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Molecular mobility in natrolite and NMR line shape

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The mineral natrolite ($Na_2Al_2Si_3O_{10}2H_2O$) is the 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 [1]. The dynamic of water molecules in natrolite has studied by NMR (see references in [1]). It has been established that there are two different kind of the water molecular motion. The molecular motion of the first kind is the 180^0 flip motion and second one is the diffusion of the water molecules. The chemically and structurally equivalence of water molecules suggests that the diffusive jumps of water molecules may be characterised by the same correlation time τ_c. However, this suggestion does not agree to observed temperature transformations of the NMR spectra (see Fig.1) [1].

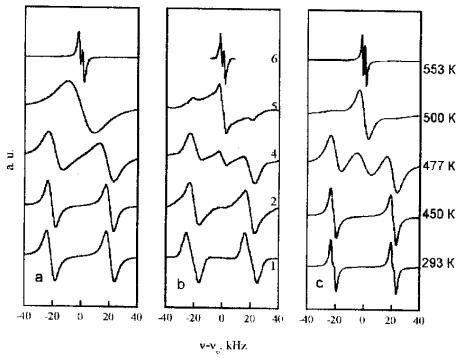

Figure 1: The temperature dependencies of the ^{1}H NMR spectrum of natrolite for the case when vector $\mathbf{B}_0$ lies in [110] direction: (a) theoretical NMR spectra obtained for the model of homogeneous diffusion of water molecules with the activation energy $E_a = 73$ kJ/mole [1]; (b) experimental NMR spectra; (c) theoretical NMR spectra obtained for the non-Markov model of water molecular motions with fluctuations driven by dichotomic noise ($E_a = 73$ kJ/mole and $\Delta = 4.2$ kJ/mole)

The existing of the additional spectral line in the central part of experimental spectra (Fig. 1b) does not explained by the simple model of Markov mobility of water molecules with one correlation time τ_c (Fig.1a) [1].

In NMR spectroscopy it is assumed mostly, that a simple Markov process with components in a configuration space only may describe the stochastic molecular dynamic in solids [2]. However the unharmonical motions in solids such as diffusion of water molecules are often connected with the large structural fluctuations in solid dynamics. These structural fluctuations are described by additional "non-observable" variables and in the consequence this leads to non-Markovian stochastic process of molecular mobility [3-6]. One of the well-known procedures of the creation of the non-Markovian process is connected with the projection from a higher-dimensional Markov process by integration over all "non-observable" states [3-6]. Similar procedure has used by Sillescu [5] in 4D-NMR method, where summation over all "non-observable" states has been done after solution of an extended master equation.

In order to explain the observed temperature transformations of the ^{1}H NMR spectra in natrolite we assume that the molecular diffusion of water molecules has been considered as the non-Markovian process. We assumed that the activation energy of the diffusion process E_a of water molecules is no constant but fluctuates in time between two positions $E_a \pm \Delta$ (Fig.2). We also assume that these fluctuations may be described by bistable process of telegraphic type (dichotomic noise [7]).

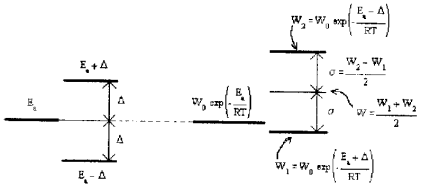

Figure 2: Schemata of transition probability distribution

From comparison of the experimental (Fig.1b) and simulated (Fig.1c) NMR spectra it can be concluded that our very 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 natrolite.

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