Spectral diffusion and decay of spin echo signals in inhomogeneously broadened systems with quadrupole interaction

S. N. Polulach

Simferopol State University, Crimea, Ukraine

N. A. Sergeev

Pedagogical High School, 76-200 Słupsk, Poland
(Submitted 13 October 1994)
Zh. Éksp. Teor. Fiz. **108**, 14–22 (July 1995)

The decay of two-pulse spin echo signals in inhomogeneously broadened systems with $I \geqslant 1$ due to fluctuations in the Hamiltonians of the Zeeman and quadrupole interactions is studied. It is shown that in the presence of selective excitation in the quadrupole spin system with $I=3/2$ of the central spectral transitions ($\pm 1/2 \leftrightarrow \mp 1/2$) and also of the three-quantum transitions ($\pm 3/2 \leftrightarrow \mp 3/2$), the decay of spin echo signals at $t=2\tau$ and $t=4\tau$ (τ is the time between pulses) is determined by the fluctuations in the Zeeman Hamiltonian only. The spin echo decay rate at $t=2\tau$ is slow compared to the spin echo decay rate at $t=4\tau$. For selective excitation of $\pm 3/2 \leftrightarrow \mp 1/2$ spectral transitions and excitation for all spectral transitions, the decay of spin echo signals at $t=2\tau$ is determined by fluctuations in both the Zeeman Hamiltonian and the quadrupole Hamiltonian.

1. INTRODUCTION

The phenomenon of a two-pulse echo in radio and optical spectroscopy is widely used to investigate the structure of matter (the structure of energy levels, the nature of the chemical bond, the spatial arrangement of particles, etc.) in various states (gases, liquids, solids).[1] Apart from their purely applied value, studies of the echo phenomenon are of general physical interest, since they yield unique information about various possible relaxation mechanisms in the evolution of nonequilibrium states of physical systems.

At present, many experimental results on the relaxation of signals of two-pulse echoes in inhomogeneously broadened two-level systems[2,3] are well explained within the framework of the spectral diffusion model, that is, in terms of temporal fluctuations (diffusion) of the resonant frequencies (the Rabi frequencies[2,3]) within the limits of the inhomogeneously broadened resonance line.[4,5]

The simplest example of an inhomogeneously broadened two-level system is a system of magnetic moments of nuclei with spin $I=1/2$, each of which is located in its own local magnetic field. In nuclear spin systems with $I=1/2$ the resonant frequencies, that is, the nuclear magnetic resonance (NMR) frequencies, are determined by the local magnetic fields acting on the magnetic moments of the nuclei. In contrast to nuclear spin systems with $I=1/2$, in systems of quadrupole nuclei with $I \geqslant 1$ the resonant NMR frequencies are determined not only by the local magnetic fields acting on the magnetic moments of the nuclei (the Zeeman interaC-tion), but also by the nonuniform local electric fields acting on the electric quadrupole moments of the nuclei (the quadrupole interaction). In this case the energy levels of the nuclear spin system are not uniformly spaced, and fluctuations in the resonant NMR frequencies of the quadrupole nuclei can be caused not only by fluctuations in the local magnetic fields, but also by fluctuations in the nonuniform electric fields acting on the nuclear quadrupole moments. A study of the relaxation of two-pulse echo signals in inhomogeneity broadened spin systems with quadrupole interactions (in systems with nonuniformity spaced energy levels) under the action of fluctuating Zeeman and quadrupole interaction Hamiltonians has yet to be carried out.

The goal of the present work is to study, within the framework of the spectral diffusion model, the kinetics of the decay of two-pulse echo signals in inhomogeneously broadened spin systems with quadrupole interaction.

2. THEORY

Let us consider the response of a system of quadrupole nuclei located in temporally fluctuating local magnetic and electric fields to two-pulse sequence R_1-τ-R_2-t, where R_1 and R_2 are operators describing the action of the radio frequency (RF) pulses on the nuclear spin system, and τ is the time interval between the RF pulses. The Hamiltonian ($\hbar=1$) of the quadrupole nucleus with spin I has the form (Ref. 6, Ch. 7)

$$H(t)=-\omega_0(t)I_Z+\omega_Q(t)[I_Z^2-(1/3)I(I+1)]. \tag{1}$$

Here $\omega_0(t)$ is the Larmor frequency of the nucleus at time t, which is determined by the magnetic field acting on the magnetic moment of the nucleus, and $\omega_Q(t)$ is the frequency of the quadrupole interaction, determined by the interaction of the quadrupole moment of the nucleus with the electric field gradient at the nucleus (Ref. 6, Ch. 7).

We represent $\omega_0(t)$ and $\omega_Q(t)$ in the form

$$\begin{aligned}\omega_0(t)&=\omega_0+\delta\omega_0(t),\\ \omega_Q(t)&=\omega_{Q0}+\delta\omega_Q(t),\end{aligned} \tag{2}$$

where $\omega_0=\langle\omega_0(t)\rangle$ is the mean value of the fluctuating Larmor frequency, $\omega_{Q0}=\langle\omega_Q(t)\rangle$ is the mean value of the fluctuating frequency of the quadrupole interaction. In a coordinate system rotating with frequency ω_{RF} (ω_{RF} is the repetition frequency of the RF pulses) the interaction Hamiltonian (1) takes the form

$$H(t)=H_0+H_1(t), \tag{3}$$

where

$$H_0=-I_Z\Delta+\omega_{Q0}[I_Z^2-(1/3)I(I+1)], \tag{4}$$

and

$$H_1(t)=-\delta\omega_0(t)I_Z+\delta\omega_Q(t)[I_Z^2-(1/3)I(I+1)], \tag{5}$$

$$\Delta=\omega_0-\omega_{RF}.$$

Assuming that the fluctuations in ω_0 and ω_Q can be neglected during the time over which the RF pulses act, in the adiabatic approximation (i.e., assuming that the fluctuations in ω_0 and ω_Q do not cause changes in the orientation of the spin I (Ref. 6, Ch. 10) we obtain for the two-pulse echo signal at time t (t is reckoned from the end of the first pulse)

$$V(\tau,t)=\sum_{m,m_1,m_2} A_{m,m_1,m_2}(\tau,t)$$
$$\times\langle[R_\omega(\tau,t)]_{S_{1\omega},S_{2\omega}}[R_Q(\tau,t)]_{S_{1Q},S_{2Q}}\rangle. \tag{6}$$

Here, $\langle...\rangle$ denotes averaging over all realizations of the random processes describing the fluctuations of $\omega_0(t)$ and $\omega_Q(t)$. The functions $A_{m,m_1,m_2}(\tau,t)$ do not depend on the fluctuations of the Larmor frequency or the quadrupole interaction frequency, and have the form

$$A_{m,m_1,m_2}(\tau,t)=\sqrt{I(I+1)-m(m+1)}\langle m|R_2|m_1\rangle$$
$$\times\langle m_1|R_1I_ZR_1^{-1}|m_2\rangle\cdot\langle m_2|R_2^{-1}|m+1\rangle$$
$$\times\exp\{-i(t-\tau)[\Delta-(2m+1)\omega_{Q0}]$$
$$-i\tau[(m_2-m_1)\Delta-(m_2^2-m_1^2)\omega_Q]\}, \tag{7}$$

where $|m\rangle$ and m are the eigenfunctions and eigenvalues of the operator $I_z(I_z|m\rangle=m|m\rangle)$.

The functions $A_{m,m_1,m_2}(\tau,t)$ describe the two-pulse response of a quadrupole nucleus when fluctuations in ω_0 and ω_Q are absent. As follows from formula (7), the echo signals are formed at times t at which the argument of the exponential in formula (7) is equal to zero simultaneously for all isochromats of the inhomogeneously broadened spectra line, i.e., formation of the echo signal is possible at times $t=k\tau$ under the condition that the quantity

$$k=1+\frac{\Delta(m_1-m_2)+(m_2^2-m_1^2)\omega_{Q0}}{\Delta-\omega_{Q0}(2m+1)} \tag{8}$$

not depend on Δ or ω_{Q0}.

The relaxation functions $[R_\omega(\tau,t)]_{S_{1\omega},S_{2\omega}}$ and $[R_Q(\tau,t)]_{S_{1Q},S_{2Q}}$, which govern the kinetics of the decay of the two-pulse spin echo signals, have the form

$$[R_\omega(\tau,t)]_{S_{1\omega},S_{2\omega}}=\exp\left\{i\int_0^t S_\omega(t_1)\delta\omega_0(t_1)dt_1\right\}, \tag{9}$$

$$[R_Q(\tau,t)]_{S_{1Q},S_{2Q}}=\exp\left\{i\int_0^t S_Q(t_1)\delta\omega_Q(t_1)dt_1\right\}. \tag{10}$$

Here

$$S_\omega(t_1)=\begin{cases} S_{1\omega}=(m_1-m_2), & t\in(0,\tau)\\ S_{2\omega}=-1, & t\in(\tau,t)\end{cases} \tag{11}$$

$$S_Q(t_1)=\begin{cases} S_{1Q}=(m_2^2-m_1^2), & t\in(0,\tau)\\ S_{2Q}=(2m+1), & t\in(\tau,t),\end{cases} \tag{12}$$

The relaxation functions (9) are determined by the fluctuations in the magnetic field, which act on the magnetic moment of the nucleus, whereas the relaxation functions (10) are determined by the fluctuations in the nonuniform electric field at the nucleus. It is reasonable to assume that the physical mechanisms that cause fluctuations in the frequencies ω_0 and ω_Q are independent, and that the random realizations of $\omega_0(t)$ and $\omega_Q(t)$ can be averaged over separately:

$$\langle[R_\omega(\tau,t)]_{S_{1\omega},S_{2\omega}}[R_Q(\tau,t)]_{S_{1Q},S_{2Q}}\rangle$$
$$=\langle[R_\omega(\tau,t)]_{S_{1\omega},S_{2\omega}}\rangle\langle[R_Q(\tau,t)]_{S_{1Q},S_{2Q}}\rangle.$$

For subsequent calculation of the contribution of spectral diffusion of the frequencies $\omega(t)$ and $\omega_Q(t)$ to the kinetics of the decay of the two-pulse echo signals, we assume that the random spectral diffusion processes are Markovian, or more specifically, Gaussian Markovian and Lorentzian Markovian.[5]

The explicit form of the relaxation functions (9) and (10) differs from the corresponding expression describing the kinetics of decay of the echo signals in two-level spin systems with $I=1/2$ (expression (1.62) in Ref. 5) only in the specific form of functions (11) and (12). Therefore, using the averaging technique detailed in Ref. 5, for a Gaussian Markov spectral diffusion process we obtain

$$\langle[R_J(\tau,t=k\tau)]_{S_{1J},S_{2J}}\rangle$$
$$=\exp\{-\sigma_J^2\tau_{cJ}^2[(S_{1J}^2+(k-1)S_{2J}^2)(\tau/\tau_{cJ})$$
$$+(S_{1J}S_{2J}-S_{1J}^2-S_{2J}^2)+S_{1J}(S_{1J}-S_{2J})\exp(-\tau/\tau_{cJ})$$
$$+S_{2J}(S_{2J}-S_{1J})\exp(-(k-1)\tau/\tau_{cJ})+S_{1J}S_{2J}$$
$$\times\exp(-k\tau)/\tau_{cJ})]\}, \tag{13}$$

and for a Lorentzian Markov spectral diffusion process,

$$\langle[R_J(\tau,t=k\tau)]_{S_{1J},S_{2J}}\rangle$$
$$=\exp\{-\sigma_J[\tau(|S_{1J}|+(k-1)|S_{2J}|)-2|S_{1J}|\tau_{cJ}$$
$$\times\ln[1+(|S_{2J}|/|S_{1J}|)(1-\exp(-(k-1)\tau/\tau_{cJ}))]]\}. \tag{14}$$

In formulas (13) and (14) the subscript J can take the values ω and Q; $\tau_{c\omega}$ and τ_{cQ} are correlation times that describe the fluctuations in $\omega_0(t)$ and $\omega_Q(t)$, respectively; σ_ω and σ_Q are parameters that define the widths of the resonant frequency distributions, which are due, respectively, to inhomogeneous magnetic and inhomogeneous quadrupole broadening.

3. DISCUSSION

We will center our discussion of the above results on quadrupole nucleus with $I=3/2$. The NMR spectrum of

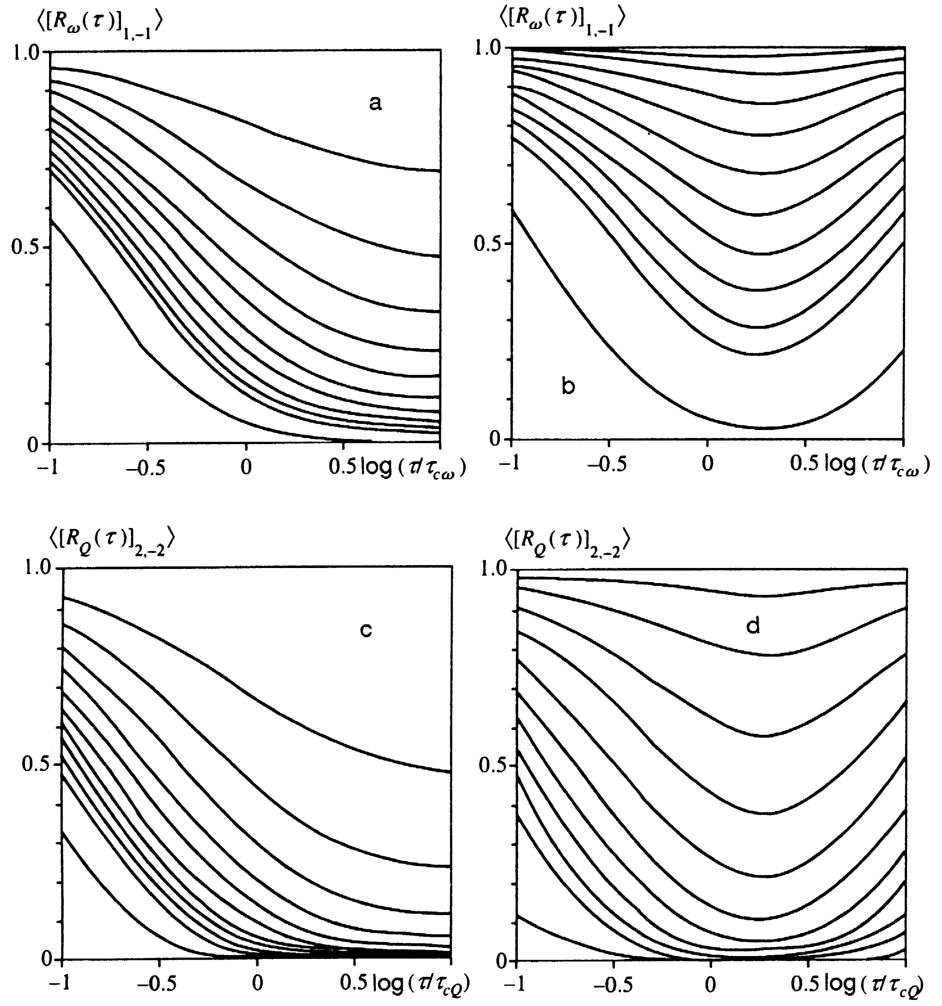

FIG. 1. Graph of $\langle[R_\omega(\tau)]_{1,-1}\rangle$ vs $\log(\tau/\tau_{c\psi})$ for a Lorentzian Markov process (a,b) and $\langle[R_Q(\tau)]_{2,-2}\rangle$ vs $\log(\tau/\tau_{cQ})$ for a Gaussian Markov process (c,d). The dimensionless parameter $\sigma_\omega\tau$ (from above down) takes the values: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0. The dimensionless parameters $\sigma_\omega\tau$ (a,b) and $\sigma_Q\tau$ (c,d) (top to bottom) take the values 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0.

such a nucleus is a triplet, with lines at $\omega_0 \pm 2\omega_{Q0}$ ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions and ω_0 ($\pm 1/2 \leftrightarrow \mp 1/2$) transition (Ref. 6, Ch. 7).

In this case, two spin echo signals can appear in a two-pulse response at times $t=2\tau$ and $t=4\tau$ (Ref. 7). The echo signal receives a contribution at $t=2\tau$, according to relation (8), from the matrix elements for which the magnetic quantum numbers m, m_1, and m_2 are

$$m=1/2, \quad m_1=3/2, \quad m_2=1/2$$
$$m=-1/2, \quad m_1=1/2, \quad m_2=-1/2 \qquad (15)$$
$$m=-3/2, \quad m_1=-1/2, \quad m_2=-3/2.$$

Substituting these values of m, m_1, and m_2 into Eqs. (6) and (7), we find that the amplitude of the echo signal $V(2\tau)$ is given by

$$V(2\tau)=A_{1/2,3/2,1/2}\langle[R_\omega(\tau)]_{1,-1}\rangle \cdot \langle[R_Q(\tau)]_{-2,2}\rangle + A_{-3/2,-1/2,-3/2}\langle[R_\omega(\tau)]_{1,-1}\rangle \times \langle[R_Q(\tau)]_{2,-2}\rangle + A_{-1/2,1/2,-1/2}\langle[R_\omega(\tau)]_{1,-1}\rangle \times \langle[R_Q(\tau)]_{0,0}\rangle. \qquad (16)$$

For the Gaussian Markov and Lorentzian Markov processes describing the fluctuations in ω_0 and ω_Q, the relaxation functions in relation (16) according to (13) and (14) have,

$$\langle[R_\omega(\tau)]_{1,-1}\rangle=\exp\{-\sigma_\omega^2\tau_{c\omega}^2[1+2(\tau/\tau_{cw}) -(2-\exp(-\tau/\tau_{cw}))^2]\}, \qquad (17)$$

$$\langle[R_Q(\tau)]_{2,-2}\rangle=\langle[R_Q(\tau)]_{-2,2}\rangle =\exp\{-4\sigma_Q^2\tau_{cQ}^2[1+2(\tau/\tau_{cQ}) -(2-\exp(-\tau/\tau_{cQ}))^2]\}, \qquad (18)$$

$$\langle[R_Q(\tau)]_{0,0}\rangle=1 \qquad (19)$$

for a Gaussian Markov process, and the form

$$\langle[R_\omega(\tau)]_{1,-1}=\exp\{-2\sigma_\omega[\tau-\tau_{c\omega}\ln(2-\exp(-\tau/\tau_{cw}))]\}, \qquad (20)$$

$$\langle[R_Q(\tau)]_{2,-2}\rangle=\langle[R_Q(\tau)]_{-2,2}\rangle =\exp\{-4\sigma_Q[\tau-\tau_{cQ}\ln(2-\exp(-\tau/\tau_{cQ}))]\}, \qquad (21)$$

$$\langle[R_Q(\tau)]_{0,0}\rangle=1. \qquad (22)$$

for a Gaussian Markov process.

Graphs of the relaxation functions (17), (18), and (20), (21) as functions of the dimensionless parameter τ/τ_{cJ} for various values of the parameter $\sigma_J \cdot \tau$ are plotted in Fig. 1. It follows from expression (17), (18) and (20), (21) and the curves in Fig. 1 that the relaxation functions describing the

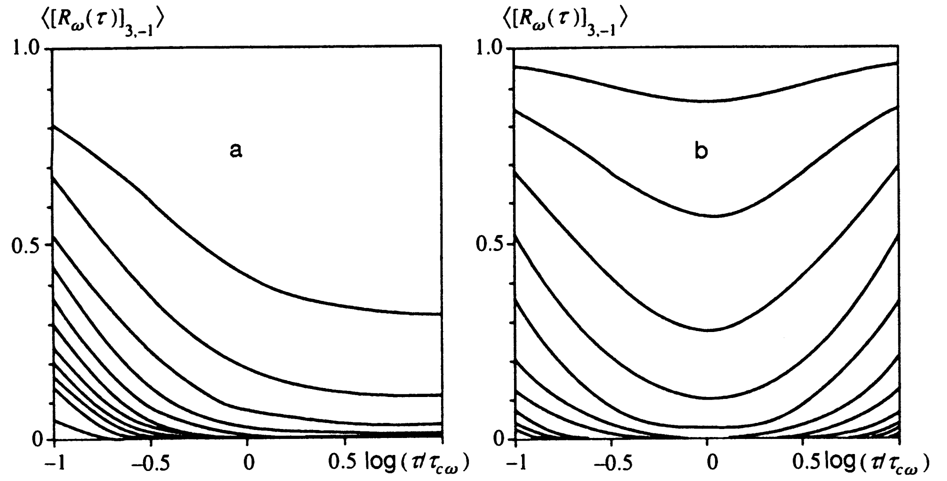

FIG. 2. Graph of $\langle[R_\omega(\tau)]_{3,-1}\rangle$ vs $\log(\tau/\tau_{c\omega})$ for a Lorentzian Markov process (a) and a Gaussian Markov process (b). The dimensionless parameter $\sigma_\omega\tau$ (top to bottom) takes the values 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0

decay of the echo signal do not have a simple $\exp(-\tau/T_2)$ form and consequently the relaxation process cannot be described by a relaxation time T_2. It is also interesting to note that the relaxation functions have a completely different dependence on the parameter τ/τ_{cJ} for the Lorentzian Markov and Gaussian Markov processes. Whereas for the Lorentzian Markov spectral diffusion process the relaxation of the echo is described by a monotonically decaying function of τ/τ_{cJ}, for a Gaussian Markov process there is a minimum in the dependence of $\langle[R_J(\tau)]_{S_{1J},S_{2J}}\rangle$ on τ/τ_{cJ} at $\tau/\tau_{cJ}=1.893$.

The first two terms in (16) describe the contribution to the spin echo amplitude $V(2\tau)$ due to excitation by RF pulses of the $\pm1/2\leftrightarrow\pm3/2$ transitions. The last term (16) is nonzero for excitation of the central $\pm1/2\leftrightarrow\mp1/2$ transition. If the amplitude of the magnetic field ω_1 of the RF pulses, expressed in frequency units, significantly exceeds ω_{Q0}, then the RF pulses excite all of the spectral transitions (nonselective excitation) and all three terms in (6) contribute to the echo signal at $t=2\tau$.

For small amplitudes of the RF pulses ($\omega_1\ll\omega_{Q0}$), the transitions are excited selectively. For selective excitation of the central transition ($m=-1/2$, $m_1=1/2$, $m_2=-1/2$), we find from Eq. (16) that the kinetics of decay of the echo signal $V_c(2\tau)$ is described by the expression

$$V_c(2\tau)=V_c(0)\langle[R_\omega(\tau)]_{1,-1}\rangle. \tag{23}$$

It follows from Eq. (23) that in the case of selective excitation of the central transition, the fluctuations in the quadrupole interaction frequency ω_Q have no effect on the nature of the decay of the echo amplitude at $t=2\tau$.

For selective excitation of a spin system at frequencies of the quadrupole satellites ($\omega_0\pm2\omega_{Q0}$), the decay of the echo signal at $t=2\tau$ is described by the expression

$$V_Q(2\tau)=V_Q(0)\langle[R_\omega(\tau)]_{1,-1}\rangle\cdot\langle[R_Q(\tau)]2,-2\rangle. \tag{24}$$

Comparing (23) and (24), we see that in the case of selective excitation of the $\pm3/2\leftrightarrow\pm1/2$ transitions, the kinetics of decay of the echo signal $V_Q(2\tau)$ is governed by the fluctuations in both the Larmor frequency and the quadrupole interaction frequency.

In addition to the echo signal at $t=2\tau$, in quadrupole spin systems with $I=3/2$ the formation of an echo at $t=4\tau$ is also possible.[7,8] As was first shown in Refs. 8 and 7, the echo at $t=4\tau$ is also possible.[7,8] As was first shown in Refs. 8 and 7, the echo at $t=4\tau$ is formed as a result of excitation in the spin system by the first RF pulse of a three-quantum "transition" ($\pm3/2\leftrightarrow\mp3/2$), and the amplitude of this echo peaks when the repetition frequency of the RF pulses coincides with the frequency of the central ($\pm1/2\leftrightarrow\mp1/2$) transition. The difference between the conditions of formation of the echo at $t=4\tau$ and the conditions of formation of the echo at $t=2\tau$, observed upon selective excitation of the central transition, consists in the fact that for excitation of the three-quantum "transition" it is necessary that the amplitude ω_1 of the magnetic field of the RF pulses be of the order of ω_{Q0}.[7,8]

The echo signal at $t=4\tau$ receives a contribution, according to Ref. 8, only from the matrix element for which $m=-1/2$, $m_1=3/2$, and $m_2=-3/2$. Substituting these values for m, m_1, and m_2 into expression (6) and (7), we obtain the following expression for the amplitude of the spin echo signal $V(4\tau)$:

$$V(4\tau)=V(0)\langle[R_\omega(\tau)]_{3,-1}\rangle. \tag{25}$$

For the Gaussian Markov and Lorentzian Markov processes describing the fluctuations in ω_0 and ω_Q, the relaxation function in Eq. (25), according to Eqs. (13) and (14), has the form

$$\langle[R_\omega(\tau)]_{3,-1}\rangle=\exp\{-\sigma_\omega^2\tau_{c\omega}^2[3(1+4(\tau/\tau_{c\omega})) -(4-3\exp(-\tau/\tau_{c\omega})) \times(4-\exp(-3\tau/\tau_{c\omega}))]\}, \tag{26}$$

for a Gaussian Markov process, and

$$\langle[R_\omega(\tau)]_{3,-1}\rangle=\exp\{-6\sigma_\omega[\tau-\tau_{c\omega}\ln((4-\exp(-3\tau/\tau_{c\omega}))/3)]\}. \tag{27}$$

for a Lorentzian Markov process. Graphs of the relaxation functions (26) and (27) as functions of the dimensionless parameter $\tau/\tau_{c\omega}$ for various values of the parameter $\sigma_\omega\tau$ are plotted in Fig. 2.

From a comparison of relations (23) and (25) it follows that, as in the case of the echo at $t=2\tau$, which appears upon selective excitation of the central transition, the kinetics of the decay of the echo signal at $t=4\tau$ is governed only by the fluctuations of the Larmor frequency. However, as can be seen by comparing the curves shown in Figs. 1a, 1b, and 2, the rate of decay of the echo signal amplitude $V(4\tau)$ is greater than that of the echo signal amplitude $V_c\ (2\tau)$.

4. CONCLUSION

The foregoing of the decay of two-pulse echo signals in inhomogeneously broadened systems with quadrupole interaction shows that fluctuations of the Zeeman and quadrupole Hamiltonians are manifested in different ways in different echo signals and under various conditions of excitation of the spin system. In particular, for a spin system with $I=3/2$ an examination of the kinetics of the decay of the "three-quantum" echo at $t=4\tau$ (or of the echo at $t=2\tau$ for selective excitation of the central $\pm 1/2 \leftrightarrow \mp 1/2$ transition makes it possible to identify the random process underlying the fluctuations of the Larmor frequency ω_0 and to determine its characteristic parameters σ_ω and $\tau_{c\omega}$. The results obtained here allow one to determine the parameters σ_Q and τ_{cQ}, which underlie the fluctuations in the quadrupole interaction frequency ω_Q, by analyzing the kinetics of the decay of the echo at $t=2\tau$ formed by selective excitation of the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions.

[1] D. M. S. Bagguley (ed.), *Pulsed Magnetica Resonance: NMR, ESR, and Optics: A Recognition of E. L. Hahn*, Clarendon Press, Oxford (1992).

[2] J. D. Macomber, *The Dynamics of Spectroscopic Transitions*, Wiley, New York (1976).

[3] L. Allen and J. H. Eberly, *Optical Resonance and Two-level Atoms*, Wiley, New York (1975).

[4] J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).

[5] K. M. Salikhov, A. G. Semënov, and Yu. D. Tsvetkov, *The Electron Spin Echo and its Applications* [in Russian], Nauka, Novosibirsk (1976), Ch. 2.

[6] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).

[7] G. N. Abelyashev, V. N. Berzhanskiĭ, N. A. Sergeev, and Yu. V. Fedotov, Pis'ma Zh. Éksp. Teor. Fiz. **42**, 453 (1985) [JETP Lett. **42**, 561 (1985)].

[8] G. N. Abelyashev, V. N. Berzhanskiĭ, N. A. Sergeev, and Yu. V. Fedotov, Zh. Éksp. Teor. Fiz. **94**, 227 (1988) [Sov. Phys. JETP **67**, 127 (1988)].

Translated by Paul F. Schippnick