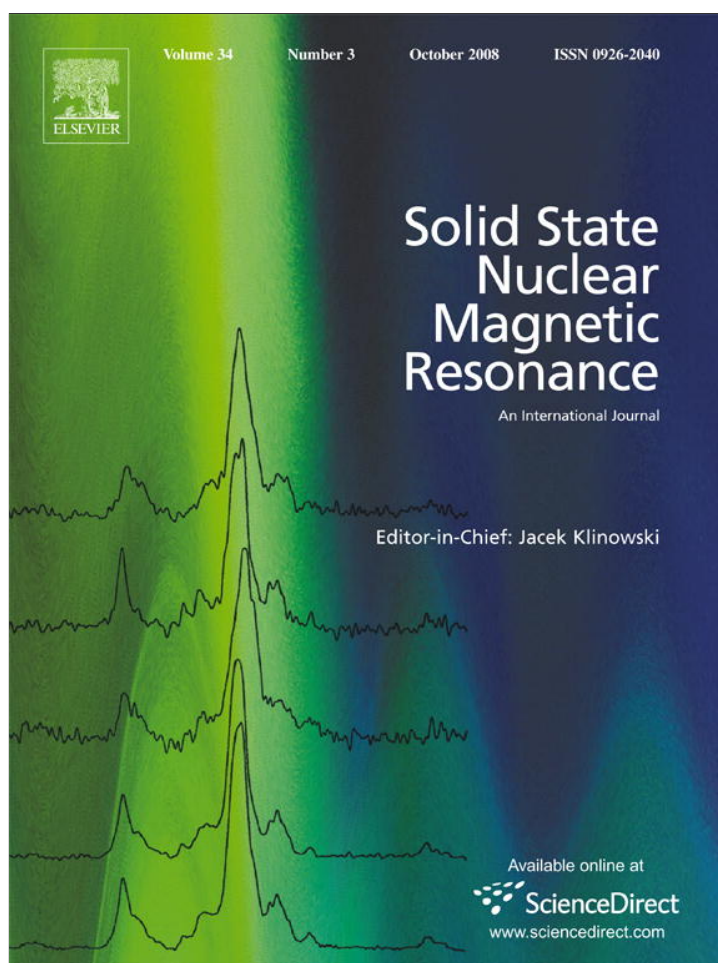


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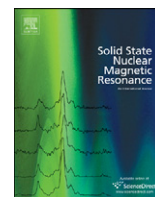
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Kubo–Anderson oscillator and NMR of solid state

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ABSTRACT

The analytical solution for the Kubo–Anderson oscillator with a fluctuating frequency ω for arbitrary distribution function $p(\omega)$ has been obtained. The obtained theoretical expression has been applied to consideration of some dynamical problems of solid state NMR, namely (1) dynamical transformation of NMR line shape and spin-echo signal and (2) the temperature transformation of the second moment of NMR line for the case, when the potential barrier for the mobility of magnetic nuclei is a stochastic function of time.

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1. Introduction

The two-level system with a stochastically fluctuating frequency has found wide applications in condensed phase physics ranging from magnetic resonance spectroscopy [1–12] and non-linear optical spectroscopy [13–17] to the problem of decoherence and dephasing in spin-based solid state quantum computers [18–20]. This model is described by Kubo–Anderson stochastic differential equation in the form [2,3]

$$\dot{x} = -i\varepsilon(t)\omega(t) \times \bar{x}, \quad (1)$$

where $\omega(t)$ is stochastically fluctuating frequency and $\varepsilon(t)$ is a non-stochastic function of time.

The formal average solution of Eq. (1) has the form

$$\langle x(t) \rangle = \left\langle x(0) \exp\left(-i \int_0^t \varepsilon(t')\omega(t') dt'\right) \right\rangle, \quad (2)$$

where symbol $\langle \dots \rangle$ means averaging over all realizations of the random process.

In pulse NMR experiments, the time decays of $M_{X,Y}$ and M_Z components of a nuclear magnetization are recorded. If $\varepsilon(t) = 1$, the function $\langle x(t) \rangle \equiv \langle M_{X,Y}(t) \rangle$ describes the linear response function or the free induction decay (FID), and for the stationary stochastic process Fourier transform of the function of Eq. (2) gives the NMR absorption line shape [1].

If $\varepsilon(t) = 1$ for $0 \leq t < \tau$ and $\varepsilon(t) = -1$ for $\tau \leq t$, the function $\langle x(t, \tau) \rangle \equiv \langle M_{X,Y}(t, \tau) \rangle$ describes the spin-echo signal observed when the ensemble of two-level systems is irradiated by two pulses at times $t = 0$ and $t = \tau$ [5,21].

The analytical solutions of Eq. (1) are well-known for the cases when (1) the frequency ω jumps between two frequencies $\pm \Delta$ (dichotomous telegraphic process) [7,9,10], when (2) the random process is diffusion Lorentz–Markov stochastic process [5,21], and when (3) the random process is diffusion Gauss–Markov stochastic process [5,21]. These analytical solutions have been obtained based on the assumption of the specific form of the distribution function $p(\omega)$, which describes the set of ω between which the frequency jumps. In the case when the frequency ω jumps between two values, the function $p(\omega)$ has a doublet form. For Lorentz–Markov and Gauss–Markov stochastic processes, the distribution function $p(\omega)$ has Lorentz or Gauss forms, correspondingly. However, in real situations the distribution function $p(\omega)$ is not Gaussian, Lorentzian or doublet-like one.

In present paper, the analytical solution of Eq. (1) has been obtained for arbitrary distribution function $p(\omega)$. In contrast to the different methods of solving the stochastic Eq. (1), described in literature [22–25], we use the method proposed in Refs. [25–28]. In our opinion, the using of this method in the case of stochastic Kubo–Anderson process considerably simplified the procedure of obtaining the solution of Eq. (1). The obtained theoretical expressions are applied to consideration of some dynamical problems of solid state NMR, namely (1) the dynamical transformation of NMR line shape and spin-echo signal and (2) transformations of the second moment of NMR line for the case, when the potential barrier for the mobility of magnetic nuclei is a stochastic function of time.

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2. Theory

We will assume that the distribution of all possible values $\omega(t)$ is described by the function $p(\omega)$ and the jumps from one value ω_1 to the other value ω_2 are independent and distributed uniformly over the time with density ν_C (the value $\nu_C dt$ determines the average jumps value in the time interval dt) (Fig. 1). This stochastic process is called in the physics as the Kubo–Anderson process (see Ref. [26]). The solution of Eq. (1) can be obtained by the different methods [22–26]. Now we will show that for the Kubo–Anderson process the solution of Eq. (1) can be easily obtained using the so-called method of the differentiation formulae [26–28]. As it was shown in Refs. [25–28] for the Kubo–Anderson processes, the differentiation formulae have the form

$$\frac{d}{dt} \langle x_k \rangle = -\nu_C \langle x_k \rangle + \nu_C \times \langle x_0 \rangle \times \langle \alpha^k \rangle + \left\langle \alpha^k \frac{\partial x_0}{\partial t} \right\rangle. \quad (3)$$

Here $k = 0, 1, 2, \dots$

$$\alpha^k = [i\varepsilon(t)\omega(t)]^k, \quad (4)$$

$$x_k = \alpha^k \times x_0, \quad (5)$$

and $x_0 \equiv x$.

Inserting Eq. (1) into Eq. (3) we obtain

$$\frac{d}{dt} \langle x_k \rangle = -\langle x_{k+1} \rangle - \nu_C \langle x_k \rangle + \nu_C \times \langle \alpha^k \rangle \times \langle x_0 \rangle. \quad (6)$$

The Laplace transformation of Eq. (6) has the form

$$s \times \bar{x}_k - \langle x_k(0) \rangle = -\bar{x}_{k+1} - \nu_C \bar{x}_k + \nu_C \times \bar{\beta}_k, \quad (7)$$

where

$$\bar{x}_k = \int_0^\infty e^{-st} \times \langle x_k \rangle dt. \quad (8)$$

and

$$\bar{\beta}_k = \int_0^\infty e^{-st} \langle \alpha^k \rangle \langle x_0 \rangle dt, \quad (9)$$

are the Laplace images of $\langle x_k \rangle$ and $\langle \alpha^k \rangle \langle x_0 \rangle$, respectively.

Denoting $l = (s + \nu_C)^{-1}$ we can rewrite Eq. (7) as

$$\bar{x}_k = l \times [\langle x_k(0) \rangle - \bar{x}_{k+1} + \nu_C \times \bar{\beta}_k]. \quad (10)$$

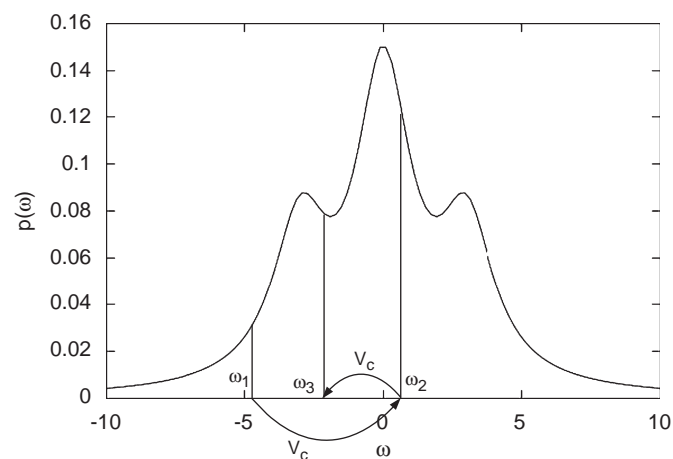


Fig. 1. Schematic presentation of the distribution function $p(\omega)$. The arrows designate the jumps of the frequency $\omega(t)$ from the value ω_1 to the value ω_2 and from the value ω_2 to the value ω_3 . The value ν_C determines the density of these jumps.

Using this recurrent relation, we obtain

$$\begin{aligned} \bar{x}_0(s) &= \left\langle l \times x_0(0) \sum_{k=0}^{\infty} (-1)^k l^k \alpha^k(0) \right\rangle + l \times \nu_C \sum_{k=0}^{\infty} (-1)^k l^k \bar{\beta}_k \\ &= \left\langle \frac{x_0(0)}{s + \nu_C + i\varepsilon(0)\omega(0)} \right\rangle + \nu_C \int_0^\infty e^{-st} \langle x_0(t) \rangle dt \\ &\quad \times \left\langle \frac{1}{s + \nu_C + i\varepsilon(t) \times \omega(t)} \right\rangle. \end{aligned} \quad (11)$$

Now we consider the case for which $\varepsilon(t) = 1$. If we assume that $x_0(0) = 1$ and the stochastic process is the stationary process

$$\left\langle \frac{1}{s + \nu_C + i\omega(t)} \right\rangle = \left\langle \frac{1}{s + \nu_C + i\omega(0)} \right\rangle, \quad (12)$$

then from Eq. (11) it follows:

$$\bar{x}_0(s) = \frac{g(s)}{1 - \nu_C \times g(s)}, \quad (13)$$

where

$$g(s) = \left\langle \frac{1}{s + \nu_C + i\omega} \right\rangle \equiv \int_{-\infty}^{\infty} \frac{p(\omega) d\omega}{s + i\omega + \nu_C}. \quad (14)$$

Eq. (13) describes the dynamical transformation of the Laplace image of the FID signal (i.e., the NMR absorption line) for the arbitrary distribution function $p(\omega)$.

Now we consider the case for which $\varepsilon(t) = 1$ for $0 \leq t < \tau$ and $\varepsilon(t) = -1$ for $\tau \leq t$. For the time interval (τ, ∞) , for which $\varepsilon(t) = -1$, from Eq. (3), entering analogously as with the conclusion (13), we obtain for the stationary stochastic process

$$\bar{x}_0(z, \tau) = \frac{\langle x_0(\tau) \rangle / (z + \nu_C - i\omega)}{1 - \nu_C \times h(z)}, \quad (15)$$

where

$$h(z) = \int_{-\infty}^{\infty} \frac{p(\omega) d\omega}{z - i\omega + \nu_C}. \quad (16)$$

The Laplace transformation of Eq. (15) relatively of the variable τ gives

$$\bar{x}_0(z, s) = \frac{\langle \tilde{x}_0(s) \rangle / (z + \nu_C - i\omega)}{1 - \nu_C \times h(z)}, \quad (17)$$

where

$$\tilde{x}_0(s) = \int_0^\infty e^{-s\tau} \times x_0(\tau) d\tau. \quad (18)$$

From Eq. (13), it may be conclude that $\tilde{x}_0(s)$:

$$\tilde{x}_0(s) = \frac{1 / (s + \nu_C + i\omega)}{1 - \nu_C \times g(s)}. \quad (19)$$

Inserting Eq. (19) into Eq. (17) gives

$$\bar{x}_0(z, s) = \frac{k(z, s)}{[1 - \nu_C \times h(z)][1 - \nu_C \times p(s)]}, \quad (20)$$

where

$$\begin{aligned} k(z, s) &= \left\langle \frac{1}{(z - i\omega + \nu_C)(s + i\omega + \nu_C)} \right\rangle \\ &\equiv \int_{-\infty}^{\infty} \frac{p(\omega) d\omega}{(z - i\omega + \nu_C)(s + i\omega + \nu_C)}. \end{aligned} \quad (21)$$

Obtained Eq. (20) fully describes the dynamical transformation of Laplace image of the echo signal for arbitrary distribution function $p(\omega)$.

3. Dynamical transformation of NMR line shape

In the present section, using Eq. (13) we consider the dynamical transformation of NMR line shape for some distribution functions $p(\omega)$.

- (1) In the case, when the distribution function $p(\omega)$ has a doublet form:

$$p(\omega) = \frac{1}{2}\delta(\omega + \Delta) + \frac{1}{2}\delta(\omega - \Delta), \quad (22)$$

from Eq. (13) it follows the well-known result [1,7,9,10]

$$\overline{\chi_0(s)} = \frac{s + v_C}{s(s + v_C) + \Delta^2}. \quad (23)$$

The Laplace transformation of Eq. (23) gives [1,9,10]:

$$\langle \chi(t) \rangle = e^{-v_C t} \left[\left(\frac{v_C}{R} \right) \sinh(Rt) + \cosh(Rt) \right], \quad (24)$$

where $R^2 = v_C^2 - \Delta^2$.

- (2) Transformations of the NMR line shape for the case, when the distribution function $p(\omega)$ has the form

$$p(\omega) = \sum_{j=1}^n p_j \delta(\omega \pm \omega_{pj}), \quad (25)$$

where $\sum_{i=1}^n p_i = 1$, and $n = 3$ ($p_1 = p_2 = p_3 = 1/3$) are shown in Fig. 2. It is easy to calculate the similar transformations of NMR line shape for the case when $n > 3$.

- (3) The obtained Eq. (13) gives an opportunity to study the influence of intermolecular dipolar interaction on the

transformations of NMR line of mobile water molecules. Using the distribution function $p(\omega)$ in the form

$$p(\omega) = \frac{1}{\sqrt{2\pi}\sigma^2} \sum_{j=1}^n p_j \exp\left(-\frac{(\omega - \omega_{pj})^2}{2\sigma^2}\right), \quad (26)$$

where $\sum_{j=1}^n p_j = 1$, we analysed the transformation of NMR line shape of mobile water molecule jumps between $n \geq 2$ non-equivalent position. The results of this consideration will be published in Ref. [29].

- (4) If the function $p(\omega)$ has Lorentz form

$$p(\omega) = \frac{\sigma}{\pi \times (\omega^2 + \sigma^2)}, \quad (27)$$

from Eq. (13) it follows:

$$\langle \chi(t) \rangle = \exp(-\sigma t). \quad (28)$$

Thus, for Lorentz distribution function $p(\omega)$, the stochastic jumps of the frequency $\omega(t)$ do not influence the NMR line shape. This unusual result was obtained at the first time in Refs. [2,7,30]. It is of interest to note also that Lorentz distribution (27) is the limit case of the Pareto–Lévy distributions for which only the first moment has the finite quantity [31].

- (5) For the Gauss form of the function $p(\omega)$

$$p(\omega) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\omega^2}{2\sigma^2}\right), \quad (29)$$

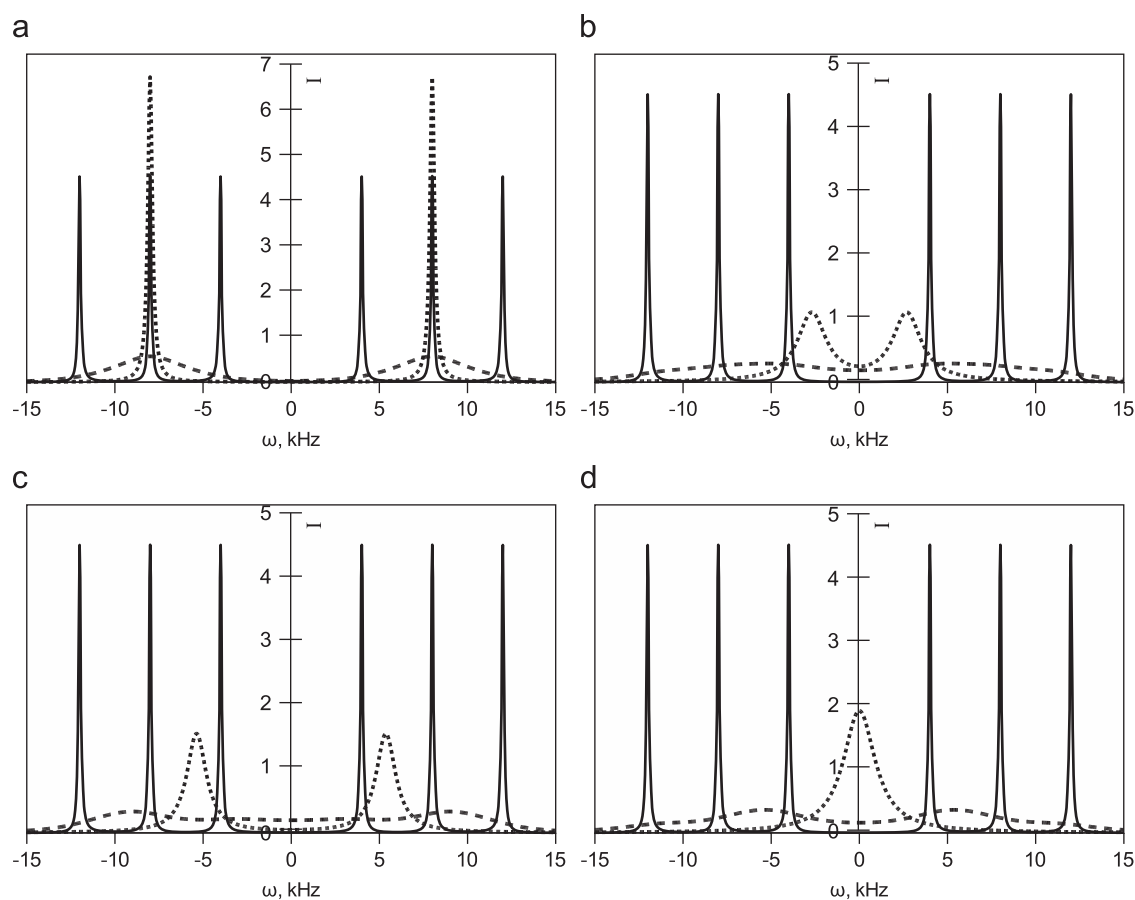


Fig. 2. The temperature transformations of NMR line shape in the case when $p(\omega)$ is described by the function (25). $n = 3$; $p_1 = p_2 = p_3 = 1/3$; $v_C = 1.2 \times 10^{13} \exp(-25 \text{ kJ/mol}/\text{K}) \text{ Hz}$. The bold continuous line represents the line shape at $T = 130 \text{ K}$; the bold broken line represents the line shape at $T = 155 \text{ K}$; the broken-point line represents the line shape at $T = 180 \text{ K}$: (a) $\omega_1 = 4 \text{ kHz}$; $\omega_2 = 8 \text{ kHz}$; $\omega_3 = 12 \text{ kHz}$; (b) $\omega_1 = -4 \text{ kHz}$; $\omega_2 = 8 \text{ kHz}$; $\omega_3 = -12 \text{ kHz}$; (c) $\omega_1 = 4 \text{ kHz}$; $\omega_2 = -8 \text{ kHz}$; $\omega_3 = 12 \text{ kHz}$; (d) $\omega_1 = 4 \text{ kHz}$; $\omega_2 = 8 \text{ kHz}$; $\omega_3 = -12 \text{ kHz}$.

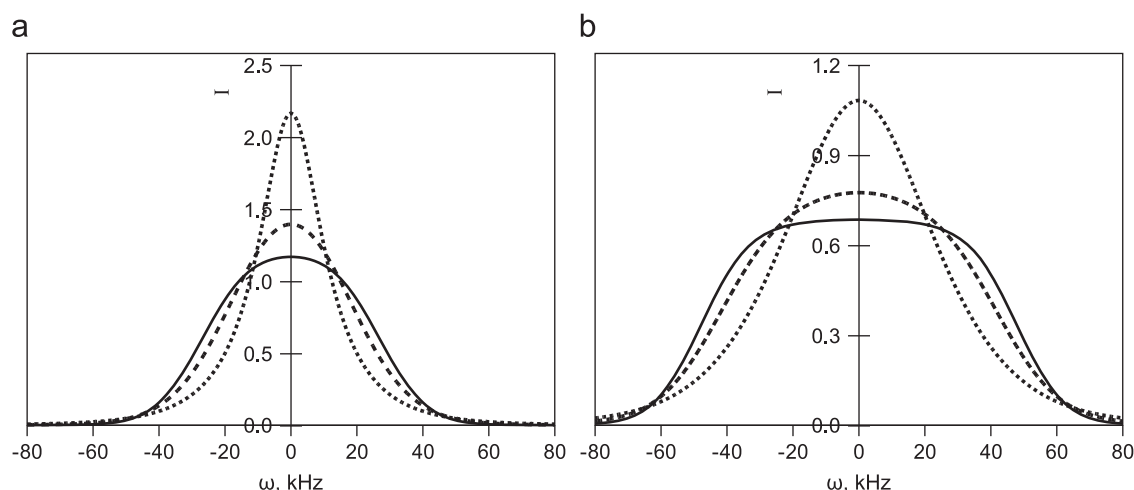


Fig. 3. The temperature transformations of NMR line shape in the case when $p(\omega)$ is described by the function (32). $\sigma = 10^{-2}$ MHz; $\nu_0 = 1.2 \times 10^7 \exp(-25 \text{ kJ/mol/RT})$ MHz $\exp(-25 \text{ kJ/mol/RT})$ Hz. The bold continuous line represents the line shape at $T = 136$ K; the bold broken line represents the line shape at $T = 144$ K; the broken-point line represents the line shape at $T = 152$ K: (a) $b = 3\sigma$ and (b) $b = 5\sigma$.

we have from Eq. (13)

$$\overline{x_0(s)} = \frac{(\sqrt{\pi/2}/\sigma)\text{erfc}[(s + \nu_C)/\sigma\sqrt{2}]}{\exp[-(s + \nu_C)^2/2\sigma^2] - \sqrt{\pi/2}(\nu_C/\sigma)\text{erfc}[(s + \nu_C)/\sigma\sqrt{2}]}. \quad (30)$$

Kubo and Tomita obtained the following expression for the transformations of the Gauss NMR line shape (29) [32]

$$\text{Re}\overline{x_0(s)} = \frac{\exp(\sigma^2\tau_C^2)}{2\pi\sigma} \times \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} (\sigma \times \tau_C)^{2n} \times \frac{\sigma\tau_C + n/\sigma\tau_C}{(\sigma\tau_C + n/\sigma\tau_C)^2 + (\omega/\sigma)^2}, \quad (31)$$

where $\tau_C = \nu_C^{-1}$.

Using Eqs. (30) and (31), we calculated the transformations of NMR line shape. Both Eqs. (30) and (31) give the similar numerical results for the same sets of parameters σ and τ_C .

(6) In his classical book [1], Abragam suggested to describe the FID in solid state NMR by the function

$$G(t) = \exp\left(-\frac{\sigma^2 t^2}{2}\right) \times \frac{\sin(bt)}{bt}, \quad (32)$$

The other function $G(t)$ was proposed in Ref. [33]

$$G(t) = \frac{J_1(2\sqrt{M_2}t)}{\sqrt{M_2}t}, \quad (33)$$

where $J_1(x)$ is the Bessel function of the first kind and M_2 the second moment of NMR line shape.

The results of calculations of the transformation of NMR line shape, whose FID's is described by the function (32), are shown in Fig. 3.

4. Dynamical transformations of spin-echo signals

In the present section, using Eq. (20), we consider the dynamical transformations of spin-echo signal for some distribution functions $p(\omega)$.

(1) If the distribution function $p(\omega)$ has a doublet form Eq. (22), from Eq. (20) we have

$$\overline{x_0(z, s)} = \frac{1}{2} \frac{s + 2\nu_C - i\Delta}{(s + \nu_C + R)(s + \nu_C - R)} \times \frac{z + 2\nu_C + i\Delta}{(z + \nu_C + R)(z + \nu_C - R)} + \frac{1}{2} \frac{s + 2\nu_C + i\Delta}{(s + \nu_C + R)(s + \nu_C - R)} \times \frac{z + 2\nu_C - i\Delta}{(z + \nu_C + R)(z + \nu_C - R)}, \quad (34)$$

where $R^2 = \nu_C^2 - \Delta^2$.

The Laplace transformation of Eq. (34) gives the well-known result [9,10]

$$\langle x(t, \tau) \rangle = \frac{e^{-\nu_C(t+\tau)}}{R^2} \times [\nu_C^2 \cosh R(t + \tau) + \nu_C R \sinh R(t + \tau) - \Delta^2 \cosh R(t - \tau)], \quad (35)$$

(2) The results of calculations of the dynamical transformation of the Laplace image of echo signals for the cases when the signal FID is described by the Eqs. (32) and (33) are shown in Fig. 4.

(3) The dynamical transformations of the two-dimensional NMR spectrum $\overline{x_0(z = i\omega_1, s = i\omega_2)}$ for the case when the distribution function $p(\omega)$ has the doublet form (22) are shown in Fig. 5.

5. NMR and dynamic disorder in solid state

The concept of a distribution of the correlation times has been widely used in interpreting NMR data, such as line shape, second moment and relaxation times [34–38]. In the most works in which the concept of the correlation times distribution has been discussed, it was assumed that the randomness of correlation times appears due to a static set of random barriers and an atom (or molecule) moves without changing them. However, randomness of potential barriers must be dynamic rather than static, since, due to the collective character of the diffusion process, the fluctuations of the potential barriers would occur simultaneously with each jump of a moving particle [39–41]. Now we consider

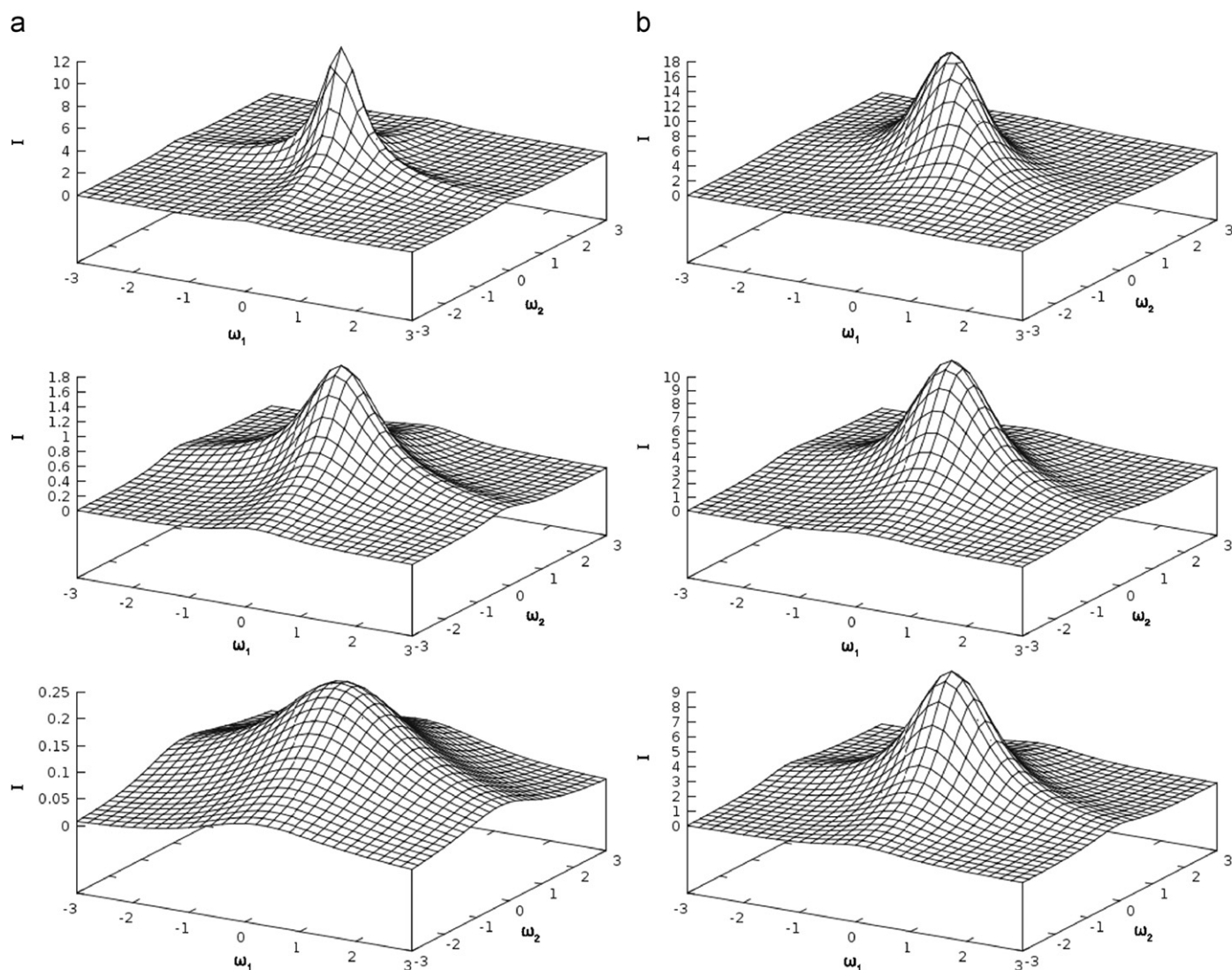


Fig. 4. The temperature transformations of two-dimensional NMR spectra in the case when $p(\omega)$ is described (a) by the function (33) and (b) by the function (32). $\sigma = \sqrt{M_2} = 0.5$, $b = 1$. From top to bottom: $\tau_c = 2$, $\tau_c = 1$, $\tau_c = 0.5$.

the transformations of the second moment of NMR line shape for the case, when the potential barrier for the mobility of magnetic nuclei is the stochastic function of the time.

The temperature dependences of the second moment M_2 of NMR line and spin-lattice relaxation rates in laboratory T_1^{-1} and rotating $T_{1\rho}^{-1}$ frames are determined by the dipolar correlation function $h(t)$ [1,42]. Here we will consider for simplicity only the temperature dependence of the second moment M_2 , which is determined by equation [1,42–44],

$$M_2(T) = \frac{1}{\pi} \int_{-\delta\omega}^{\delta\omega} J_0(\omega) d\omega, \quad (36)$$

where the spectral density $J_0(\omega)$ is determined by

$$J_0(\omega) = \text{Re} \int_{-\infty}^{\infty} d(t) \exp(i\omega t) dt, \quad (37)$$

and the dipolar correlation function $d(t)$ ($t > 0$) is

$$d(t) = K \sum_{ij} \langle b_{ij}(0)b_{ij}(t) \rangle. \quad (38)$$

In Eq. (38) the angular brackets denote again the averaged value of $b_{ij}(0)b_{ij}(t)$ for the random motions of spin-pair $i-j$;

$$K = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N} \quad (39)$$

and

$$b_{ij}(t) = R_{ij}^{-3}(t)[1 - 3 \cos^2 \theta_{ij}(t)]. \quad (40)$$

Assuming that the nuclear $i-j$ pair, in the result of the molecular motion (diffusion or molecular reorientation) of i and j nuclei, occupies the lattice sites Ω_k ($k = 1, 2, 3, \dots, n$) and the correlation frequency ν_C , describing the molecular motion is the random function of time, it is easy to obtain [45]

$$d(t) = \langle M_2 \rangle + \Delta M_2 \times f(t), \quad (41)$$

where

$$f(t) = \left\langle \exp \left[- \int_0^t \nu_C(t') dt' \right] \right\rangle. \quad (42)$$

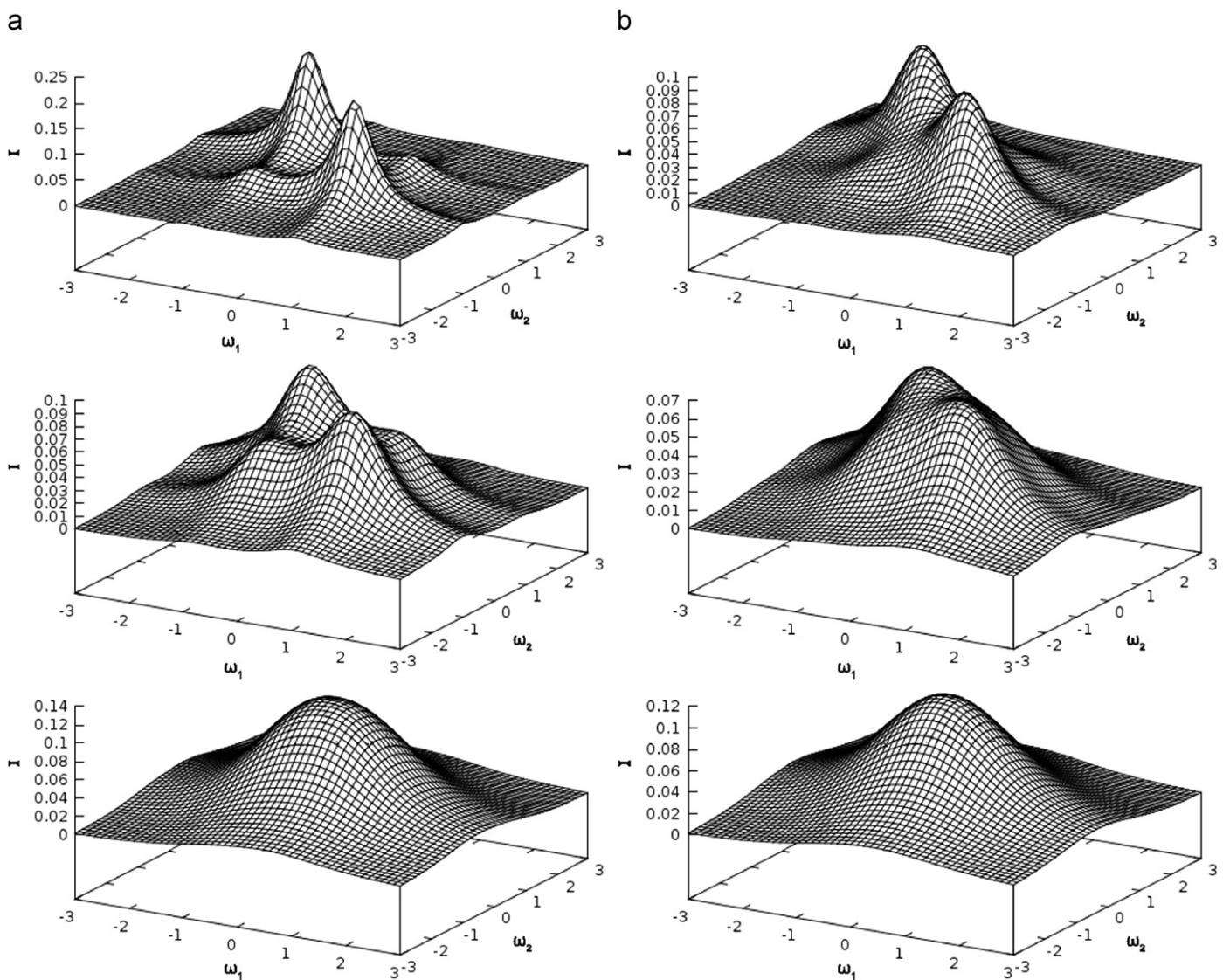


Fig. 5. The temperature transformations of two-dimensional NMR spectra in the case when $p(\omega)$ is described by the function (26). $n = 2$, $\omega_{p1} = -\omega_{p2} = 1$. From top to bottom: $\tau_c = 2$, $\tau_c = 1$, $\tau_c = 0.5$: (a) $\sigma = 0.1$ and (b) $\sigma = 0.5$.

In Eq. (41)

$$\langle M_2 \rangle = K \sum_{ij} \left[\frac{1}{n} \sum_{k=1}^n b_{ij}(\Omega_k) \right]^2 \equiv K \sum_{ij} \langle b_{ij} \rangle^2, \quad (43)$$

is the second moment of motionally narrowed NMR line [1,44],

$$\Delta M_2 = M_2 - \langle M_2 \rangle \quad (44)$$

and

$$M_2 = K \sum_{ij} b_{ij}^2 \quad (45)$$

is the second moment of NMR line in rigid lattice [1,44].

Comparing Eqs. (42) and (2), we see that the function $f(t)$ is the solution of the Kubo–Anderson stochastic differential Eq. (1) with $x(0) = 1$ and $i\epsilon(t')\omega(t') = \nu_c(t')$.

Using the solution of the Kubo–Anderson equation Eq. (13) we have from Eqs. (41) and (37)

$$J_0(\omega) = 2\langle M_2 \rangle \delta(\omega) + 2\Delta M_2 \times \text{Re}f(i\omega), \quad (46)$$

where

$$f(i\omega) = \frac{r(i\omega)}{1 - \nu_0 \times r(i\omega)}, \quad (47)$$

and

$$r(i\omega) = \int_0^\infty \frac{q(\nu_c) d\nu_c}{i\omega + \nu_c + \nu_0}. \quad (48)$$

In Eq. (48) the function $q(\nu_c)$ describes the distribution of all possible values of the correlation frequency $\nu_c(t)$. The jump from one value of the correlation frequency $\nu_c(t)$ to the other one is determined by the frequency ν_0 .

Insertion of Eq. (46) into Eq. (36) gives

$$M_2(T) = \langle M_2 \rangle + \Delta M_2 \frac{1}{\pi} \int_{-\delta\omega}^{\delta\omega} \text{Re}f(i\omega) d\omega, \quad (49)$$

At first, we note that in the case when both dynamic and static randomness of the potential barriers are absent and the molecular motions in solids are described by one correlation frequency $\nu_{c0} = \tau_{c0}^{-1}$ (for this case $\nu_0 = 0$ and $p(\nu_c) = \delta(\nu_c - \nu_{c0})$),

from Eq. (47) and Eq. (48) it follows that:

$$\operatorname{Re}f(i\omega) = \frac{\tau_{c0}}{1 + (\omega\tau_{c0})^2}. \quad (50)$$

Insertion of Eq. (50) into Eq. (49) gives the well-known results [1,42–44]

$$M_2(\nu_C) = \langle M_2 \rangle + \Delta M_2 \frac{2}{\pi} \tan^{-1} \left(\frac{\delta\omega}{\nu_C} \right). \quad (51)$$

The concept of a static distribution of the correlation times in solids assumes the static (but not dynamic) scattering of the correlation frequencies $\nu_C = \tau_C^{-1}$, which is described by the distribution function $q(\nu_C)$. In this case $\nu_0 = 0$, and from Eqs. (47) and (48) it follows that:

$$\operatorname{Re}f(i\omega) = \int_0^\infty q(\nu_C) \frac{\tau_C}{1 + (\omega\tau_C)^2} d\nu_C \quad (52)$$

and

$$M_2 = \int_0^\infty M_2(\nu_C) \times q(\nu_C) d\nu_C. \quad (53)$$

The value $M_2(\nu_C)$ in Eq. (53) is determined by Eq. (51).

Now we consider the case of dynamic distribution of the potential barriers for which the distribution of the correlation frequencies ν_C is described by the log-normal function

$$q(\nu_C) = \frac{kT}{\sigma_E \times \nu \sqrt{2\pi}} \exp \left[-\frac{(kT \ln(\nu_C/\nu_\infty) + \bar{E})^2}{2\sigma_E^2} \right]. \quad (54)$$

The log-normal distribution of ν_C corresponds to the case when ν_C follows the Arrhenius activation law

$$\nu_C = \nu_\infty \exp \left(-\frac{E}{kT} \right), \quad (55)$$

in which activation energy E has a normal (Gauss) distribution

$$y(E) = \frac{1}{\sigma_E \sqrt{2\pi}} \exp \left[-\frac{(E - \bar{E})^2}{2\sigma_E^2} \right]. \quad (56)$$

For simplicity, we will assume that the frequency ν_0 also follows the Arrhenius activation law

$$\nu_0 = \nu_\infty \exp \left(-\frac{E_b}{kT} \right), \quad (57)$$

where E_b is the activation energy, which determines the temperature dependence of jump frequency ν_0 from one value

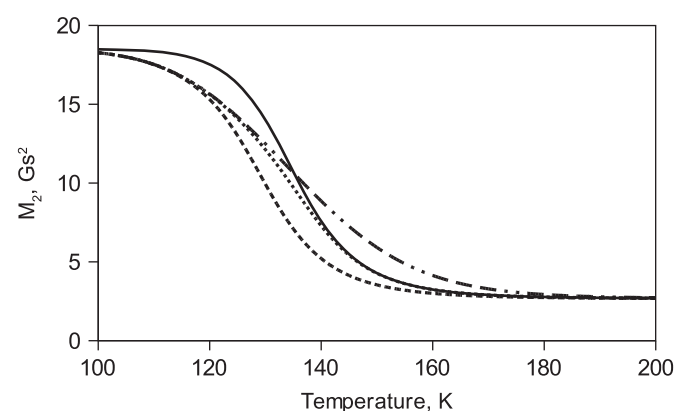


Fig. 6. Temperature dependences of the second moment of NMR line M_2 . The graphs were obtained for the following parameters: $M_2 = 18.5 \times 10^{-8} T^2$, $\bar{M}_2 = 2.67 \times 10^{-8} T^2$, $\bar{E} = 20.8$ kJ/mol, $\sigma_E = 0.1\bar{E}$ and $\nu_\infty = 1.2 \times 10^{-13}$ Hz. The bold continuous line represents Eq. (51). The broken-point line represents Eq. (53) (the case of static disorder) obtained with the normal distribution of E . Eq. (49) (the case of dynamic disorder) is represented by the short broken line ($E_b = \bar{E}$) and by the broken line ($E_b = 0.88\bar{E}$).

of the correlation frequency ν_C to the other. Using Eqs. (54), (57) and (49), we calculated the temperature transformations of the second moment M_2 of NMR line. The results of these calculations are shown in Fig. 6. From Fig. 6, it follows that in the case of static distribution of the potential barriers the temperature dependence of M_2 is a symmetrical function of the temperature at which $M_2(T) = \Delta M_2/2$. In the case of dynamic distribution of the potential barriers, the temperature dependence of $M_2(T)$ exhibits a significant dependence on the type of the standard deviation σ_E of the distribution function $y(E)$ (Eq. (56)) and on the form of the activation energy E_b at jump frequency ν_0 (Eq. (57)). It can also be seen that in the case of the dynamic disorder of the activation energy E , the temperature interval in which the reduction of the second moment is observed is smaller than that in the case of the static disorder of E . This effect reflects the motional average of the correlation frequency ν_C induced by its temporal fluctuations with the jump frequency ν_0 . It should be also noted that the temperature at which the reduction of the second moment is observed shifts in the dynamic case to the side of the lower temperatures.

We applied the model of the dynamical disorder of the potential barriers to the interpretation of the temperature transformations of the second moment of ^1H NMR spectra of the diffusing water molecules in the mineral natrolite. In this compound, unusual temperature transformations of the ^1H NMR line shapes have been observed [36,46]. The mineral natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) is a typical channel-type compound with porous structure. According to the NMR data [46–48], at $T > 250$ K, the diffusion of the water molecules occurs along the vacancies whose positions coincide with regular positions of water molecules in the natrolite lattice. The anomalous temperature transformations of the NMR line shapes in natrolite are connected with the appearance of the wide temperature interval in which the reduction of the second moment was observed (Fig. 7). This behaviour is not consistent with the assumption that the diffusion process of the water molecules can be described by one correlation time. In Refs. [36,46], it was assumed that the observed temperature behaviour of the NMR second moment is connected with the static distribution of the correlation times for the diffusing water molecules. However, this assumption does not agree with the NMR [47,48] and neutron diffraction data [49]

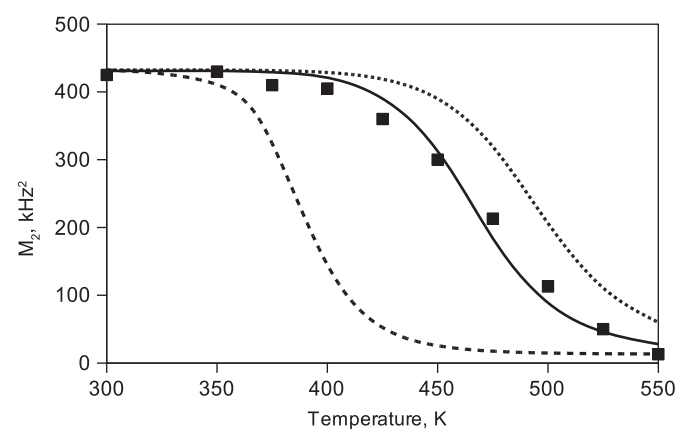


Fig. 7. The temperature dependence of the ^1H NMR second moment in natrolite for the case that the external magnetic field \bar{B}_0 lies in [110] direction. The symbol (■) represents the experimental data [36,46]; the continuous line represents Eq. (49) (dynamic disorder) obtained with the following parameters: $\bar{E} = E_b = 73$ kJ/mol, $\sigma_E = 0.02\bar{E}$; the broken line represents Eq. (51) obtained with $\nu_C = 1.2 \times 10^{-13} \exp(-73 \text{ kJ/mol}/RT)$; the short broken line represents Eq. (53) (static disorder) obtained with the normal distribution of E and $\bar{E} = 73$ kJ/mol, $\sigma_E = 0.02\bar{E}$. For the all graphs, $M_2 = 432.3$ (kHz) 2 , $\bar{M}_2 = 13$ (kHz) 2 .

showing that all water molecules in the channels of natrolite are chemically and structurally equivalent.

From the results obtained in this paper, it follows that the unusual temperature transformation of the NMR second moment in natrolite may be explained assuming that the potential barrier for the diffusion of the water molecules fluctuates chaotically as a function of time. The results of our calculations for this model are shown in Fig. 7. The data presented in this figure show that the model of the dynamical fluctuations of the potential barrier describes well the experimentally observed unusual temperature transformations of the second moment of NMR spectra in natrolite.

6. Conclusion

We obtained the analytical solution of stochastic differential equation for the two-level quantum system, assuming that the stochastic process described a fluctuation of the frequency ω is the Kubo–Anderson process. The obtained solution is right for arbitrary distribution function $p(\omega)$ of the fluctuating frequency ω . The obtained theoretical expressions (13) and (20) allowed for the first time to consider of the dynamical transformation of NMR line shape and spin-echo signal for different (arbitrary, in principle) distribution function $p(\omega)$. The obtained theoretical expression (13) allowed us also for the first time to investigate the temperature dependences of the second moment of NMR line shape in solids with dynamic disorder. In our consideration, it was assumed that the potential barrier E for the moving atom (or molecule) is a stochastic function of time. The proposed model of the dynamical disorder of the potential barrier was applied to the interpretation of the temperature transformations of the second moment of ^1H NMR spectra of the diffusing water molecules in the mineral natrolite.

In conclusion, it should be noted that the model of the two-level system with a stochastic fluctuating frequency is only the approximation to the reality, especially in the case of solids. This model can be applied to the ensemble of mobile nuclei with spin $I = 1/2$ for which NMR line shape is inhomogeneous broadened.

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