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

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The decay of two-pulse spin echo signals in inhomogeneously broadened systems with \( I = 1 \) due to exchange of electromagnetic fields 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 \( (\pm 1/2 \rightarrow \pm 1/2) \) and also of the three-quantum transitions \( (\pm 3/2 \rightarrow \pm 3/2) \), the decay of spin echo signals at \( t = 2\tau \) and \( t = 4\tau \) (\( \tau \) 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 \( \pm 3/2 \rightarrow \pm 1/2 \) 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). 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 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) within the limits of the inhomogeneously broadened resonance line.

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 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 \( I = 1 \) the resonant NMR frequencies are determined not only by the local magnetic fields acting on the magnetic moments of the nuclei (the Zeeman interaction), 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 inhomogeneously broadened spin systems with quadrupole interactions (in systems with nonuniformly 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 \( R_1 \tau R_2 \tau \), where \( R_1 \) and \( R_2 \) are operators describing the action of the radio frequency (RF) pulses on the nuclear spin system, and \( \tau \) is the time interval between the RF pulses. The Hamiltonian \( \{k=1\} \) of the quadrupole nucleus with spin \( I \) has the form (Ref. 6, Ch. 7)

\[
H(t) = -\omega_0(t)I_z + \omega_Q(t)(I_z^2 - (1/3)(I_+ I_-)).
\]

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

\[
\omega_0(t) = \omega_0 + \delta\omega_0(t),
\]

\[
\omega_Q(t) = \omega_Q + \delta\omega_Q(t),
\]

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

$$H(t) = H_0 + H_1(t),$$

where

$$H_0 = -i2\Delta + \omega_Q(I_2^2 - (1/3)I(I+1)),$$

and

$$H_1(t) = -\Delta \omega(t)I_2(12 - (1/3)I(I+1)), \quad \Delta = \omega_{RF} - \omega_{RF}.$$

Assuming that the fluctuations in $\omega_0$ and $\omega_Q$ can be neglected during the time over which the RF pulses act, in the adiabatic approximation (i.e., assuming that the fluctuations in $\omega_0$ and $\omega_Q$ 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 $t$ (it is reckoned from the end of the first pulse)

$$V(t,\tau) = \sum_{m_1, m_2} A_{m_1, m_2}(\tau, \tau') \times \langle \{R(\tau, \tau')\}_{m_2} \{R(\tau, \tau')\}_{m_1} \rangle,$$

(6)

Here, (...) denotes averaging over all realizations of the random processes describing the fluctuations of $\omega_0(t)$ and $\omega_Q(t)$.

The functions $A_{m_1, m_2}(\tau, \tau')$ do not depend on the fluctuations of the Larmor frequency or the quadrupole interaction frequency, and have the form

$$A_{m_1, m_2}(\tau, \tau') = \langle \{I(t, \tau)\}_{m_1} \{I(t, \tau')\}_{m_2} \rangle.$$

The explicit form of the relaxation functions (9) and (10) differs from the corresponding expression describing the kinetics of 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.

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For subsequent calculation of the contribution of spectral diffusion of the frequencies $\omega_0$ and $\omega_Q$ 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.

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such a nucleus is a triplet, with lines at $\pm 3/2 \rightarrow \pm 1/2$ transitions and $\pm 1/2 \rightarrow \mp 1/2$ transition (Ref. 6, Ch. 7).

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

\begin{align*}
  m &= 1/2, \quad m_1 = 1/2, \quad m_2 = 1/2 \\
  m &= -1/2, \quad m_1 = 1/2, \quad m_2 = -1/2 \\
  m &= -3/2, \quad m_1 = -1/2, \quad m_2 = -3/2. 
\end{align*}

Substituting these values of $m_1$, $m_2$, and $m_3$ into Eqs. (6) and (7), we find that the amplitude of the echo signal $V(2T)$ is given by

\begin{align*}
  V(2T) &= A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) - A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) - A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) \\
  &+ A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) - A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) - A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) \\
  &\times \langle R_\sigma(\tau) \rangle_{1/2,1} - A_{11/2,1/2,1}(\langle R_\sigma(\tau) \rangle_{1/2,1}) \\
  &\times \langle R_\sigma(\tau) \rangle_{1/2,1}. 
\end{align*}

For the Gaussian Markov and Lorentzian Markov processes describing the fluctuations in $\sigma_\theta$ and $\sigma_\phi$, the relaxation functions in relation (16) according to (13) and (14) have,

\begin{align*}
  \langle R_\sigma(\tau) \rangle_{1/2,1} &= \exp(-\sigma^2 \tau^2 [1 + 2(\sigma_\tau \tau)]) \\
  &- (2 - \exp(-\sigma_\tau \tau))^2, \\
  \langle R_{\sigma}(\tau) \rangle_{1/2,1} &= \exp(-4\sigma^2 \tau^2 [1 + 2(\sigma_\tau \tau)]) \\
  &- (2 - \exp(-\sigma_\tau \tau))^2, \\
  \langle R_{\sigma}(\tau) \rangle_{1/2,1} &= 1. 
\end{align*}

for a Gaussian Markov process, and the form

\begin{align*}
  \langle R_\sigma(\tau) \rangle_{1/2,1} &= \exp(-2\sigma^2 \tau^2 (2 - \exp(-\sigma_\tau \tau))) \\
  \langle R_{\sigma}(\tau) \rangle_{1/2,1} &= \exp(-4\sigma^2 \tau^2 (2 - \exp(-\sigma_\tau \tau)))). 
\end{align*}

for a Gaussian Markov process.

Graphs of the relaxation functions (17), (18), and (20), (21) as functions of the dimensionless parameter $\sigma_\tau \tau$ for various values of the parameter $\sigma_\tau \tau$ 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
frequency. The echo signal at $t=2\tau$ receives a contribution, according to Ref. 8, only from the matrix element for which $m=-1/2, m_1=1/2, m_2=-1/2$. 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 $V(4\tau)$:

$$V(4\tau) = V(0)|\langle R_d(4\tau)|l_{1-1}\rangle|.$$  (25)

For the Gaussian Markov and Lorentzian Markov processes describing the fluctuations in $s_0$ and $s_0$, the relaxation function in Eq. (25), according to Eqs. (13) and (14), has the form

$$|\langle R_d(4\tau)|l_{1-1}\rangle| = \exp\left[-\sigma_\tau^2\sigma_\tau^2(1 + 4(\tau\tau)) - (4 - 3 \exp(-\tau\tau_\omega)) \times (4 - \exp(-3\tau\tau_\omega))\right].$$  (26)

For a Gaussian Markov process, and

$$|\langle R_d(4\tau)|l_{1-1}\rangle| = \exp\left[-6\sigma_\tau^2\tau - \tau_\omega\ln(4 - \exp(-3\tau\tau_\omega))\right].$$  (27)

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

In addition to the echo signal at $t=2\tau$, in quadrupole spin systems with $t=3/2$ the formation of an echo at $t=4\tau$ is also possible. As was first shown in Refs. 8 and 7, the echo at $t=4\tau$ is described by the expression for a Lorentzian Markov process (a) and a Gaussian Markov process (b). The dimensionless parameter $\sigma_\tau\tau$ (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.

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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 $V(t)$ (27).

4. CONCLUSION

The foregoing of the decay of two-pulse echo signals in inhomogeneously broadened systems with quadruple 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 $\pm 1/2\rightarrow \pm 1/2$ transition makes it possible to identify the random process underlying the fluctuations of the Larmor frequency $\omega_0$ and to determine its characteristic parameters $\sigma_\omega$ and $\tau_\omega$. The results obtained here allow one to determine the parameters $\sigma_Q$ and $\tau_Q$, which underlie the fluctuations in the quadrupole interaction frequency $\omega_Q$, by analyzing the kinetics of the decay of the echo at $t = 2\tau$ formed by selective excitation of the $\pm 3/2\rightarrow \pm 1/2$ transitions.


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