1 - 3 \cos^2 \theta_j / 2 \theta_j) \), \( \theta_j \) is the angle between the internuclear vector \( r_j \) and the constant magnetic field \( H_0 \), and \( \{ S_i^j, S_j^j S_k^k \} \) denotes the components of the vector operator of the spin at site \( i \) in a coordinate system with its \( z \) axis parallel to the effective field \( \omega_0 \).

The relaxation of the component of the magnetization which is orthogonal to the effective field in a doubly rotating frame (the second rotation is about the effective field) is given by the spin temporal correlation function

\[
M_\alpha(t) = \text{Tr}[S^* S^* U - \alpha(t)], 
\]

\[
U(t) = T \exp \left[ \int_0^t \mathcal{H}_{\text{eff}}(t') dt' \right], 
\]

where \( T \) is the Dyson chronological ordering operator. The time dependence of the Hamiltonian in (2.4) is either a result of variation of the coupling constants \( b_{ij} \) due to the motions of the atoms or a result of variation of the spin orientations resulting from the isotropic exchange interaction

\[
\mathcal{H}_{\text{ex}} = \sum_{ij} b_{ij} S_i^j S_j^j. 
\]

Nuclear spin systems with an exchange interaction include, for example, solid \(^3\)He (Ref. 14).

In the general case the spin temporal correlation function (2.3) cannot be calculated exactly. A qualitative representation can be obtained by following Refs. 12 and 13 and retaining the interaction between the \( z \) components of the spins in the Hamiltonian (2.2). Then from (2.3) we find

\[
M_\alpha(t) = M_{(i)z}(t) + iM_{(i)x}(t) = \exp \left[ \int_0^t \omega_0(t') dt' \right], 
\]

where

\[
\omega_0 = -\omega_1 - \omega_2 z / 2 - \omega_3 \omega_z, 
\]

\[
\omega_1 = 3B / 8 \omega_0, \quad B = \frac{1}{2} \frac{b_{ij}^2}{\omega_0}, 
\]

\[
\omega_2 = \frac{4}{B} \sum_{ij} b_{ij} S_i^j S_j^j S_i^j, \quad \omega_3 = \frac{4}{B} \sum_{ij} b_{ij} S_i^j S_j^j S_k^k. 
\]

In (2.7) two constants \( \omega_2 \) and \( \omega_3 \) were introduced for convenience in the further transformations, although it follows from Hamiltonian (2.2) that \( \omega_2 = \omega_3 = B / 2 \omega_0 \). Expression (2.6) was obtained by taking into account the fundamental property of the raising operators \( S^* \) and the translational invariance of the crystal. The subscript 0 refers to one of the

V. E. Zobov and M. A. Popov
spins of the system, whose precession is described by expression (2.6). It is assumed that all the spins occupy equivalent sites in the crystal; therefore, we include an identical frequency shift \(\omega_0\) for all of them in \(\omega_\ell\). The angle brackets denote averaging with respect to the random process.

In this section we consider the exchange narrowing of an NMR line in the rotating frame. To describe it we assume that \(S_\ell\) in the expression for the precession frequency (2.7) is a classical variable, which varies randomly with time. We first focus on the thoroughly studied case of a two-spin dipolar interaction, in which the precession frequency is determined by the projection of the local field on \(H_\ell\):

\[
as(t) = \sqrt{B} h(t), \quad h(t) = \frac{4}{\beta} \sum b_{2j} S_j. \tag{2.8}
\]

When there is a large number of neighbors, Anderson and Weiss\(^1\) proposed representing the variation of the precession frequency with time by a Gaussian random process \(\xi(t)\), i.e.,

\[
h(t) = \xi(t), \quad \text{with the correlation function}
\]

\[
g(t_1 - t_2) = \langle \xi(t_1) \xi(t_2) \rangle \tag{2.9}
\]

in the form of the Gaussian function

\[
\phi(t) = \exp(-at^2). \tag{2.10}
\]

Extending the Anderson–Weiss approximation to systems with the three-spin interaction (2.2), we note that the contribution \(\omega_3\) is expressed in terms of the square of the 2 component of the local field:

\[
\omega_3(t) = \vec{\eta}^2(t) - \langle \vec{\eta}^2 \rangle. \tag{2.11}
\]

Although the third contribution \(\omega_3(t)\) is also quadratic with respect to the spin projections, it differs from \(\omega_2\) with respect to the position of the selected spin with the label 0, which is located on the end, rather than in the middle, of the chain of three coupled spins.

Due to the special form of the last term in (2.7), to average (2.6) it is not sufficient to specify the stochastic properties of the local field as such. We must proceed further and ascertain the corresponding microscopic conditions imposed on the motion of the spins themselves. The analysis which we previously performed in Refs. 15 and 16 showed that a random local field whose fluctuations are caused by a two-spin interaction is Gaussian, if the correlation between the contributions of different spins to the local field is discarded. Since lattice sums having the form of loops of the interactions \(b_{ij}\) are responsible for the correlation in the power series in time for the spin temporal correlation functions, such sums should be discarded. This can be achieved, for example, by considering spin systems in lattices of large dimensionality \(d\), for which the contribution of the lattice sums with loops becomes negligible in the limit \(d \to \infty\) (Ref. 16) in comparison with the contribution of the lattice sums without loops, which have the form of trees. However, as the calculations in Refs. 5 and 16 show, these contributions differ by a large factor even in real systems.

We now proceed to the averaging of (2.6), for which we expand the exponential function in a series:

\[
M_\ell(t) = \sum_n \frac{1}{n!} \left[ \int_0^t \exp \left( \int_0^t \omega_\ell(t') dt' \right) \right]^n. \tag{2.12}
\]

We substitute the powers of the frequency (2.7) into the series (2.12). For \(n = 2\) we have three terms:

\[
\langle \omega_2(t_1)\omega_2(t_2) \rangle = \frac{4}{B} \sum b_{02} b_{02} b_{02} \times (S_0(t_1)S_0(t_2)S_2(t_1)S_2(t_2)), \tag{2.13}
\]

\[
\langle \omega_2(t_1)\omega_3(t_2) \rangle = \frac{4}{B} \sum b_{02} b_{02} b_{02} \times (S_0(t_1)S_0(t_2)S_2(t_1)S_2(t_2)), \tag{2.14}
\]

\[
\langle \omega_2(t_1)\omega_3(t_2) \rangle = \frac{4}{B} \sum b_{02} b_{02} b_{02} \times (S_0(t_1)S_0(t_2)S_2(t_1)S_2(t_2)). \tag{2.15}
\]

Here the subscript 0 is fixed, and the summation is carried out over all the other site labels under the condition that the labels on each individual interaction constant are unequal; the averaging \(\langle \ldots \rangle\) now means taking the trace and dividing it by the total number of states.

The difference between the contributions \(\omega_2(t)\) and \(\omega_3(t)\) with respect to the position of the subject spin at the end or in the middle of the chain of three coupled spins causes loops of interactions to unavoidably form when spins from \(\omega_2(t)\) and \(\omega_3(t)\) are coupled. An illustration is provided by expression (2.14). Loop formation can be avoided only when the spins in the product of \(\omega_3(t)\) contributions are coupled with one another and the spins in the product of \(\omega_2(t)\) contributions are coupled with one another. Therefore, in the approximation under consideration, after the terms forming interaction loops are neglected in the time series, the two contributions to the precession frequency \(\omega_3(t)\) and \(\omega_2(t)\) become statistically independent, i.e.,

\[
M_\ell(t) = V_2(t)V_3(t), \tag{2.16}
\]

where

\[
V_2(t) = \exp \left[ -ia_2 \int_0^t \omega_2(t') dt'/2 \right], \tag{2.17}
\]

\[
V_3(t) = \exp \left[ -ia_3 \int_0^t \omega_3(t') dt' \right]. \tag{2.18}
\]

Moreover, as is shown in Appendix A, in this approximation \(\omega_2(t)\) is a new Gaussian random process, and, therefore, \(V_2(t)\) is expressed by the Anderson–Weiss formula

\[
V_2(t) = \exp \left[ -a_2 \int_0^t \langle \xi(t) \rangle dt' \right]. \tag{2.19}
\]

\[
g_2(t) = \langle \omega_2(t)\omega_2(0) \rangle. \tag{2.20}
\]

For \(g_2(t)\) we shall use the approximate expression (A3).

A different result is obtained when \(V_3(t)\) is averaged. In the product of \(\omega_3(t)\) contributions in the series (2.12) for (2.17), each of the two Gaussian variables in the square \(\xi^2(t_\ell)\) of one cofactor can be coupled with \(\xi(t_\ell)\) from dif-
Different cofactors. As a result, loops of different numbers of the correlation functions $g(t_0-t_0)$ form (they should not be confused with the already discarded loops of the interactions $b_{ij}$). For example, a loop of $n$ correlation functions is described by the expression

$$V_n = \int_0^T \ldots \int_0^T g(t_1-t_2) g(t_2-t_3) \ldots g(t_{n-1}-t_n) dt_1 dt_2 \ldots dt_n,$$

(2.21)

Therefore, while $\xi(t)$ breaks down during the averaging into a product of pair averages, $\xi'(t)$ breaks down into a product of group averages in the form of loops described by (2.21). Thus, the result of averaging $\xi(t)$ in the series (2.12) for $V_n(t)$ is the sum of every possible way of subdividing it with respect to loop length and number of loops. After summation of the series described in Appendix B, we obtain

$$V_n(t) = \exp \left( F_n(t) \right),$$

(2.22)

where

$$F_n(t) = -i b \int_0^T \left[ (R(t', t') - 1) dt'/2 \right],$$

(2.23)

and $R(t, t_1)$ is a solution of the equation

$$R(t, t_1) = g(t-t_1) - i b \int_0^T R(t, t_2) g(t_1-t_2) dt_2.$$

(2.24)

Equations (2.22)–(2.24) make it possible to calculate the spin temporal correlation function for $g(t)$ of arbitrary form. A special averaging method was developed for the special case of an Ornstein–Uhlenbeck process, i.e., when

$$g(t) = \exp(-a t),$$

(2.25)

in Ref. 17. For our case we find

$$V_{g}(t) = \left[ \cosh(a t) + (a^2 + 1)/2 t \right] \sinh(a t)/a,$$

(2.26)

where $\Omega = (1 + i a t)/\sigma$.

For $g(t) = 1$ the expressions given for $M_4(t)$ transform into the expression which we obtained in Ref. 5

$$M_4(t) = (1 + i a t)^2 \cosh(a t)/2,$$

(2.27)

Following the Anderson–Weiss approach, we take $g(t)$ in the form (2.10), and we determine the parameters $a_2$, $a_3$, and $\sigma$ from the moments. On the basis of expressions (2.16), (2.19), and (2.22) we have

$$a_2 = M_2^{1/3}, \quad a_3 = M_3 - M_2^{1/2}, \quad \sigma = M_4/4 M_2 - 3 M_2^{1/2} - 3 a_3^2/16 M_2,$$

(2.28)

We found the moments appearing in (2.28) in Ref. 5 in the approximation of lattices of large dimensionality in the absence of an exchange interaction [in Ref. 5 the term $72a^2$ in expression (16) for $M_2^{\text{ex}}$ should be corrected to 78$a^2$]:

$$M_1 = 33 R^2/32 a_1^2, \quad M_2 = 0.86 M_1^{1/2}, \quad M_4 = 4.11 M_2,$$

(2.29)

The isotropic exchange interaction (2.5) does not alter $M_2$ and $M_4$, but it increases the fourth moment by $M_4^{\text{ex}}$. In the same approximation for $M_4^{\text{ex}}$ we find

$$M_4^{\text{ex}} = 10(56/3)^{3/2} M_2 \sum_j (J_j^2/R^2).$$

(2.30)

Equations (2.28)–(2.30) completely specify the parameters needed. In particular, when there is no exchange interaction and the fluctuations of the precession frequency are caused by the interaction between the transverse components of the spins in effective Hamiltonian (2.2), we have

$$a_2 = 0.95 \sqrt{M_2}, \quad a_3 = 0.55 M_2, \quad \sigma = 0.124 M_2.$$

(2.31)

The solution of Eq. (2.24) and the integrals in (2.19) and (2.23) were found numerically for various values of $\sigma$. The results of the calculations are shown in Figs. 1 and 2. The parameter chosen to characterize the nonexponential decays obtained was $T_2$, which can be determined from the condition

$$[M_4(T_2)] = 1/e.$$ 

(2.32)

For comparison, Fig. 2 shows the dependence of $T_2$ on $a$, which was found using Eqs. (2.19) and (2.26). According to the calculations, the value of $T_2$ corresponding to $\sigma = 0.12 M_2$ is attained for $\alpha = \alpha_0 = 0.1 M_2^{1/2}$. The decays calculated for these values of the parameters nearly coincided; therefore, when we take into account the mobility of the atoms in the next section, we shall use the simple expression (2.26) instead of the numerical solution of Eq. (2.24).

One of the fundamental differences between the FID in the case of a three-spin interaction and the FID in the case of a two-spin interaction is the presence of an imaginary part, which attests to the time variation of the phase of the magnetization vector in the doubly rotating frame. We discussed these features in detail in Ref. 5. Now, in our analysis of the narrowing of an NMR line in the rotating frame we are interested primarily in the behavior of the absolute value of the FID.
The first term coincides with the single cumulant in curves in Fig. 2 converge as the Anderson-Weiss formula (2.19) or (2.33) taken with this result is obtained for the relationship between $a$ and $\xi$, obtained when $a=\sqrt{3}$.

The microscopic model theory devised above makes it possible to elucidate the role of the large number of neighbors in the dynamics. When $Z$ increases both the mean square of the precession frequency $\langle M_z \rangle^2$ (2.29) and the higher moments increase, but, according to our calculations, they increase in such a manner that the ratio $\langle M_z \rangle^2 / \langle M_z^2 \rangle$ ceases to depend on $Z$ for sufficiently large $Z$. Thus, the number of neighbors $Z$ appears in the scalar factor for the frequency and the time, while the line shape or the FID ceases to depend on $Z$ at $Z \gg 1$ and is determined by the form of the Hamiltonian. The disparate conclusion in Ref. 6 was drawn after the characteristic time of the variation of the precession frequency was compared, not with that frequency itself, but with the contribution to it from the interaction with one of the neighbors, which is $Z$ times smaller.

Closing this section, we note that the averaging performed above [see (2.22)-(2.24)] of an exponential function of the quadratical Gaussian noise with a correlation function of general form is of value in itself and may be useful in studying other phenomena described by such noise in physics, chemistry, biology, etc.

Thus, when there is a strong exchange interaction in systems with a three-spin effective interaction, we obtain exponential FID's corresponding to a Lorentzian line shape. However, the presence of the higher terms of the cumulant series results in a deviation from the Anderson-Weiss formula: a frequency shift appears, and the relationship between the width of the spectrum and the exchange integral changes.

Besides the change in the form of the equations in the transition from systems with a two-spin interaction to systems with a three-spin interaction, there is a twofold increase in the relative rate of variation of the precession frequency. This is seen from the replacement of $g(t)$ with $g^3(t)$ which occurred in the precession frequency correlation function. This relation is obtained in an especially simple form for $\omega_1(t)$ on the basis of (2.7) and (2.8).

The doubling of the rate occurred as a result of the fact that in the case of a two-spin interaction the precession frequency is linear in the spin variables, while in the case of a three-spin interaction it is quadratic. The increase which occurred in the rate of variation of the precession frequency has a significant effect on the spin dynamics of systems with a three-spin interaction, but it is still insufficient, if we look at the analogy to the dynamics of spins in a liquid discussed in Ref. 6. In the opinion of the authors of this analogy, it can be substantiated by the large number of nearest neighbors $Z$.

The microscopic model theory devised above makes it possible to elucidate the role of the large number of neighbors in the dynamics. When $Z$ increases both the mean square of the precession frequency $\langle M_z \rangle^2$ (2.29) and the higher moments increase, but, according to our calculations, they increase in such a manner that the ratio $\langle M_z \rangle^2 / \langle M_z^2 \rangle$ ceases to depend on $Z$ for sufficiently large $Z$. Thus, the number of neighbors $Z$ appears in the scalar factor for the frequency and the time, while the line shape or the FID ceases to depend on $Z$ at $Z \gg 1$ and is determined by the form of the Hamiltonian. The disparate conclusion in Ref. 6 was drawn after the characteristic time of the variation of the precession frequency was compared, not with that frequency itself, but with the contribution to it from the interaction with one of the neighbors, which is $Z$ times smaller.

Closing this section, we note that the averaging performed above [see (2.22)-(2.24)] of an exponential function of the quadratical Gaussian noise with a correlation function of general form is of value in itself and may be useful in studying other phenomena described by such noise in physics, chemistry, biology, etc.

3. MOTIONAL NARROWING

Let us now consider the influence of atomic and molecular motions in a solid on FID's in the rotating frame. To perform the averaging in (2.6) we must concretize the motion model and assign the characteristics of the random process. The atoms in a crystal can occupy only a definite set of sites, between which there are rare transitions, the lifetime in each site exceeding the transition time. Therefore, we assume
that changes in the position of atoms and the precession frequency occur abruptly and are described, as usual, by a Markovian random process. We also assume that the probability of the new value which a random quantity takes after a random jump does not depend on the previous value and is determined only by the set of possible sites in the lattice. Such an approximation is often used in theory\textsuperscript{6,18-23} since it makes it possible to easily obtain results which are in relatively good agreement with experiment.

We shall analyze three typical motion models.

1. Independent atomic motions with a dipolar coupling constant correlation function:

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 \exp(-2|t|/\tau_c), \quad (3.1) \]

where \( 1/\tau_c \) is the mean jumping frequency of an atom. The diffusion of atoms may be included in this category.

2. Simultaneously activated atomic motions, under which all the atoms in a certain region simultaneously change their positions:

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 \exp(-|t|/\tau_c). \quad (3.2) \]

This occurs for the atoms in a single molecule when it undergoes rotation, as well as for the atoms in several molecules when they rotate simultaneously.\textsuperscript{22} When a molecule rotates around a single axis, the dipolar interaction can be averaged only partially, i.e., a part \( b_{ij} \), which is invariant to motion, can be isolated in the dipolar coupling constant. The coupling constant correlation function under such motion is written in the form

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 - \langle b_i^0 \rangle^2 \exp(-|t|/\tau_c) + \Delta b_{ij}^2, \quad (3.3) \]

3. Independent rotation of different molecules.\textsuperscript{22} In this case the correlation constant function has the form (3.2) for atoms belonging to the same molecule and the form (3.1) for the atoms of other molecules.

We begin the calculation of the FID (2.6) from the second motion model, assuming that the value of the precession frequency changes abruptly at arbitrary moments in time and does not vary between jumps. The probability density of the frequency values after a jump coincides with that in a rigid-lattice model, assuming that the value of the precession frequency in response to such jumps can be measured experimentally, instead of \( M_{2}(t) \). For example, in solid benzene\textsuperscript{24}

\[ M_{2}(t) = 9.7 \text{Oe}^2, \quad M_{2\text{in}} = 3.1 \text{Oe}^2, \quad M_{2\text{k}} = 1.6 \text{Oe}^2, \]

where \( M_{2\text{in}} \) is the intramolecular contribution to \( M_{2}(t) \), and \( M_{2\text{k}} \) is the second moment averaged over the fast rotational acts of the molecules.

Now we turn to the first motion model. The jumps of atoms which create a local field at the subject spin and the jumps of the subject spin itself should be distinguished. Under the condition of a large number of neighbors, the jumps of the selected spins cause virtually continuous variation of the field, and they will be taken into account in expressions (2.19) and (2.26) by means of the Gaussian field correlation function (2.25):

\[ M_{2}(t) = M_{20} \exp(-u_{2}^{2}/2) \]

where \( M_{20} = 9.7 \text{Oe}^2, \quad M_{2\text{in}} = 3.1 \text{Oe}^2, \quad M_{2\text{k}} = 1.6 \text{Oe}^2 \]

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 \exp(-2|t|/\tau_c), \quad (3.1) \]

where \( 1/\tau_c \) is the mean jumping frequency of an atom. The diffusion of atoms may be included in this category.

Finally, if the third model of molecular rotation does not contain the part of the dipolar interaction which is invariant to the motion, this model can also be described by Eq. (3.4) when the Gaussian field correlation function is taken in the form

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 \exp(-2|t|/\tau_c), \quad (3.1) \]

where \( 1/\tau_c \) is the mean jumping frequency of an atom. The diffusion of atoms may be included in this category.

Now we turn to the first motion model. The jumps of atoms which create a local field at the subject spin and the jumps of the subject spin itself should be distinguished. Under the condition of a large number of neighbors, the jumps of the selected spins cause virtually continuous variation of the field, and they will be taken into account in expressions (2.19) and (2.26) by means of the Gaussian field correlation function (2.25):

\[ \langle b_i(t)b_j(t) \rangle = \langle b_i^0 \rangle^2 \exp(-2|t|/\tau_c), \quad (3.1) \]

where \( 1/\tau_c \) is the mean jumping frequency of an atom. The diffusion of atoms may be included in this category.
Hamiltonian was described above, we approached it as a real by the strong dependences of presented in Fig. 3. The three motion models give different relaxations processes. The constants $p_1$ and $p_2$ are determined by the fractions of the inter- and intramolecular interactions in the mean square of the local field:

$$g(t) = p_1 \exp(-|t|/\tau_c) + p_2 \exp(-a_2|t|).$$

(3.7)

where the constants $p_1$ and $p_2$ are determined by the fractions of the motion models in the text. The values of $\tau_c$ and $\tau_r$ are given in units of $t_f^{3/2}$.

In particular, after substitution of the values from (3.5) for benzene, we find $p_1 = 0.7$ and $p_2 = 0.3$. The function $V_2(t)$ in $M_2^r(t)$ is now given numerically according to Eqs. (2.22)–(2.24).

The FID's in the rotating frame were calculated for the three motion models, and $T_2^r$, as specified by condition (3.32), was calculated from them. The results obtained are given in Fig. 3. The three motion models give different dependences of $T_2^r$ on $1/\tau_c$. The curve is steeper in the case of independent motion than in the case of correlated motion. This is reasonable, since in the former case variation of the frequency is caused by the movement of any of the atoms coupled by the three-spin interaction. When there is intense motion, different asymptotic dependences are obtained in the three cases. They are:

$$T_2^r = \frac{M_2^r}{\gamma_2^r}$$

$$T_2^r = \frac{M_2^r}{\gamma_2^r}$$

$$T_2^r = \frac{M_2^r}{\gamma_2^r}$$

When the influence of motion on the effective three-spin Hamiltonian was described above, we approached it as a real interaction, which exists at any frequency of motion. However, this Hamiltonian is formed from a time-dependent dipolar interaction having rapid oscillations with time caused by the strong rf field. The effective Hamiltonian is observed in high-order perturbation theory after averaging with respect to these oscillations for the purpose of describing the slow relaxation processes. The analysis of such averaging in the presence of an additional stochastic time dependence of the Hamiltonian of the dipolar interaction showed that the separation of the effective Hamiltonian is substantiated until $\tau_2, \omega_1 \approx 1$. At high frequencies of motion, relaxation occurs directly under the action of the dipolar interaction and is described well by the familiar formulas for the spin–lattice relaxation rate of the magnetization in a rotating frame

$$T_2^r = \frac{\Delta M_{22}^r 5 \omega_2 + I(2 \omega_2)}{9},$$

(3.8)

where

$$I(\omega) = c \tau_c / (1 + \tau_c^2 \omega^4) + 2 \tau_c (1 - c) (4 + \tau_c^2 \omega^4).$$

(3.9)

$\Delta M_{22}^r = M_{22}^r - M_{22}^r$ is the part of the second moment averaged over the motion, and the coefficient $c$ is specified by the motion model: $c = 0$ for model 1, $c = 1$ for model 2, and, finally, $c = 0.6$ for model 3 in the case of benzene.

In the slow-motion region both relaxation mechanisms should be taken into account simultaneously. Therefore, to describe real FID's, the expression for $M_2(t)$ obtained as a result of the solution of Eq. (3.4) should be multiplied by $\exp(-t/T_2^r)$.

In addition, the equations must be modified for types of motion which dipolar interactions do not average completely. Consideration of the invariant part $b_{ij}$ is, in principle, important in the rapid-motion region, in which the relaxation mechanisms described above become ineffective. In this region the Hamiltonian of the dipolar interaction becomes temperature-independent with the constant $b_{ij}$. For example, in the case of benzene, the dipolar interaction between the spins of the atoms is transformed into the dipolar interaction between the total spins of the molecules as a result of the rapid rotation of the molecules. Therefore, the FID in the rotating frame is described by the equations for a rigid lattice, in which the constants are modified as a result of the replacement of $b_{ij}$ by $b_{ij}$.

In the slow-motion region Eq. (3.4) is replaced by a considerably more complicated expression when the invariant part of the dipolar interaction is rigorously taken into account. Since the invariant part is usually small in magnitude in many-particle systems [see, for example (3.5)], it would not be useful, in our opinion, to concern ourselves with this complication. Therefore, we shall utilize the simple interpolating formula

$$M_2(t) = M_{2,2}(t)M_{2,2}(t)\exp(-t/T_2^r),$$

(3.10)

in which the contributions to the relaxation $M_{2,2}(t)$ from the invariant and variable parts of the effective interaction are completely separated.

We performed a specific calculation for solid benzene, for which the temperature dependence of the transverse relaxation time in the rotating frame has been measured. We calculated $M_{2,2}(t)$ from Eqs. (2.16), (2.19), and (2.26) and found $M_{2,2}(t)$ from Eq. (3.4). We calculated the constants $\delta_2$, $\delta_3$, $\gamma_2$ in the first case and $\delta_3^{\pm}$, $\delta_3^{\pm}$, and $\delta_2$ in the second case from Eqs. (2.28) using the corresponding values of the moments

$$M_2 = 11 M_2^r 54 \omega_2^m = 7 \times 10^5 \text{ s}^{-1}$$

and

$$\Delta M_2 = 11 (M_2^r - M_2^r)/54 \omega_2^m = 2.41 \times 10^7 \text{ s}^{-2}.$$

The numerical values were obtained here after plugging in (3.5) and $\omega_2 = 100$ kHz for the experimental conditions in
The characteristic of the experimental FID's in the rotating frame \(1/T_{2p}\) was determined in Ref. 11 according to a different rule: the initial portions of the decays were approximated by a Gaussian dependence with the half-width \(1/T_{2p}\) and the portions at later times were approximated by an exponential (Lorentzian) dependence with the half-width \(1/T_{2p}\), which was found at different temperatures, was presented in the figure in Ref. 11, which were measured according to (3.11). The theoretical curves presented in Fig. 4 demonstrate the sensitivity of \(1/T_{2p}\) to the motion model. A choice in favor of the model of correlated molecular motions (model 2) was made in Ref. 22 for solid benzene on the basis of measurements of \(T_{1}\) for deuterated samples. The curve in Fig. 4 corresponding to this model is also closer to the experimental curve. Nevertheless, we must proceed from a comparison of the transverse relaxation times to a comparison of the FID's in the rotating frame themselves to draw an unequivocal conclusion.

Thus, the proposed theory accounts for the differences in the dynamics of systems with a two-spin dipolar interaction and a three-spin effective interaction. It makes it possible to describe the slow-motional narrowing of NMR lines in the rotating frame. The theoretically predicted sensitivity of the temperature changes in FID's in the rotating frame to the motion model should serve as a basis for devising a new highly sensitive method for investigating them.

We thank A. E. Mefed for some useful discussions and A. V. Ponomarenko for assisting in this study.

This research was performed with financial support from the Krasnoyarsk Regional Science Fund (grant 3F0074).

APPENDIX A

Let us study the statistical properties of the contribution \(\omega_j(t)\) to the precession frequency (2.27) in the approximation under consideration. We start with the correlation function \(g_{ij}(t)\) (2.15). In order for the lattice sum not to contain loops of interactions, the site labels of the spins next to the selected spin must coincide: \(i = k\). The other two labels may coincide or not coincide. We analyze these cases.

1. \(j = i\). After elimination of the loops we have

\[
\langle S_j(t_1)S_j(t_2)S_j(t_2)S_j(t_2)\rangle = \langle S_j(t_1)S_j(t_2)\rangle
\]

2. \(j \neq i\).
\[ \langle S_j(t_1)S_j(t_2) \rangle = \langle S_j(t_1)S_j(t_2) \rangle - g(t_1-t_2) \langle S_j^2 \rangle, \]

(A1)

describes a Gaussian random process. The function \( g(t) \) in the approximation under consideration is the local field correlation function (2.8). In fact, although

\[ \langle h(t)h \rangle = g(t) + \frac{4}{\pi} \sum_{j \neq j' \neq n} b_{j} b_{j'} \langle S_j S_j' \rangle, \]

the lattice sum in the second term contains a loop of interactions and should be omitted. Substituting (A1) and (A2) into (2.15), we find (in the case of \( j = j' \))

\[ g_3(t_1-t_2) = g^2(t_1-t_2). \]

(A3)

2. \( j \neq j' \). Terms which satisfy the condition of the absence of interaction loops are possible in this case, if the coupling between spins \( j \) and \( j' \) is realized strictly through spin \( i \). These terms appear at large values of \( t_1-t_2 \) and cause \( g_3(t_1-t_2) \) to differ somewhat from \( g^2(t_1-t_2) \).

We now consider the mean of the product \( \Pi_{j} \omega_{j}(t_{j}) \). If we couple the outer spins of some factors in the product and the inner spins of others, loops of interactions form. Therefore, the different \( \omega_{j}(t_{j}) \) must be coupled entirely to one another by both of their spins. Consequently, when there is an even number of factors, we have

\[ \langle \omega_{j_1}(t_{j_1})\omega_{j_2}(t_{j_2})...\omega_{j_n}(t_{j_n}) \rangle = \sum \prod g^2(t_{j_k}-t_{j_k'}), \]

(A4)

where the sum is taken over all the possible interactions and the product is taken over the \( n \) pairs formed. When there is an odd number of factors, the mean is equal to zero. The property (A4) indicates that \( \omega_{j}(t_{j}) \) describes a Gaussian random process in the approximation under consideration.

APPENDIX B

Let us average the exponential function \( V_{2}(t) \) of the quadratic Gaussian noise. To determine the combination factors in the \( n \)th term of the series (2.12) for \( V_{2}(t) \), we note that all \( n \) factors are identical, since the integration in each of them is carried out over the entire interval \((0,t)\) independently of the others. When we average a difference appears in the way (order) the \( \omega_{j}(t_{j}) \) from different factors combine.

We consider two methods:

1) Loops of \( n \) variables. Since a loop does not have a beginning or an end and since all the factors are identical, the first factor can be selected as the starting point for constructing the loop, and the remaining \( n-1 \) variables can be rearranged by varying their sequence in \((n-1)!/2\) different ways.

2) A total of \( n \) variables are distributed among \( k \) loops: \( n_1+n_2+...+n_k = n \). The \( n \) factors in (2.12) can be distributed among these loops in \( n! / n_1! n_2! ... n_k! \) ways. Then a combination factor is written for each individual loop according to rule 1). If some of the loops are identical, substitution of the factors in one of them into another identical loop does not give a new combination; therefore, the resultant product of combination factors should be divided by \( m_{1}!m_{2}!...m_{k}! \), where \( m_{i} \) is the number of identical loops of the \( i \)th kind.

The combination factor obtained according to rules 1) and 2) should first be divided, according to (2.12), by \( n! \). Second, it should be multiplied by \( 2^{k} \) because there are two ways to place the two Gaussian random variables in \( \omega_{j}(t) \) in a loop. The latter factor has already been taken into account in (2.21) by replacing \( (a_{2}^{2})^{n} \) by \( (a_{2}^{2})^{k} \). As a result, before the product of \( k \) contributions of the form (2.21) for the loops

\[ O_{1}(t)O_{2}(t)...O_{k}(t) \]

we obtain the following combination factor

\[ \frac{(2^{k}m_{1}!m_{2}!...m_{k}!)^{n}}{n!} \]

(B1)

Determining the first members of the series in (2.12) for \( V_{2}(t) \) according to the rules described, we can easily see that if this series is differentiated with respect to time, we obtain the original series multiplied by a sum of loops with a different number of time variables, one of which is fixed at the time \( t \):

\[ \frac{d}{dt} V_{2}(t) = \sum_{n=2}^{\infty} K_{n}(t) V_{2}(t), \]

(B2)

where the cumulant \( K_{n}(t) \) equals

\[ (-i a_{2})^{n} \int_{0}^{t} dt_{1}...\int_{0}^{t} dt_{n-1} g(t-t_{1})g(t-t_{2})...g(t-t_{n-1}) \]

\[ \times dt_{n}, \]

(B3)

Integrating Eq. (B2), we obtain expression (2.22), where

\[ F_{2}(t) = \sum_{n=2}^{\infty} \int_{0}^{t} K_{n}(t')dt'. \]

(B4)

The simple structure of the series (B4) makes it possible to reduce the calculation of its sum to the solution of the integral equation (2.24) for \( R(t',t) \), which is the sum of an auxiliary series of broken loops. The \( n \)th term in the latter is obtained from (B3) after removing the integration with respect to \( t_{n-1} = t' \) and the factor \( g(t_{n-1} - t) \). If the integrand in the \( n \)th-order term is multiplied by \( g(t'-t'') \) and integrated with respect to \( t'' \), we obtain an \((n+1)\)th-order term (after a trivial replacement of variables). Just this property of the auxiliary series is expressed by Eq. (2.24).

Finally, we obtain the series (2.34) from the series (B4). We transform expression (2.21) into

\[ O_{2}(t) = \left( -i a_{2} \right)^{n} \int_{-\infty}^{t} dt_{1}...\int_{-\infty}^{t} dt_{n-1} g(t_{1})...g(t_{n-1}) \]

\[ \times g(-t_{n-1} - ... - t_{1}), \]

(B5)

which was derived with consideration of the fact that the product of correlation functions differs appreciably from
zero only in a small part of the integration region in the vicinity of the diagonal $t_1 = t_2 = \ldots = t_\nu$ and does not depend on the position on this diagonal. The convolution in (B5) is easily calculated after obtaining the Fourier transform.


