Non-Markovian Dynamic and NMR Spectra in Solids

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The influence of non-Markov molecular motions on NMR absorption spectra has been investigated. It has been shown that the simple non-Markov model of water molecular motion with fluctuations driven by dichotomic noise very well explains the observed temperature dependence of NMR spectra in the mineral natrolite. – PACS number: 05.40.+j, 33.25.+k, 76.20.+q

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1. Introduction

The NMR spectroscopy is one of the important method of internal mobility investigations in solids. Motions (reorientation, diffusion etc.) of molecules or molecular groups in solids are considered as a stochastic process in the majority of theories analyzing the influence of molecular dynamics on the NMR [1]. It is also mostly assumed that stochastic molecular dynamics in solids may be described by a simple Markov process with components in a configuration space only [1 – 3]. However, not taking into account additional "non-observable" states, it is not always reasonable, especially in condensed matter [3]. The unharmonical motions such as reorientations or diffusion of molecular groups are often connected with the large structural fluctuations in solid dynamics. These structural fluctuations are described by additional "non-observable" variables, and this leads to non-Markovian stochastic processes of the molecular mobility [3 – 6]. One of the well-known procedures of the creation of non-Markovian processes is connected with the projection from a higher-dimensional Markov process by integrating over all "non-observable" states. A similar procedure has been used by Sillescu [5] in the 4D-NMR method, where summation over all "non-observable" states has been done after solution of an extended master equation.

In the present paper we also investigate the influence of non-Markov molecular motions on NMR absorption spectra. We have taken the existence of additional states into consideration when the transition probability matrix becomes random, and master equation changes into the stochastic equation, driven by a bistable process of telegraphic type, called dichotomic noise (DN). In Sect. 4 we have applied the obtained theoretical results to the interpretation of experimental NMR spectra in mineral natrolite [6].

2. Theory

The NMR absorption spectrum $J(\omega)$ can be calculated from the free induction decay signal (FID) $G(t)$. According to the Lowe-Norberg theorem, both representations are connected with each other by the Fourier transform [1]:

$$J(\omega) = \mathrm{Re} \int_0^\infty G(t) e^{-i\omega t} \mathrm{d}t. \tag{1}$$

When the spin system can jump between two (or more) positions in a lattice, the observed FID is [1]:

$$\begin{aligned} G(t) &= \left\langle \exp\left[i \int_0^t \omega(t') \mathrm{d}t' \right] \right\rangle = \\ &\lim_{n\to\infty} \sum_{(\omega_1,\ldots,\omega_n)} P(\omega_1,t_1;\ldots;\omega_n,t_n) e^{i \frac{\omega_1+\ldots+\omega_n}{n} t}, \end{aligned} \tag{2}$$

where $\omega(t)$ represents the NMR frequencies between which the spin system jumps, $t_k = k\Delta t$, and $P(\omega_1,t_1;\ldots;\omega_n,t_n)$ is the n-point probability distribution. For the Markov process the joint probability can be written as a chain of conditional probabilities [2]:

$$\begin{aligned} &P(\omega_1,t_1;\ldots;\omega_n,t_n) = \\ &P(\omega_1,t_1) P(\omega_2,|\omega_1;\Delta t) \ldots P(\omega_n,|\omega_{n-1};\Delta t), \end{aligned} \tag{3}$$

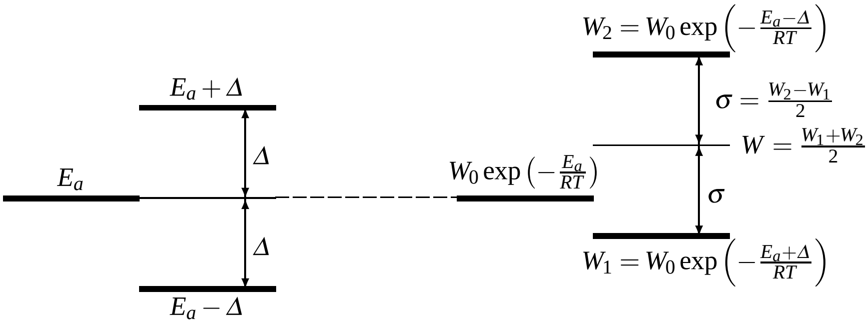

Fig. 1. Scheme of the transition propability distribution.

and according to [1] the equation for $G(t)$ has the form

$$\frac{\mathrm{d}\boldsymbol{G}(t)}{\mathrm{d}t} = (i\omega + \boldsymbol{W})\boldsymbol{G}(t), \tag{4}$$

where $\boldsymbol{W}$ is the transition probability matrix, ω is the diagonal matrix with elements equal to possible resonance frequencies of the spin system. $\boldsymbol{G}(t)$ is the vector with the components $G_\alpha(t)$ representing sums of terms in (2) corresponding to one frequency ω_α:

$$G(t) = \sum_{\omega_\alpha} G_\alpha(t) = \mathbf{1}^T \boldsymbol{G}(t), \tag{5}$$

where $\mathbf{1}$ is the vector, in which all components are equal to 1. Denoting by $G(s)$ the Laplace transformation of $G(t)$ we have for the NMR lineshape (1) the formula [1]

$$J(\omega) = \frac{1}{2}[G(-i\omega) + G(i\omega)]. \tag{6}$$

3. Fluctuations Driven by Dichotomic Noise

Let us consider the spin system which jumps between two equivalent positions in a crystal lattice. For the Markov model (4) has the form [7, 8]

$$\frac{\mathrm{d}\boldsymbol{G}(t)}{\mathrm{d}t} = \boldsymbol{N}\boldsymbol{G}(t), \tag{7}$$

where

$$\boldsymbol{N} = i\omega + \boldsymbol{W} = \begin{bmatrix} i\delta - W & W \\ W & -i\delta - W \end{bmatrix}. \tag{8}$$

In (8), W is the rate of the spin-system-jump between two positions; $\pm\delta$ are the NMR frequencies between which the spin system jumps. We will assume that W fulfills the Arhenius activation law

$$W = W_0 \exp(-\beta E_a), \tag{9}$$

where $\beta = 1/RT$ and E_a is the activation energy of the jump process.

In case of non-Markovian molecular motions we assume that the activation energy fluctuates and causes the transformation of the matrix $\boldsymbol{N}$ into the stochastic matrix $\boldsymbol{N}(t)$. Then (7) takes the form

$$\frac{\mathrm{d}\boldsymbol{G}(t)}{\mathrm{d}t} = \boldsymbol{N}(t)\boldsymbol{G}(t), \tag{10}$$

where

$$\boldsymbol{N}(t) = \boldsymbol{N} + \alpha(t)\boldsymbol{B}, \tag{11}$$

$$\boldsymbol{B} = \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}, \tag{12}$$

and $\alpha(t)$ is a scalar random function.

Using these equations, we have the following equation of motion for the average $\boldsymbol{G}(t)$ vector:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{G}\rangle = \boldsymbol{N}\langle \boldsymbol{G}\rangle + \boldsymbol{B}\langle \alpha \boldsymbol{G}\rangle. \tag{13}$$

The Eq. (13) contains the unknown average value $\langle \alpha \boldsymbol{G}\rangle$.

For the case when $\alpha(t)$ is the dichotomic noise, we solved (10) with the time dependent perturbation using the Shapiro-Loginov theorem [9]. In this case the transitional rate is no longer constant but jumps between two states W_1 and W_2 (see Fig. 1) with the exchange rate ν.

For the DN the following equation was obtained in [9]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \alpha \boldsymbol{\Phi}_t\rangle = -\nu \langle \alpha \boldsymbol{\Phi}_t\rangle + \langle \alpha \dot{\boldsymbol{\Phi}}_t\rangle, \tag{14}$$

where $\boldsymbol{\Phi}_t$ is a function of time. Inserting $\boldsymbol{\Phi}_t = \boldsymbol{G}(t)$ in (14), we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \alpha \boldsymbol{G}\rangle = -\nu\langle \alpha \boldsymbol{G}\rangle + \langle \alpha \dot{\boldsymbol{G}}\rangle. \tag{15}$$

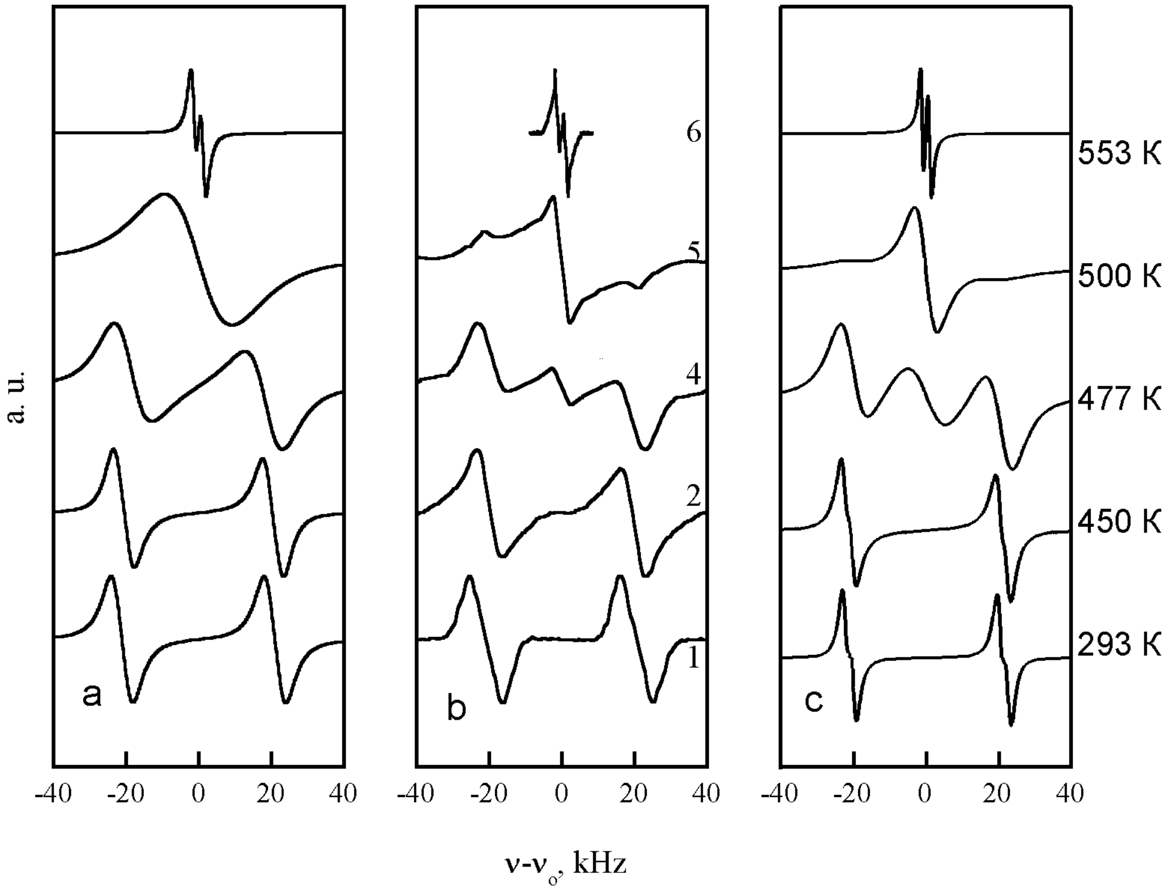

Fig. 2. The temperature dependence of the ^{1}H NMR spectrum of natrolite for the case when the vector B_0 lies in [110] direction: (a) theoretical NMR spectra obtained for the model of homogeneous diffusion of water molecules with the activation energy $E_a = 73$ kJ/mole; (b) experimental NMR spectra; (c) theoretical NMR spectra obtained for the non-Markov model of motion ($E_a = 73$ kJ/mole and $\Delta = 4.2$ kJ/mole).

Denoting $\boldsymbol{G}_0(t) = \langle \boldsymbol{G}(t) \rangle$, $\boldsymbol{G}_1(t) = \langle \alpha(t)\boldsymbol{G}(t) \rangle$, and using the property of dichotomic noise $\alpha^2(t) = \sigma^2 =$ const [2, 9], we obtain a closed system equations for the average values $\boldsymbol{G}_0$ and $\boldsymbol{G}_1$:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{G}_0 &= \boldsymbol{N}\boldsymbol{G}_0 + \boldsymbol{B}\boldsymbol{G}_1 \\ \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{G}_1 &= (\boldsymbol{N} - \nu)\boldsymbol{G}_1 + \sigma^2\boldsymbol{B}\boldsymbol{G}_0. \end{aligned} \tag{16}$$

The Laplace transformations of (16) gives:

$$\begin{aligned} s\boldsymbol{G}_0(s) - \boldsymbol{G}_0(0) &= \boldsymbol{N}\boldsymbol{G}_0(s) + \boldsymbol{B}\boldsymbol{G}_1(s) \\ s\boldsymbol{G}_1(s) &= (\boldsymbol{N} - \nu)\boldsymbol{G}_1(s) + \sigma^2\boldsymbol{B}\boldsymbol{G}_0(s), \end{aligned} \tag{17}$$

where the initial condition $\boldsymbol{G}_0(0)$ is the equilibrium value of the $\boldsymbol{G}_0(t)$, and in our case is equal to $[1/2, 1/2]^T$ [7, 8]. The solution of the system (17) is

$$\boldsymbol{G}_0(s) = \left[(s - \boldsymbol{N}) - \sigma^2\boldsymbol{B}(s + \nu - \boldsymbol{N})^{-1}\boldsymbol{B}\right]^{-1}\boldsymbol{G}_0(0). \tag{18}$$

4. Comparison to Experimental Data

The mineral natrolite ($\mathrm{Na_2Al_2Si_3O_{10} \cdot 2H_2O}$) is a typical channel-type compound with porous structure (zeolite). The water molecules are situated at regular positions within the channels and form hydrogen bonds to oxygen of the aluminosilicate structure. According to the NMR and neutron diffraction data, all water molecules are chemically and structurally equivalent at room temperature [10]. The dynamic of water molecules in natrolite has been studied by NMR [10]. It has been established that there are two kinds of water molecular motions [10]. The molecular motion of the first kind is the 180° flip motion, and the second one is the diffusion of the water molecules along the vacancies whose positions coincide with regular positions of water molecules in the lattice of natrolite. The structural and chemical equivalence of the water molecules suggests that the diffusive jumps of water molecules may be characterized by the same correlation time τ_c. However this suggestion does not agree with the observed temperature transformations of NMR spectra [10]. The existence of the additional spectral line in the central part of the experimental NMR spectra (Fig. 2b) can not be explained by the simple model of Markov mobility of water molecules with one correlation time τ_c (Fig. 2a). However the comparison of the theoretical NMR spectra (Fig. 2c) obtained with (18) with the experimental ones (Fig. 2b) demonstrates good agreement between them.

5. Conclusions

From comparison of the experimental and theoretical NMR spectra of water molecules in natrolite it follows that the model of the water molecules diffusion with a single correlation time τ_c does not agree with the experiment. We have shown that the existence of the additional spectral lines in the central part of the NMR spectra (see Fig. 2) may be explained by assuming that the water mobility in natrolite is not a Markov process. In particular, it is shown that the simple non-Markov model of water molecular motion with fluctuations driven by dichotomic noise very well explains the observed temperature dependence of NMR spectra in natrolite.

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