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ABSTRACTS

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ACTIVATION OVER A FLUCTUATING BARRIER: CALCULATION OF DIPOLAR CORRELATION FUNCTION

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Many of NMR experimental values such as the second moment of NMR spectrum, spin-lattice relaxation rates, the time position and the amplitude of the solid echo signals, and others are governed by the dipolar correlation function [1]:

$$h(t'',t') = W\sum_{i,j}\overline{a_{ij}(t'')a_{ij}(t')}\,, \quad (1)$$

where $a_{ij}(t)$ are the values, which describe dipolar interactions between nuclear magnetic moments. The upper bar denotes the average on the random motions of spin pair i-j.
Motions of molecules or molecular groups in solids are usually described by the potential wells model, in which minima correspond to possible positions of these groups in lattice. The assumption of static potential barrier leads to well-known Markov processes [2,3]. It is reasonable to expect that motions can not be Markovian for the sake of the barrier is able to be non-static, modulated by some internal degrees of freedom [4,5]. We have taken into account the existence of possible additional states when the transition probability matrix become random, and the master equation transforms into the stochastic equation.

We have considered two-site model with fluctuating activation energy E, which as we expect is the Ornstein-Uhlenbeck (OU) process (Markov Gaussian process). Since rate constant W and E are connected with each other by the Arhenius activation law, W is described by the Markov log-normal process with drift and diffusion coefficients (Fokker-Planck equation) [3]:

$$a(W) = -\nu W_a \ln\frac{W}{W_a}, \quad b(W) = 2\nu W_a\left(\frac{\sigma}{RT}\right)^2 W\,, \qquad (2)$$

where $W_a = W_0\exp\left(-\frac{E_a}{RT}\right)$, ν and σ^2 are rate constant and dispersion of the fluctuations. In linear approximation of the drift we can write coefficients (2) in the form:

$$a(W) = -\nu(W-(z+1)g) \quad b(W) = 2\nu gW\,, \quad (3)$$

where $g = W_a\left(\frac{\sigma}{RT}\right)^2$ and $z+1 = \left(\frac{RT}{\sigma}\right)^2$. This is the well-known gamma Pearson process. The stochastic master equation driven by gamma Pearson process may be solve by method described in [6]. The final solution for dipolar correlation function in Laplace representation is:

$$h(s) = \overline{M_2}\frac{1}{s} + \Delta M_2\frac{2\gamma_1 - 1 + 2\sum_{k=2}^{\infty}(-2)^{k-1}\alpha_1\alpha_2\ldots\alpha_{k-1}\gamma_k}{s + 2\delta_1 + 2\sum_{k=2}^{\infty}(-2)^{k-1}\alpha_1\alpha_2\ldots\alpha_{k-1}\delta_k}\,, \quad (4)$$

where $\overline{M_2}$ is the second moment of motionally narrowed NMR line and $\Delta M_2 = M_2 - \overline{M_2}$ where M_2 is the second moment of NMR line in "rigid" lattice, α_l, γ_l, δ_l are determined by recurrent relations:

$$\alpha_i = \frac{1}{l_i + 2a_i\alpha_{i-1}},$$
$$\delta_i = a_i\alpha_i\delta_{i-1}, \quad (5)$$
$$\gamma_i = \alpha_i(a_i\gamma_{i-1} + f_i),$$
with initial conditions:
$$\alpha_0 = 0, \delta_0 = 1, \gamma_0 = 0. \qquad (6)$$
In Eq.(5)
$$a_i = i(z+i)g\nu,$$
$$l_i = s + i\nu, \quad (7)$$
$$f_i = g^i \frac{\Gamma(z+i+1)}{\Gamma(z+1)}.$$
The obtained result (Eq.(4)) has been used for the calculation of the temperature dependences of spin-lattice relaxation times in the laboratory and rotating frames.

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