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**NMR spin-lattice relaxation time T1 calculation for
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4 **through inequivalent potential barriers**
5 **in the case of n -fold ($n=2,3,4,6$) symmetry axis**
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10 *Asja Kozak*¹

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22 reorientation from the spin-lattice T_1 time measurements in the NMR experiment. For the model of
23 n potential wells of which one is deeper than the others, for $n = 2, 3, 4, 6$ the analytical formulae have
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1. Introduction

The aim of the study is to show new possibilities of investigation of molecular reorientations about the axis of the multiplicity greater than 3 (C_n , where $n > 3$). Interpretation of the nuclear relaxation on the basis of the NMR results depends on the model of reorientation assumed. The NMR data permit verification of different models of molecular reorientations considered, especially in the solids, and select the most probable one. Assuming a very short time of jumping, the time of the molecule rest in the well is characterised by the correlation time. The temperature study of the nuclear relaxation time and NMR line changes permits determination of the activation parameters of the molecular motion and drawing conclusions on the shape of the potential barriers for a given reorientation.

The simplest molecular motion is the jump between two potential wells, let's say A and B described at first by Look and Lowe for proton NMR relaxation [1] and applied by Waścicki in description of molecular reorientation in p-diphenyl [2]. The molecular reorientation through the inequivalent energy barriers is observed or expected in the compounds with hydrogen bonds, the motion of C_2 symmetry described by the matrix method for dicarboxylic acids by Nagaoka [3], then supplemented by the tunnelling effect by Horsewill and Aibout [4]. Changes in the proton – proton distance related to the jumps to the alternative well have been described by Latanowicz [5]. For the molecular groups of the C_3 symmetry, the reorientation between inequivalent barriers has been described by Anderson [6]. Many groups of this symmetry undergo reorientations through three different barriers, such a situation has been analysed by Knop [7]. Recently a review on this subject has been published by Latanowicz [8]. Reorientations about the C_3 , C_4 , C_5 and C_6 axes have been considered by Hoffman in calculation of the correlation function for interpretation of dielectric relaxation results [9]. The guest molecules in the inclusion compounds of the C_4

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2
3 symmetry can perform motion of the same symmetry. For substituted benzene and pyridine
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5 compounds the motion is expected to have the C_6 symmetry. However, because of the lack of
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7 theoretical solution for the T_1 spin-lattice relaxation time for such a reorientation, the
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9 description developed for the C_3 symmetry was applied for these compounds, in particular in
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11 view of the fact that Ripmeester obtained the same result T_1 for the model of jumps at every
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13 60° degrees in the six-well potential for the jumps to the nearest wells only [10] (which is the
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15 application of the solution of the C_3 model) and the successful application of the Anderson
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17 and Ripmeester results by Ito for description of the dynamics of pyridinium ions [11]. The
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19 dynamics of the three-well model has been also applied by Wąsicki group to approximate the
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21 dynamics of other pyridinium ions [12-14]. Attempts were also made to describe the
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23 dielectric polarization data for pyridinium tetrafluoroborate by the model of reorientation
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25 about the C_6 axis [15]. According to Roduner, the deuterated spectra of pyridinium ions are
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27 well described by the three-well and six-well models [16]. The calculations of the shape of the
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29 six-well potential of pyridinium iodide by Latosińska [17] also indicate a more complex
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31 character of the barrier heights. The T_1 relaxation time measurements by Ishikawa have
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33 confirmed the calculations of the potential of the C_6 symmetry in iodine and bromide 5-
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35 methylbenzene [18].
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46 In this paper the expected correlation and T_1 spin-lattice relaxation times have been
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48 calculated for particular models of reorientation taken as random steps with respect to the C_2 ,
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50 C_3 , C_4 , C_6 axes, for inequivalent and equivalent energy barriers. It was assumed that one
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52 potential well is deeper and all others have the same depth and that the particle can jump from
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54 each well to all others. Knowing the function describing the time changes in the population of
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56 the wells it is possible to calculate the autocorrelation function describing changes in the
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58 position of the dipole moment vector. On the basis of the latter it is possible to find the spectra
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density function related to a given type of reorientation and the physical value that could be measured in experiment, e.g. the spin-lattice correlation time measured in NMR.

The analytical results obtained for the first time for the reorientation about the C_4 and C_6 axes have shown that when the reorientation takes place between inequivalent barriers about the C_n axis, where $n \geq 3$, the T_1 data from the NMR experiment allow concluding about the multiplicity of the reorientation axis. However, such a conclusion cannot be drawn when the reorientation takes place among equivalent barriers.

2. The method for the relaxation time calculations for the angular reorientation among inequivalent barriers

The spin-lattice relaxation time T_1 is still the subject of interest in scientific research. In solid state the reorientations of molecules, molecular groups or ions are considered assuming different models of reorientations, in particular those taking into account not only the equivalent positions in the crystal lattice, but also those describing the reorientation through inequivalent potential barriers. In general to be able to make comparisons with experiment, the relaxation time is calculated from the BPP formula [19]:

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) (J_1(\omega) + J_2(2\omega)), \quad (1)$$

Where γ is the gyromagnetic coefficient of the atomic nucleus of the spin I , $J_1(\omega)$ and $J_2(2\omega)$ are the spectral density functions and depend on the model of reorientation chosen. The coefficient $3/2 \gamma^4 \hbar^2 I(I+1)$ describes the dipole interaction of two identical magnetic nuclei. The spectral density of the order of l is defined as:

$$J_l(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} \text{Re } F_l(t) d\tau. \quad (2)$$

The integral is calculated from the real component of the correlation function $F_l(t)$.

• *Correlation functions for reorientations*

The molecular reorientation in the plane can be described in terms of the correlation functions calculated for different models of reorientation with the help of the linear combinations of Legendre polynomials. The reorientational correlation function of the order of l is:

$$F_l(t) = \langle F(t) F_l^*(t + \tau) \rangle, \quad (3)$$

Where $\langle \rangle$ is the averaging over the whole set of nuclear spins and $l = 0, 1, 2$ is the order of the Legendre polynomial. The asterisk stands for the coupled function. For the reorientations in plane about an axis e.g. perpendicular to the plane, the function $F_l(t)$ is a function of the Θ angle. Knowing the possible angular Θ_i reorientations and the probability P_i of finding a molecule or particle at this orientation, it is possible to relate the previous and subsequent position of the molecule through the conditional probability $P_i(\Theta_o | \Theta, \tau)$. Then, the mean value of the autocorrelation function is defined as

$$F_l(t) = \langle F_l(\Theta_o) F_l^*(\Theta) \rangle = \sum_{i,j} F_{l,i}(\Theta_o) F_{l,j}^*(\Theta) P_i(\Theta_o) P_j(\Theta_o | \Theta, \tau) \quad (4)$$

where j is the i -th position of the molecule or its fragment, if the molecule or its fragment before the time τ were at the position i . For the sake of simplicity, P_i stands for $P_i(\Theta_o)$ and P_{ij} stands for the conditional probability $P_j(\Theta_o | \Theta, \tau)$. For the reorientation e.g. about the C_2 axis, $i=1, 2$ the sum is composed of $2*2 = 4$ products, while for the reorientation about the C_6 axis; $i = 1, 2, \dots, 6$; so the sum is composed of 36 products. If the vector of a length r reorients about the axis of reorientation from the position Θ_o to the position Θ , and if the axis takes random positions with respect to the external distinguished direction (e.g. the direction of the external magnetic field), the averaging over the orientation of this axis must be taken into regard, which is denoted by the symbols $\langle \rangle$ used below. The mean values of the correlation functions are [19,7]:

$$\langle F_{0,i}(\Theta_o) F_{0,i}^*(\Theta) \rangle = 4/5 r^{-6},$$

$$\begin{aligned}
\langle F_{1,i}(\Theta_0)F_{1,i}^*(\Theta) \rangle &= 2/15 r^{-6}, \\
\langle F_{2,i}(\Theta_0)F_{2,i}^*(\Theta) \rangle &= 8/15 r^{-6}, \\
\langle F_{0,i}(\Theta_0)F_{0,j}^*(\Theta) \rangle &= 4/5 r^{-6} P_2(\cos \alpha), \\
\langle F_{1,i}(\Theta_0)F_{1,j}^*(\Theta) \rangle &= 2/15 r^{-6} P_2(\cos \alpha), \\
\langle F_{2,i}(\Theta_0)F_{2,j}^*(\Theta) \rangle &= 8/15 r^{-6} P_2(\cos \alpha).
\end{aligned} \tag{5}$$

The Legendre function $P_2(\cos \alpha)$ will be henceforth denoted by G because P stands for the probability of the well population for a system of molecules.

$$\text{Here } \alpha_{ij} = \Theta_j - \Theta_i, \tag{6}$$

$$\text{and } G_{ij} = 1/2 (3 \cos^2 \alpha_{ij} - 1). \tag{7}$$

Therefore, for the n -fold reorientation we get a set of G_{ij} , making a matrix $[G]$.

As follows from the above, the only problem to get the spectral density function is to find the set of the conditional probabilities. This search is related to the choice of the model of reorientation, the number of the equilibrium positions or the multiplicity of the reorientation axis and the choice of the equivalent or inequivalent reorientational barriers.

- **Probability of jumps between the wells and the probability of well population**

The particle in the equilibrium position, i.e. in the steady state, is in the potential well. A transition to another position, i.e. to the neighbouring well, needs overcoming of the potential barrier. If P_i is the probability of the particle resting in the i -th well, the change in the probability of population dP_i/dt is related to the probability P_i through the factor W [6]:

$$dP_i/dt = W \cdot P_i. \tag{8}$$

The factor W or the probability of transition to another potential well depends exponentially on the height of the potential barrier E :

$$W = W_0 \exp(-E/RT), \tag{9}$$

where R is the gas constant, and T is temperature [K].

The differential equation for dP/dt can be generalised on n wells and then $[dP/dt]$ and $[P]$ are the column matrices of n rows, and $[A]$ is the square matrix of the size $n \cdot n$ containing all probabilities of transitions.

The number of wells is n , and the height of the barrier is involved in the matrix $[A]$.

Therefore, in the matrix formulation:

$$\left[\frac{d\mathbf{P}}{dt} \right] = [\mathbf{A}][\mathbf{P}] \quad (10)$$

The solution of the differential equations gives the exponential dependence of the probability of population of the i -th well $P_i(t)$ at the known initial probability $P_i(0)$.

In general, the solution is:

$$[\mathbf{P}] = \exp([\mathbf{A}]t) [\mathbf{P}(0)] \quad (11)$$

At the initial moment at $t=0$ we can have $P_1(0)=1$ or $P_2(0)=1$, or $P_3(0)=1$ and the same for the other wells P_i , which means that the preliminary position of the molecule is in well 1, 2 or 3 or i -th. Depending on the preliminary situation, after the time t we get different values of P_1 , P_2 , P_3 , in general P_i , making the column matrix $[\mathbf{P}]$, which is the solution of the differential equation. To avoid getting a solution with the matrix in the exponent we use the transformation [20]:

$$\exp([\mathbf{A}]t) = [\mathbf{U}] \exp([\mathbf{D}]t) [\mathbf{U}^{-1}], \quad (12)$$

in which $[\mathbf{D}]$ is the diagonal matrix of different eigenvalues λ_i of the matrix $[\mathbf{A}]$.

The exponent of the matrix $[\mathbf{D}]t$ is as follows:

$$e^{[\mathbf{D}]t} = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 & 0 \\ 0 & e^{\lambda_2 t} & 0 & 0 \\ 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & e^{\lambda_n t} \end{bmatrix}. \quad (13)$$

The columns U_i of the unitary matrix of the eigenvectors $[\mathbf{U}]$ are most frequently found from the set of n equations:

$$([\mathbf{A}] - \lambda_i[\mathbf{I}]) [\mathbf{U}] = 0. \quad (14)$$

If matrix $[\mathbf{U}]$ is well obtained it should diagonalise matrix $[\mathbf{A}]$, according to the following transformation:

$$[D] = [U^{-1}][A][U]. \quad (15)$$

The conditional probability P_{ij} is obtained by solving equation (10) n times, for $P_j(0)=1$ and for the other $(n-1)$ values $P_j(0)=0$, then $P_2(0)=0$ etc. until $P_n(0)=1$ and all the others $P_j(0)=0$. It means that we assume the molecule to be initially in well 1 and later in any of n wells. The results are the n column matrices for the n initial positions of the molecule. They can be arranged in the matrix $[P]$ of the P_{ij} terms, where i stands for the conditional probability of the molecule to be in the j -th well if it initially was in the well i .

- **Correlation functions, spectral density functions and T_1 spin-lattice relaxation times**

According to formulae 4, 5, 7 and 11, the correlation functions are composed of the sum of the products:

$$F_1(t) = \frac{2}{15} \cdot r^{-6} \cdot \sum_{j=1}^n \sum_{i=1}^n P_{oi} \cdot G_{ij} \cdot P_{ij} \quad (16)$$

and

$$F_2(t) = 4 \cdot F_1(t). \quad (17)$$

The spectral density function is calculated from the formulae given by BPP [19]:

$$J^{(0)}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} F_0(t) d\tau,$$

$$J^{(1)}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} F_1(t) d\tau, \quad (18)$$

$$J^{(2)}(2\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} F_2(t) d\tau.$$

As will be shown later, in selected models of reorientation through n walls, the diagonalization of matrix $[A]$ gives $n-1$ eigenvalues λ_i different from zero. The correlation times were calculated for the models of reorientation related to the molecular symmetries C_2 ,

C_3 , C_4 and C_6 , assuming the presence of one deeper potential well and the possibility of jumps from each well to each of the other wells. This means that matrix $[A]$ does not have zero elements. Then, biexponential solutions are obtained as one of the exponents includes the multiple root of the characteristic equation of the matrix of the jump probability $[A]$.

• *Potential well models; an example of C_2*

For the two inequivalent potential wells the reorientation takes place about the twofold axis C_2 . The position of the wells and the probabilities of transitions between them are shown in Fig. 1. if the vector \mathbf{r} performs reorientation from the position defined by the angle Θ_0 to Θ , so performs the angular jump α , we obtain the following matrix G :

$$[G] = \begin{bmatrix} 1 & \frac{1}{2} \cdot (3 \cdot \cos^2 \alpha - 1) \\ \frac{1}{2} \cdot (3 \cdot \cos^2 \alpha - 1) & 1 \end{bmatrix}. \quad (19)$$

description of the jumps between two energy levels 1- lower and 2- higher (Fig. 1.):

transition 1 \rightarrow 2 with the probability W_{12} requires the energy E_{12} ,

transition 2 \rightarrow 1 with the probability W_{21} requires the energy E_{21} .

The energy difference between the levels is $\Delta = E_{12} - E_{21}$. (20)

According to the Boltzmann distribution :

$$W_{12} = W_0 \exp(-E_{12}/RT), \quad (21)$$

$$W_{21} = W_0 \exp(-E_{21}/RT), \quad (22)$$

$a = \frac{P_2}{P_1}$ (population of well 2 relative to that of well 1), so

$$a = \exp(-\Delta/RT). \quad (23)$$

Change in the population of well 1 and well 2:

$$\frac{dP_1}{dt} = -W_{12}P_1 + W_{21}P_2, \quad (24)$$

$$\frac{dP_2}{dt} = W_{12}P_1 - W_{21}P_2$$

Matrix $[A]$ of the probabilities of transitions

$$[A] = \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}, \quad \text{or} \quad [A] = W_{21} \cdot \begin{bmatrix} -a & 1 \\ a & -1 \end{bmatrix}. \quad (25)$$

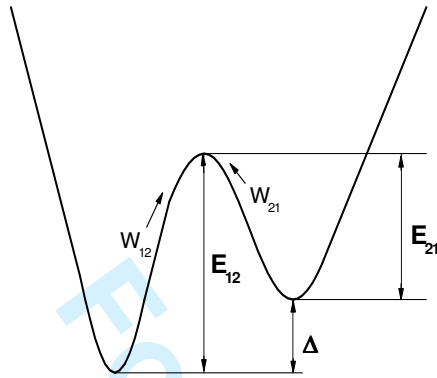


Fig.1 Two-well potential.

Therefore, the set of differential equations can be presented in the matrix form (equation 10):

$$\begin{bmatrix} \frac{dP_1}{dt} \\ \frac{dP_2}{dt} \end{bmatrix} = [A] \cdot \begin{bmatrix} P_1 \\ P_2 \end{bmatrix}. \quad (26)$$

The eigenvalues of the characteristic equation of matrix $[A]$ can be presented in the column matrix

$$\begin{bmatrix} 0 \\ -W_{21} \cdot (a+1) \end{bmatrix} \quad (27)$$

or in the diagonal matrix $[D]$:

$$[D] = W_{21} \cdot \begin{bmatrix} 0 & 0 \\ 0 & -(a+1) \end{bmatrix}. \quad (28)$$

The matrix of the eigenvectors (unitary) is:

$$[U] = \begin{bmatrix} \frac{1}{a+1} & -1 \\ \frac{a}{a+1} & 1 \end{bmatrix}. \quad (29)$$

The inverse matrix is

$$[U^{-1}] = \begin{bmatrix} 1 & 1 \\ -a & 1 \\ a+1 & a+1 \end{bmatrix}. \quad (30)$$

Now, we check if the matrix of eigenvectors transforms the matrix of the probabilities of transitions W_{21} in the diagonal matrix D :

$$\begin{bmatrix} 1 & 1 \\ -a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} -W_{21} \cdot a & W_{21} \\ W_{21} \cdot a & -W_{21} \cdot a \end{bmatrix} \cdot \begin{bmatrix} 1 & -1 \\ a & 1 \\ a+1 & a+1 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & -W_{21} \cdot (a+1) \end{bmatrix}, \quad (31)$$

which has to be proved.

Differential equation (26) is solved according to eq.(11) and the solution is:

$$\begin{bmatrix} P_1 \\ P_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{a+1} & -1 \\ a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ 0 & e^{-W_{21} \cdot (a+1) \cdot t} \end{bmatrix} \cdot \begin{bmatrix} 1 & 1 \\ -a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} P_1(0) \\ P_2(0) \end{bmatrix}. \quad (32)$$

The conditional probabilities are calculated assuming $P_i(0)=1$:

$$\begin{bmatrix} P_1(P_1(0)=1) \\ P_2(P_1(0)=1) \end{bmatrix} = \begin{bmatrix} \frac{1}{a+1} & -1 \\ a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ 0 & e^{-W_{21} \cdot (a+1) \cdot t} \end{bmatrix} \cdot \begin{bmatrix} 1 & 1 \\ -a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad (33)$$

and then $P_2(0)=1$:

$$\begin{bmatrix} P_1(P_2(0)=1) \\ P_2(P_2(0)=1) \end{bmatrix} = \begin{bmatrix} \frac{1}{a+1} & -1 \\ a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ 0 & e^{-W_{21} \cdot (a+1) \cdot t} \end{bmatrix} \cdot \begin{bmatrix} 1 & 1 \\ -a & 1 \\ a+1 & a+1 \end{bmatrix} \cdot \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \quad (34)$$

After the calculations we get:

$$\begin{bmatrix} P_1(P_1(0)=1) \\ P_2(P_1(0)=1) \end{bmatrix} = \begin{bmatrix} \frac{1+a \cdot e^{-W_{21}(a+1)t}}{a+1} \\ \frac{a-a \cdot e^{-W_{21}(a+1)t}}{a+1} \end{bmatrix} \quad \begin{bmatrix} P_1(P_2(0)=1) \\ P_2(P_2(0)=1) \end{bmatrix} = \begin{bmatrix} \frac{1-a \cdot e^{-W_{21}(a+1)t}}{a+1} \\ \frac{a+a \cdot e^{-W_{21}(a+1)t}}{a+1} \end{bmatrix} \quad (35)$$

It can be substituted as follows:

$$P_{11} = P_1(P_1(0)=1), P_{12} = P_2(P_1(0)=1), P_{21} = P_2(P_2(0)=1), P_{22} = P_2(P_2(0)=1).$$

Therefore, P_{ij} is the probability of finding the molecule in the j th well after the time t , if the molecule was initially in the i th well.

Assuming the notation $\frac{1}{\tau} = W_{21} \cdot (a + 1)$ and setting the P_{ij} in one matrix $[P]$ we get the matrix of the conditional probabilities:

$$\begin{bmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{bmatrix} = \frac{1}{a+1} \begin{bmatrix} 1 + a \cdot e^{-\frac{t}{\tau}} & a \cdot (1 - e^{-\frac{t}{\tau}}) \\ 1 - e^{-\frac{t}{\tau}} & a + e^{-\frac{t}{\tau}} \end{bmatrix}. \quad (36)$$

The first index in $[P]$ defines the initial situation, that is informs in which well the molecule was at $t=0$. The above matrix is exactly $[P(\Theta_0 | \Theta, \tau)]$, however, for the sake of simplicity it is denoted as $[P]$. The matrix $[P(\Theta_0)]$ (row matrix) is for the sake of simplicity denoted as $[P_o]$ and has elements P_{oi} defined as the probability of population of the wells in thermodynamic equilibrium (steady state) for the whole ensemble of particles. Since, according to (23), the probability of population of individual wells in the steady-state is:

$$P_{o2} = a \cdot P_{o1} \text{ and}$$

the sum

$$P_{o1} + P_{o2} = 1.$$

We have

$$P_{o1} = \frac{1}{a+1} \text{ and } P_{o2} = \frac{a}{a+1}. \quad (37)$$

Therefore

$$[P_o] = [P_{o1} \quad P_{o2}] = \left[\frac{1}{a+1} \quad \frac{a}{a+1} \right]. \quad (38)$$

Now, the calculation of the correlation function is simple, and should be performed according to scheme (16).²

The correlation function is

$$F_1(t) = \frac{2}{15} \cdot r^{-6} \cdot \frac{1}{(a+1)^2} \cdot \left\{ 3 \cdot a \cdot \sin^2 \alpha \cdot e^{-\frac{t}{\tau}} + a^2 + 1 + a \cdot (3 \cdot \cos^2 \alpha - 1) \right\}, \quad (39)$$

² The above sum [16] can be showed as the matrix multiplicity

$F_1(t) = 2/15 r^{-6} [P_o][G_{ij}P_{ij}][K]$,

where elements of middle matrix become from the multiplying G_{ij} by P_{ij} , and matrix $[K]$ is only one column matrix with amounts equaled to 1 [28, 3. 34].

$$F_2(t) = \frac{8}{15} \cdot r^{-6} \cdot \frac{1}{(a+1)^2} \cdot \left\{ 3 \cdot a \cdot \sin^2 \alpha \cdot e^{-t/\tau} + a^2 + 1 + a \cdot (3 \cdot \cos^2 \alpha - 1) \right\}. \quad (40)$$

Therefore, the spectral densities calculated from equation (18) are:

$$J^{(1)}(\omega) = \frac{4}{5} \cdot r^{-6} \cdot \frac{a \cdot \sin^2 \alpha}{(a+1)^2} \cdot \frac{\tau}{1 + \omega^2 \tau^2}, \quad (41)$$

$$J^{(2)}(2\omega) = \frac{16}{5} \cdot r^{-6} \cdot \frac{a \cdot \sin^2 \alpha}{(a+1)^2} \cdot \frac{\tau}{1 + 4 \cdot \omega^2 \tau^2}. \quad (42)$$

The T_1 spin-lattice relaxation in NMR provides information on the molecular jumps through the potential barriers and the type of the barrier is included in the spectral density function, eq. (1). For the reorientations through the inequivalent barrier of the C_2 type, with a single correlation time τ , substituting the spectral densities expressed by eq. (41) and (42) into eq. (1) we get the relaxation rate

$$\frac{1}{T_1} = \frac{6}{5} \gamma^4 h^2 I(I+1) r_{m,n}^{-6} \frac{a \sin^2 \alpha}{(a+1)^2} g_1(\omega_0, \tau), \quad (43)$$

Where $r_{m,n}$ is the distance between the nuclei m and n (n is not the multiplicity of the barrier)

and

$$g_1(\omega_0, \tau_i) = \frac{\tau_i}{1 + \omega_0^2 \tau_i^2} + \frac{4\tau_i}{1 + 4\omega_0^2 \tau_i^2}. \quad (44)$$

If in a given substance there is more than one pair of interacting atomic nuclei, the summation should be performed over all possible N pairs [21], so in eq. (43) the term $\frac{1}{N} \sum_{n>m} r_{m,n}^{-6}$ should replace $r_{m,n}^{-6}$.

• Multiple reorientation barriers

Following the analogous procedure for reorientation through multiple potential barriers it is possible to get the formulae describing the relaxation rate as a function of the parameter of inequivalence α but also as a function of the barrier multiplicity n . The terms G_{ij} were calculated from eq. (7). Results are collected in Tables 1-4.

Table 1. Model description of the reorientation about the C_n , axis when one potential well is deeper than the others

| | C_2 | C_3 | C_4 | C_6 |
|----------------------|--|---|--|--|
| $[A]$ | $= W_{21} \begin{bmatrix} \alpha & 1 \\ \alpha & -1 \end{bmatrix}$ | $= W_{21} \begin{bmatrix} -2\alpha & 1 & 1 \\ \alpha & -2 & 1 \\ \alpha & 1 & -2 \end{bmatrix}$ | $= W_{21} \begin{bmatrix} -3\alpha & 1 & 1 & 1 \\ \alpha & -3 & 1 & 1 \\ \alpha & 1 & -3 & 1 \\ \alpha & 1 & 1 & -3 \end{bmatrix}$ | $= W_{21} \begin{bmatrix} -5\alpha & \dots & 1 \\ \vdots & \ddots & \vdots \\ \alpha & \dots & -5 \end{bmatrix}$ |
| P_{01} | $= \frac{1}{\alpha + 1}$ | $= \frac{1}{2\alpha + 1}$ | $= \frac{1}{3\alpha + 1}$ | $= \frac{1}{5\alpha + 1}$ |
| P_{02} | $= \frac{\alpha}{\alpha + 1}$ | $= \frac{\alpha}{2\alpha + 1}$ | $= \frac{\alpha}{3\alpha + 1}$ | $= \frac{\alpha}{5\alpha + 1}$ |
| τ_1 τ_2 | $= (W_{21}(\alpha + 1))^{-1}$ | $= (W_{21}(2\alpha + 1))^{-1}$ $= (3W_{21})^{-1}$ | $= (W_{21}(3\alpha + 1))^{-1}$ $= (4W_{21})^{-1}$ | $= (W_{21}(5\alpha + 1))^{-1}$ $= (6W_{21})^{-1}$ |
| $[G]$ | $= \begin{bmatrix} 1 & -\frac{1}{2} \\ -\frac{1}{2} & 1 \end{bmatrix}$ | $= \begin{bmatrix} 1 & -\frac{1}{3} & -\frac{1}{3} \\ -\frac{1}{3} & 1 & -\frac{1}{3} \\ -\frac{1}{3} & -\frac{1}{3} & 1 \end{bmatrix}$ | $= \begin{bmatrix} 1 & -\frac{1}{4} & 1 & -\frac{1}{4} \\ -\frac{1}{4} & 1 & -\frac{1}{4} & 1 \\ 1 & -\frac{1}{4} & 1 & -\frac{1}{4} \\ -\frac{1}{4} & 1 & -\frac{1}{4} & 1 \end{bmatrix}$ | $= \begin{bmatrix} 1 & -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} \\ -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} \\ -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} & 1 \\ 1 & -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} \\ -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} \\ -\frac{1}{5} & -\frac{1}{5} & 1 & -\frac{1}{5} & -\frac{1}{5} & 1 \end{bmatrix}$ |

As follows from the table the terms A_{ij} , P_{01} , P_{02} , τ_1 and τ_2 can be expressed as functions of the multiplicity of the barrier.

The elements of the matrix of the jump probability A_{ij} are:

$$\begin{aligned}
 A_{11} &= -(n-1)aW_{21}, \\
 A_{ii, i \neq 1} &= -(n-1)W_{21}, \\
 A_{i1, i \neq 1} &= aW_{21}, \\
 A_{ij, i, j \neq 1, j > 1, i \neq j} &= W_{21}.
 \end{aligned} \tag{45}$$

The steady-state probability of the population of the deeper potential well is:

$$P_{01} = \frac{1}{(n-1)a + 1}, \tag{46}$$

And the probabilities of population of the other wells are:

$$P_{02} = aP_{01}. \tag{47}$$

There are exactly two correlation times (inverse eigenvalues of matrix $[A]$): one corresponding the population of the deeper well:

$$\tau_1 = [W_{21}(n-1)a + 1]^{-1}, \tag{48}$$

And the other corresponding to the population of the other equivalent wells:

$$\tau_2 = [nW_{21}]^{-1}. \tag{49}$$

For the sake of simplicity the elements P_{ij} of the matrix of the conditional probabilities [\mathbf{P}] can be expressed in the form of recurrent formulae:

$$\begin{aligned}
 P_{11} &= 1 + (n-1)a(1 - e^{-t/\tau_1}), \\
 P_{1j} &= a \cdot (1 - e^{-t/\tau_1}), \\
 j > 1 \\
 P_{i1} &= 1 - e^{-t/\tau_1}, \\
 i > 1 \\
 P_{ii} &= \frac{1}{n-1} \left[(n-1)a + (n-2)e^{-t/\tau_2} + (n-2)(n-1)ae^{-t/\tau_2} + e^{-t/\tau_1} \right], \\
 i > 1 \\
 P_{ij} &= \frac{1}{n-1} \left[(n-1)a - e^{-t/\tau_2} - (n-1)ae^{-t/\tau_2} + e^{-t/\tau_1} \right], \\
 i, j > 1, i \neq j
 \end{aligned} \tag{50}$$

At this point we have all the expressions needed to calculate the correlation function according to eq. (16). We have derived the formulae describing the correlation function F_l , the spectral density and the T_1 spin-lattice relaxation rate as functions of the correlation time and the formulae are given in Tables 2a, b, c, for each multiplicity of the reorientation axis considered.

Table 2a. Correlation functions for different multiplicities of the reorientation axis C_n

| | $F_1(t)$ |
|-------|--|
| C_2 | $= \frac{2}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} e^{-t/\tau} (3\alpha \sin^2 \alpha e^{-t/\tau} + \alpha^2 - \alpha + 1)$ |
| C_3 | $= \frac{2}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{27}{8} \frac{\alpha}{(2\alpha+1)^2} e^{-t/\tau_1} + \frac{9}{8} \frac{\alpha}{(2\alpha+1)} e^{-t/\tau_2} + \frac{7\alpha^2 - 2\alpha + 4}{4(2\alpha+1)^2} \right)$ |
| C_4 | $= \frac{2}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{4\alpha}{(3\alpha+1)^2} e^{-t/\tau_1} + \frac{2\alpha}{(3\alpha+1)} e^{-t/\tau_2} + \frac{1}{(3\alpha+1)} \right)$ |
| C_6 | $= \frac{2}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{27\alpha}{5(5\alpha+1)^2} e^{-t/\tau_1} + \frac{18\alpha}{5(5\alpha+1)} e^{-t/\tau_2} + \frac{7\alpha^2 + \alpha + 1}{(5\alpha+1)^2} \right)$ |

Table 2b. Spectral densities for different multiplicities of the reorientation axis C_n

| | $J_1(\omega)$ |
|-------|---|
| C_2 | $= \frac{4}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \cdot \frac{\tau}{1 + \omega_0^2 \tau^2}$ |
| C_3 | $= \frac{3}{10} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{\alpha}{(2\alpha+1)} \cdot \frac{\tau_2}{1 + \omega_0^2 \tau_2^2} \right)$ |
| C_4 | $= \frac{8}{15} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{\alpha}{(3\alpha+1)} \cdot \frac{\tau_2}{1 + \omega_0^2 \tau_2^2} \right)$ |
| C_6 | $= \frac{12}{25} \frac{3\alpha \sin^2 \alpha}{(\alpha+1)^2} \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{2\alpha}{(5\alpha+1)} \cdot \frac{\tau_2}{1 + \omega_0^2 \tau_2^2} \right)$ |

Table 2c. Relaxation rates for different multiplicities of the reorientation axis C_n

| | $\frac{1}{T_1}$ |
|-------|--|
| C_2 | $= \frac{6}{5} \gamma^4 \hbar^2 \tau_{n,n}^{-6} I(I+1) \frac{a \sin^2 \alpha}{(\alpha+1)^2} g^1(\omega_0, \tau)$ |
| C_3 | $= \frac{9}{20} \gamma^4 \hbar^2 \tau_{n,n}^{-6} I(I+1) \left(\frac{3a}{(2\alpha+1)^2} g_1(\omega_0, \tau_1) + \frac{a}{(2\alpha+1)} g_1(\omega_0, \tau_2) \right)$ |
| C_4 | $= \frac{4}{5} \gamma^4 \hbar^2 \tau_{n,n}^{-6} I(I+1) \left(\frac{2a}{(3\alpha+1)^2} g_1(\omega_0, \tau_1) + \frac{a}{(3\alpha+1)} g_1(\omega_0, \tau_2) \right)$ |
| C_6 | $= \frac{18}{25} \gamma^4 \hbar^2 \tau_{n,n}^{-6} I(I+1) \left(\frac{3a}{(5\alpha+1)^2} g_1(\omega_0, \tau_1) + \frac{2a}{(5\alpha+1)} g_1(\omega_0, \tau_2) \right)$ |

The formulae given in Table 2c reveal that the relaxation rate is determined by two contributions related to proper correlation times. Fig. 2 presents the T_1 spin-lattice relaxation time as a function of temperature T for different multiplicities of the axis of reorientation when the ratio of Δ to E_{21} is $1/2$. Analogous plots can be made for different values of this ratio. Their application is discussed in the following part of the paper. Fig. 3 illustrates the effect of the correlation times on the T_1 relaxation time, on the example of C_6 type reorientation.

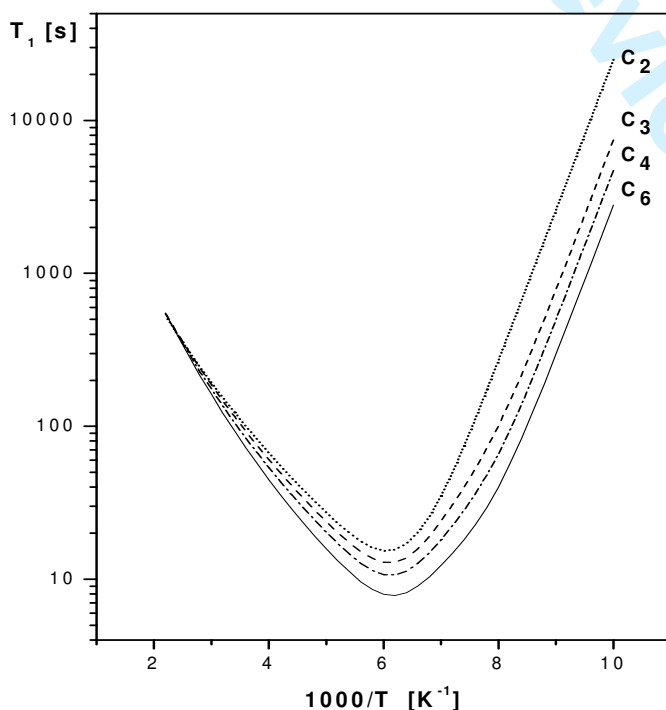


Fig. 2. Temperature dependence of the T_1 relaxation time for different multiplicities of the axis of reorientation; the calculations are performed for $E_{21} = 3$ kcal/mole; $\Delta = 1,5$ kcal/mole; $K = 1 \cdot 10^{13} \text{ s}^{-1}$; $\omega_0 = 2\pi \cdot 60$ MHz.

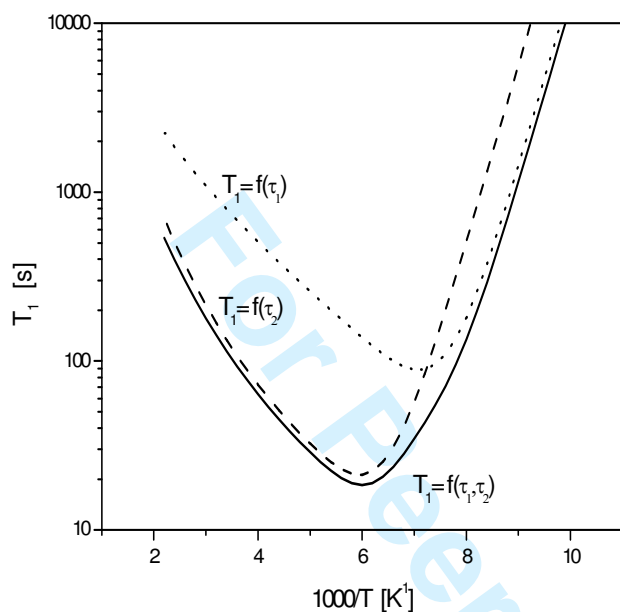


Fig. 3. T_1 relaxation time as a function of inverse temperature T for the reorientations about the C_6 axis ; $E_{21}=3$ kcal/mole; $\Delta=1$ kcal/mole; $K=1\cdot 10^{13} \text{ s}^{-1}$; $\omega_0=2\pi\cdot 60$ MHz.

If $\Delta > E_{21}$, the plot of the T_1 relaxation time versus inverse temperature does not have a minimum but only an inflection point, see Fig. 4.

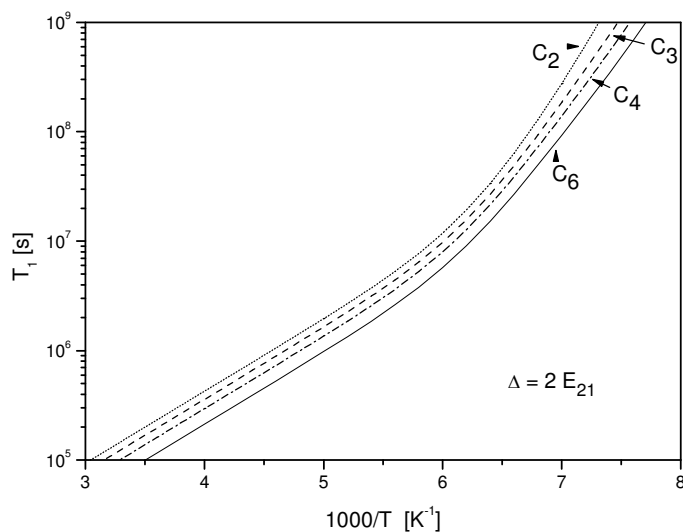


Fig. 4. T_1 relaxation time versus inverse temperature for different multiplicities of the axis of reorientation, for $E_{21}=3$ kcal/mole; $\Delta=6$ kcal/mole; $K=1\cdot 10^{13} \text{ s}^{-1}$; $\omega_0=2\pi\cdot 60$ MHz

3. Discussion

As follows from Fig. 2, the higher the value of n , the shorter the T_1 relaxation time. The changes in the position of the T_1 time minima are almost unnoticeable. The minima are asymmetric with the greater slope on the low-temperature side. This observation will be analysed further on in the text. The temperature of the relaxation time minimum is related to the correlation time $\tau_1 = 1/[W_{21}(n-1)a+1]$. The slope of the function near the relaxation time minimum is not steeper on the low-temperature side than on the high-temperature side. When in the experiment the times no longer than $10 \cdot T_1$ at the minimum are available, it is easy to confuse the reorientation through inequivalent barriers with other types of motion, e.g. a combination of two types of molecular motions. It should be emphasised that near the relaxation time minimum, the illusion of the symmetric minimum is the more pronounced the greater the multiplicity of the reorientation n .

On the basis of the results presented in Table 1, the relation between the inverse correlation time $1/\tau$ and the inequivalence parameter a , where $a \in \langle 0, 1 \rangle$ and $W_{12} = a \cdot W_{21}$ has been analysed for the reorientations C_n . For $a \rightarrow 0$, the probability of jump from a deeper well is $W_{12} \rightarrow 0$, while for $a = 1$, the potential wells are equivalent. Since the functions $g_i(\omega, \tau_i)$ for $i=1$ and $i=2$ have different amplitudes, (fraction coefficients) A_1 and A_2 , their behaviour as a function of the inequivalence parameter a for different multiplicities of the reorientation axes has been analysed. Results are presented in Fig. 5.

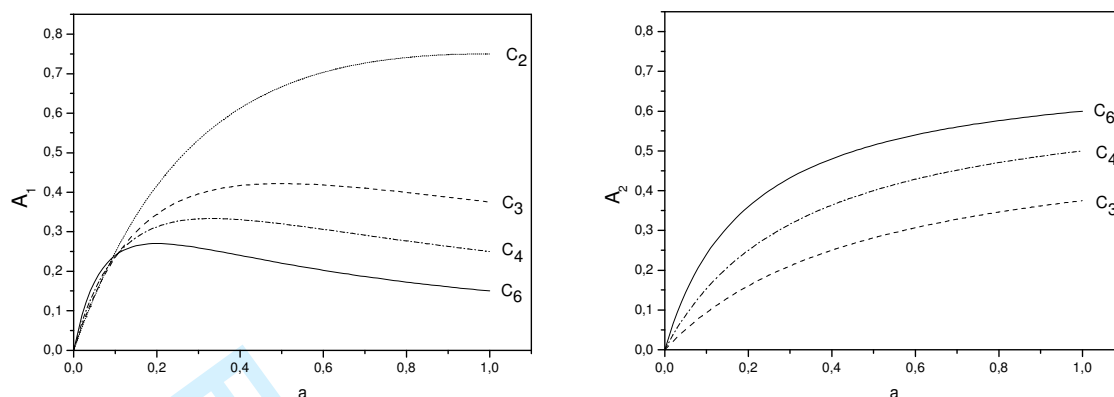


Fig. 5. The behaviour of amplitudes A_1 and A_2 as a function of the inequivalence parameter a for different multiplicities of the reorientation axis C_n .

As follows from Fig. 5, with increasing a , the amplitudes A_1 very slowly decrease, except the C_2 reorientation, while the amplitudes A_2 grow. This means that with the process of the barrier equalisation the contribution of the relaxation time expressed by the formula $\tau_2^{-1} = 1/(nW_{21})$ related to the occupation of the wells of higher energy separated by the equivalent barriers, increases. The shape of the high-temperature side of the plot of the relaxation time versus the inverse temperature is determined by the contribution related to the correlation time τ_2 , while that of the high-temperature of this plot is determined by the contribution described by the correlation time τ_1 . The greater the multiplicity of the barrier, the higher A_2 and the lower A_1 . For $a = 1$, the correlation times $\tau_1 = \tau_2$, and the sum of the amplitudes multiplied by the relaxation constant gives the same relaxation time for all multiplicities of the reorientation axis, consistent with the result [22] for the three-spin groups reorienting about the C_3 axis. Therefore, it is interesting to look at the relation between the increase in the relaxation time at the T_1 time minimum relative to $T_{1\min}$ of reorientation through inequivalent barriers [23] and the parameter $x = \Delta/E_{21}$, see Fig. 6.

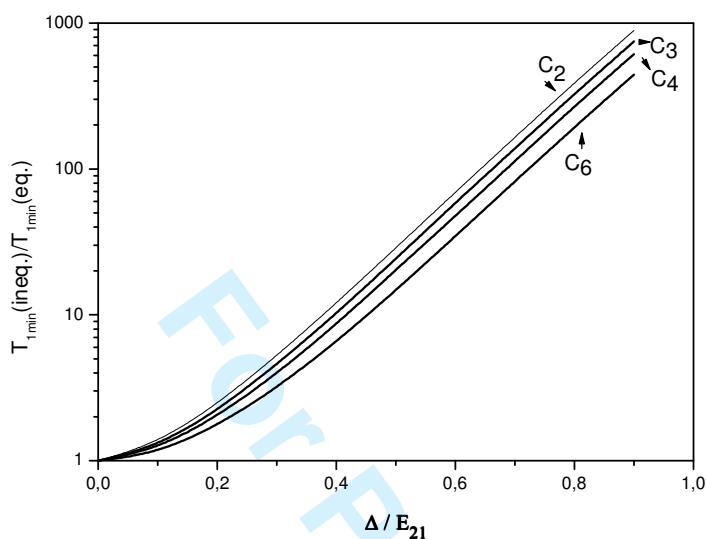


Fig. 6. The increase in T_1 at its minimum versus the ratio of Δ to the activation energy E_{21} .

Interestingly, for $x > 0.3$ the T_1 at its minimum become well discernible for different types of reorientations. If we knew the energy E_{21} and Δ , we could be able to conclude about the multiplicity of the reorientation axis from the increase in T_1 . The low-temperature side of the plot of T_1 as a function of $1000/T$ (Fig. 2.) is characterised by a steeper slope so a higher activation energy E_l than the high-temperature side corresponding to the activation energy E_h . To find Δ and E_{21} , the slopes of the two sides of the plot minimum for the multiplicity of reorientation considered were analysed (taking into regard the relaxation times $> 10 \cdot T_1$ at minimum). For the high- and low-temperature sides the following expressions were obtained:

$$\begin{aligned}
 E_h &= (0,020n + 1,140)\Delta - (0,037n + 1,223)E_{21} \\
 E_l &= (0,019n + 0,916)\Delta - (0,024n - 1,040)E_{21}.
 \end{aligned}
 \tag{51}$$

In the first approximation it can be assumed that in the above equations the dependence on the multiplicity of reorientations n is neglected, E_{21} and Δ can be found from the above equations, and then n is found from the increase in T_1 versus Δ/E_{21} . In the second approximation we use the equations containing n and for a given n we find E_{21} and Δ . When the activation energies

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3 E_h and E_l are determined to an accuracy of 5 % , determination of the multiplicity of the
4 reorientation axis n is ambiguous. Only knowing n , E_{2l} , Δ it is reliable to fit the T_1 relaxation
5 time dependence on the inverse temperature. However, in experiment it is very rare that on
6 both sides of the T_1 relaxation time minimum the increase in the relaxation time is sufficiently
7 high. If it is not, then the course of the T_1 relaxation time dependence on the inverse
8 temperature should be found for each model of the reorientation and the model ensuring the
9 best fit to the experimental data is assumed. This procedure was applied to choose the model
10 of reorientation about the C_6 axis for the pyridinium ring in thiourea pyridinium nitrate
11 inclusion compound [13]. The study of proton relaxation in bromo- and
12 iodopentamethylbenzene reported in [24] was undertaken to show that the temperature
13 dependence of the T_1 relaxation time could be explained by their jumps about the C_6 axis
14 between the potential wells of different depth.
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31 In this paper the simplest possible model of one well deeper than the other five equivalent
32 wells was chosen in order to obtain the analytical expressions for the rate of relaxation that
33 can be applied by any experimenter. This model of reorientation about the C_6 axis with only
34 one well deeper than the others has been recently applied for description of the reorientation
35 of the pyridine ring in pyridinium nitrate and in its inclusion compound with thiourea [25].
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The confirmation of this model obtained in the deuterium experiment [26] in pyridinium
periodate in low temperature phase suggests that it could also be applied for interpretation of
the earlier T_1 time relaxation results in pyridinium nitrate reported in [27].

4. Conclusions

1. The analytical formulae have been derived in the matrix formulation for the T_1 spin-lattice relaxation rate of the nuclear spins undergoing reorientation through inequivalent potential barriers between n wells of which only one is deeper than the others ($n=2, 3, 4, 6$).
2. The recurrent form of the formulae for the matrix elements containing the conditional probabilities of jumps between the wells permits the calculation of the elements for an arbitrary number of wells, if only one of them is deeper than the others.
3. The T_1 spin-lattice relaxation time minimum is expected to occur if the difference in the energy levels of the wells is lower than the potential barrier for the jump from the higher well to the other wells. Otherwise, not a minimum in T_1 relaxation time but an inflection point is expected.
4. The higher the barrier multiplicity, the shorter the relaxation time at the T_1 minimum.
5. If the experiments permits observation of both sides of the asymmetric relaxation time T_1 minimum as a function of $1000/T$, it is possible to determine the multiplicity of the axis of reorientation on the basis of the activation energies of the jumps corresponding to the low- and high-temperature sides of the minimum and the relative increase of $T_{1 \text{ min}}$ with respect to the T_1 minimum expected for the equivalent barriers. .
6. If temperature $T \rightarrow \infty$ or if the energy level difference between the wells tends to zero all the potentials become the same and the multiplicity of the reorientation axis is impossible to be found from the T_1 experiment data. The relaxation time takes the same value for all $n \geq 3$.
7. If a reorientation through inequivalent potential barriers is supposed on the basis of some data, measurements of the spin-lattice relaxation time can be important argument for or against confirmation of this supposition by other methods.

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Tables

Table 1. Model description of the reorientation about the C_n axis when one potential well is deeper than the others

Table 2a. Correlation functions for different multiplicities of the reorientation axis C_n

Table 2b. Spectral densities for different multiplicities of the reorientation axis C_n

Table 2c. Relaxation rates for different multiplicities of the reorientation axis C_n

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Figure captions

Fig.1 Two-well potential

Fig. 2. Temperature dependence of the T_1 relaxation time for different multiplicities of the axis of reorientation; the calculations are performed for $E_{21}= 3$ kcal/mole; $\Delta= 1,5$ kcal/mole; $K= 1 \cdot 10^{13} \text{ s}^{-1}$; $\omega_0=2\pi \cdot 60$ MHz.

Fig. 3. T_1 relaxation time as a function of inverse temperature T for the reorientations about the C_6 axis ; $E_{21}= 3$ kcal/mole; $\Delta= 1$ kcal/mole; $K= 1 \cdot 10^{13} \text{ s}^{-1}$; $\omega_0=2\pi \cdot 60$ MHz.

Fig. 4. T_1 relaxation time versus inverse temperature for different multiplicities of the axis of reorientation, for $E_{21}= 3$ kcal/mole; $\Delta= 6$ kcal/mole; $K= 1 \cdot 10^{13} \text{ s}^{-1}$; $\omega_0=2\pi \cdot 60$ MHz.

Fig. 5. The behaviour of amplitudes A_1 and A_2 as a function of the inequivalence parameter a for different multiplicities of the reorientation axis C_n .

Fig. 6. The increase in T_1 at its minimum versus the ratio of Δ to the activation energy E_{21} .