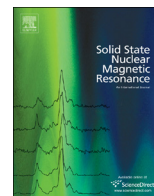




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The effect of a broad activation energy distribution on deuteron spin–lattice relaxation

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ABSTRACT

Deuteron NMR spectra and spin–lattice relaxation were studied experimentally in zeolite NaY(2.4) samples containing 100% or 200% of CD₃OH or CD₃OD molecules of the total coverage of Na atoms in the temperature range 20–150 K. The activation energies describing the methyl and hydroxyl motions show broad distributions. The relaxation data were interpreted by improving a recent model (Stoch et al., 2013 [16]) in which the nonexponential relaxation curves are at first described by a sum of three exponentials with adjustable relaxation rates and weights. Then a broad distribution of activation energies (the mean activation energy A_0 and the width σ) was assumed for each essentially different methyl and hydroxyl position. The correlation times were calculated from the Arrhenius equation (containing the pre-exponential factor τ_0), individual relaxation rates computed and classified into three classes, and finally initial relaxation rates and weights for each class formed. These were compared with experimental data, motional parameters changed slightly and new improved rates and weights for each class calculated, etc. This method was improved by deriving for the deuterons of the A and E species methyl groups relaxation rates, which depend explicitly on the tunnel frequency ω_t . The temperature dependence of ω_t and of the low-temperature correlation time were obtained by using the solutions of the Mathieu equation for a threefold potential. These dependencies were included in the simulations and as the result sets of A_0 , σ and τ_0 obtained, which describe the methyl and hydroxyl motions in different positions in zeolite.

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1. Introduction

Deuteron NMR spectrum and spin–lattice relaxation are widely used for studying structural and motional properties of solids. Of special interest have been the samples containing deuteron tetrahedra or CD₃ groups at low temperatures, where rotational tunnelling changes spectra and relaxation in a characteristic way [1–11]. The presented models agree usually well with experimental results for single crystals of such materials.

Spectra and relaxation become more complicated to analyze if the activation energy for the motion of CD₃ or deuteron tetrahedron shows a broad distribution. Then the line-width transitions extend over a much larger temperature range than in the absence of the distribution. Similarly the normal maxima of the relaxation rate as a function of temperature, corresponding roughly to $\omega_0\tau = 1$ (ω_0 is the deuteron resonance frequency and τ the correlation time of the dominant motion), become nearly flat. Since there is practically no spin diffusion between deuterons in solids,

the relaxation appears highly nonexponential so that in principle an enormous number of exponential functions $\exp(-Rt)$ is needed to describe the magnetization recovery accurately. Of course some nonexponentiality can be related to the orientation dependence of the involved transition rates, and in the case of weakly hindered methyl groups rotational tunnelling may complicate the relaxation additionally. In general the orientation dependence remains hidden under the influence of the activation energy distribution, and the effect of tunnelling is considered in detail later on in this study. There are several methods for analyzing the deuteron spectra for such CD₃ containing samples [12–15]. However, the analysis of relaxation results for broad distributions was not possible until recently because of a lack of reliable methods. Cereghetti et al. [13] introduced a method, which is valid for roughly equivalent methyl groups, which anyway show a significant distribution of activation energies. Recently Stoch et al. [16] presented a model, which can be applied in samples, where there are two or more distinctly different CD₃ positions. In such a case the methyl groups in one kind of position are roughly equivalent, but because of their different surroundings for example in zeolites they can anyway show a broad distribution of motional activation energies, while the

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mean activation energies for different positions may deviate from each other more than the distribution widths. The model was applied to methyl and hydroxyl groups of methanol molecules in zeolite NaX.

The mentioned method [16] is an experiment-based model, which needs a quite accurate description of the observed magnetization recovery. It was done by using a sum of three exponentials with adjustable weights and characteristic relaxation rates R_f , R_m and R_s for the fast, intermediate and slow components, respectively. Two exponentials cannot in general reproduce the observed recovery with sufficient accuracy. In principle the number of exponentials could be four or even five, but in practice such an increase is limited by the fact that for a growing number of exponentials the scatter in weights and characteristic rates becomes too large. The so-called stretched-exponent function $\exp[-(t/T_c)^\alpha]$ would probably produce good fits, but so far there is no theoretical method for calculating the time constant T_c . Therefore we chose to use three exponentials. The success of such fits is demonstrated for example by Fig. 1 of Ref. [16].

For each distinctly different position of CD_3 a Gaussian distribution was introduced with the mean activation energy A_0 and the distribution width σ . When the pre-exponential factor τ_0 is defined, a numerical value R_j is calculated for each point j of the relevant distribution from the well-known expression for the relaxation rate in polycrystalline samples [5,16,17]

$$R_j = \frac{\omega_Q^2}{15} [J(\tau_j, \omega_0) + 4J(\tau_j, 2\omega_0)] \quad (1)$$

Here $\omega_Q = e^2 q Q / \hbar = 2\pi\nu_Q$ and τ_j is the correlation time of the 120° jumps about the methyl axis for the activation energy $A_0 + \Delta A_j$ of the distribution. τ_j is obtained from the Arrhenius equation

$$\tau_j = \tau_0 \exp[(A_0 + \Delta A_j) / RT] \quad (2)$$

The spectral density functions are defined by $J(\tau_j, \omega) = \tau_j / (1 + \omega^2 \tau_j^2)$. The calculated rates R_j are classified into three classes by comparing them to the limiting quantities $\sqrt{R_f R_m}$ and $\sqrt{R_m R_s}$. The distribution-related weight of the point j is

$w_j = \exp(-\Delta A_j^2 / 2\sigma^2) / \sum_j \exp(-\Delta A_j^2 / 2\sigma^2)$. Then the initial relaxation rate for each class c ($=f, m$ or s) is calculated from

$$R_{ci} = \sum_{j'} w_{j'} R_{j'} / \sum_{j'} w_{j'} \quad (3)$$

where the prime in the summation index j' means that for example the relaxation rate of the intermediate class m depends only on those $R_{j'}$ values which obey $\sqrt{R_f R_m} > R_{j'} > \sqrt{R_m R_s}$. The obtained quantities R_{ci} are compared with the experimental rates R_f , R_m and R_s at each temperature and the parameters A_0 , σ and τ_0 are then adjusted to obtain better values for R_{ci} . This cycle is repeated many times to obtain the optimal fit. The initial relaxation rates R_{ci} are used because they are easy to compute. It would be more correct to use the average relaxation rate for each class. According to our estimates R_{ci} is larger than the corresponding average rate by a factor varying between 1.1 (the fast component) and 2.0 (the slow component) [16]. Since we are mainly interested in the temperature dependence of the rates and weights, the difference between the initial rates R_{ci} and the average rates is not of critical importance.

The description above is valid when the methyl groups are located at one kind of position only. If there are two or more distinctly different positions, then for each position another set of the parameters A_0 , σ and τ_0 are needed and the iteration cycle has to take into account the corresponding relaxation rates. Furthermore, the sample may contain deuterons outside methyl groups, which can be taken into account similarly by replacing the expression (1) by a relevant one.

This model was used to explain the experimental data on deuteron spin–lattice relaxation in three samples of zeolite NaX (1.3), which contained 100% or 200% of CD_3OH or CD_3OD in comparison with the total Na^+ concentration [16]. The obtained agreement between the model and experimental data was reasonable. These experiments covered the temperature range from 20 K to $T_S = 167$ K. T_S means the temperature, below which the methanol molecules are localized at certain equilibrium positions, numbered I, II, etc. in the following. Two such positions are significantly occupied in NaX [16], while a third position is also occupied in NaY (Section 3). Above T_S methanols become free to move and the rotational motion becomes effectively isotropic.

The deuteron relaxation of heavy methanol molecules was also studied in NaX and NaY above T_S [15]. Actually the NaY sample was the same as Sample 3 of this study (Section 3) and for it $T_S = 154$ K. In both these zeolites the deuteron relaxation between T_S and 300 K was observed to be biexponential. The faster relaxation rate, related to the hydroxyl deuterons, is about 9 times the slower rate corresponding to the CD_3 deuterons in the entire temperature range. Effectively isotropic reorientation (at higher temperatures translation) is the dominant motion for both the OD and CD_3 groups, but its effectiveness in the CD_3 relaxation is reduced by even faster rotation about the methyl axis. Just above T_S there is a narrow transition region where the dominant motion of relaxation changes from effectively isotropic reorientation of methanols to the internal motion of localized molecules [16]. Below T_S the methanol molecules remain localized and their reorientation becomes nonisotropic or stops practically completely. Still the methyl groups rotate about their threefold axis and the OD vectors undergo some restricted motion about their equilibrium orientation. These motions are responsible for the deuteron relaxation below T_S in NaX [16] and in NaY samples of the present study.

Although the presented model explains reasonably well the NaX experiments [16], there are some deviations, which may at least partly originate from the fact that the model did not take into account two features: (i) In the case of very small activation energies the potential hindering the methyl rotations is so low that the rotational tunnel splitting ω_t can be equal or even larger than the deuteron resonance frequency ω_0 [18]. In such a case Eq. (1) is no more valid. (ii) It has been observed that at low temperatures the rotational correlation time cannot be obtained from the Arrhenius equation by using one constant activation energy but the apparent activation energy decreases [19,20]. In carboxylic acid dimers the hydrogen correlation time becomes practically constant [21].

These two factors are taken into account in the present study. In Supplemental Material we derive coupled differential equations governing the deuteron magnetizations M_A and M_E , corresponding to the CD_3 groups with the spin and rotational wave functions belonging to the irreducible representations A and E ($=E^a$ and E^b) of the point group C_3 , respectively. For the initial relaxation rates of these magnetizations we derive expressions, which depend on the tunnel frequency ω_t and replace Eq. (1).

The rotational energies for a one-dimensional rotor like CD_3 can be calculated from the so-called Mathieu equation as the function of the height of the potential hindering methyl rotation (Section 2). From the energy eigenvalues we can calculate the tunnel frequencies and the average rotational energies for the excited rotational states, which are then used to evaluate the temperature variation of the observed tunnel frequency, needed in the numerical calculations of the relaxation rates of M_A and M_E . For the other important factor, the temperature dependence of the rotational correlation time, we use a combination of the models by Stejskal and Gutowsky [22], Müller-Warmuth et al. [20] and Clough et al. [23].

In Section 3 at first experimental details and the methanol

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