

Proton Spin–Lattice Relaxation of Tunneling Methyl Groups: Calculation of the Time Dependent Correlation Functions

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A theory of magnetic nuclear relaxation, providing a calculation of the correlation functions of complex motion of methyl groups is presented. The complex motion consists of jumps over the barrier (classical motion) and jumps through the barrier (tunneling). The Schrödinger equation has been applied in the calculation of the rate constant of tunneling jumps through the barrier. The equations for the spectral densities $J_{is}^m(\omega)$, where $\omega = (\omega_l \pm \omega_T)$, and $\omega = (m\omega_l)$, where $m = 1$ or 2 , ω_l is the resonance angular frequency, and ω_T is the angular frequency of the tunnel splitting, are derived. These spectral densities concern the motion of spin pairs inside methyl groups (“intra”) and outside methyl groups (“inter”). The calculated spectral densities are applied to analyze the temperature dependencies of the spin–lattice relaxation rate in solids containing methyl groups. A wide regime of temperatures from 0 K up to the melting point is considered. The temperature at which the tunneling process ceases is discussed. The theory proposed explains the different temperature dependencies of T_1 for CH_3COOK obtained in the experiments caused by small amounts of CH_3COOH or water impurities. The theoretical equations derived in this paper are compared to those known in the literature.

1. Introduction

The first to investigate the mechanism of reorientation of CH_3 groups in solids by NMR were Powles and Gutowsky.¹ Andrew et al.² found that even at liquid helium temperatures the second moment of NMR line in trimethylbenzene does not reach the value predicted for the rigid molecule. Eades et al.^{3,4} and also Allen⁵ reported that NMR spectra of a number of compounds containing methyl groups measured at liquid helium temperatures are often narrow, indicating rotational motion of the methyl groups. The spin–lattice relaxation time (T_1) of a number of molecules with low potential barriers of methyl groups is long at its minimum value and much longer than any value consistent with the classical theory of 3-fold hindered rotation. The NMR relaxation study performed by Stejskal et al.^{6,7} and Clough⁸ confirmed that the tunneling mechanism is plausible for the CH_3 group reorientations. The paper⁹ is a review work on the developments in the field of methyl group tunneling.

Haupt¹⁰ proposed the spin–lattice relaxation theory of methyl group tunneling. The general Haupt equation for protons ($1/T_1$) will be applied throughout this paper (with the relaxation efficiency factor (δ^2) equal to $1/2$). However, the expressions for the spectral densities, taken by Haupt, will be revised. These spectral densities will be calculated for the proposed model of complex motion.

The temperature dependence of the spin–lattice relaxation time (T_1) enables a determination of the correlation time (τ_c) (or correlation times if there are more independent stochastic motions) over a wide temperature range. The fact that the correlation time follows simple Arrhenius behavior with a single activation energy at the high-temperature limit (E_H) and E_{01} activation energy at low temperatures was anticipated by a number of authors.^{9–24} The authors^{11,12} introduced the following

phenomenological expression for the temperature dependence of the correlation time (τ_c):

$$\frac{1}{\tau_c^{\text{total}}} = \frac{1}{\tau_0^{(\text{H})}} \exp\left(-\frac{E_H}{RT}\right) + \frac{1}{\tau_0^{(\text{L})}} \exp\left(-\frac{E_L}{RT}\right) \quad (1)$$

The apparent activation energy (E_L) has been identified with $E_{01} = E_{v1} - E_{v0}$, the energy difference between the ground and first excited torsional states of the CH_3 rotator. The activation energy (E_H) corresponds to the high-temperature classical limit, namely, the barrier height minus the zero point energy. Equation 1 is based on the assumption that at diminishing temperatures the classical dynamics, namely, thermally activated hindered C_3 reorientation, evolves smoothly into the quantum low-temperature dynamics. However, eq 1 does not imply that a methyl group can undergo the classical motion which is complex (for example, C_3 hindered rotation about the symmetry axis of the group and C_3' rotation about the symmetry axis of the molecule).^{25,26} Moreover, this equation is inserted into the spectral density equation for the single motion. Woessner²⁷ proved that it is not the total correlation time but the total spectral density of a complex motion consisting of a number of independent motions modulating simultaneously the dipolar Hamiltonian, which has to be calculated.

The purpose of this paper is to calculate the temperature dependencies of spectral densities for a complex motion consisting of Arrhenius-type jumps over the barrier (correlation time $\tau_c^{(\text{H})}$) and tunnel jumps through the barrier (correlation time $\tau_c^{(\text{T})}$) in a three-minimum potential of a methyl group. The Schrödinger equation will be used to derive the correlation time $\tau_c^{(\text{T})}$. A wide temperature regime, from the liquid helium temperature up to the melting points, is taken into account.

It will be shown that not only the motion characterized by the correlation time $\tau_c^{(\text{T})}$ but also two stochastic processes

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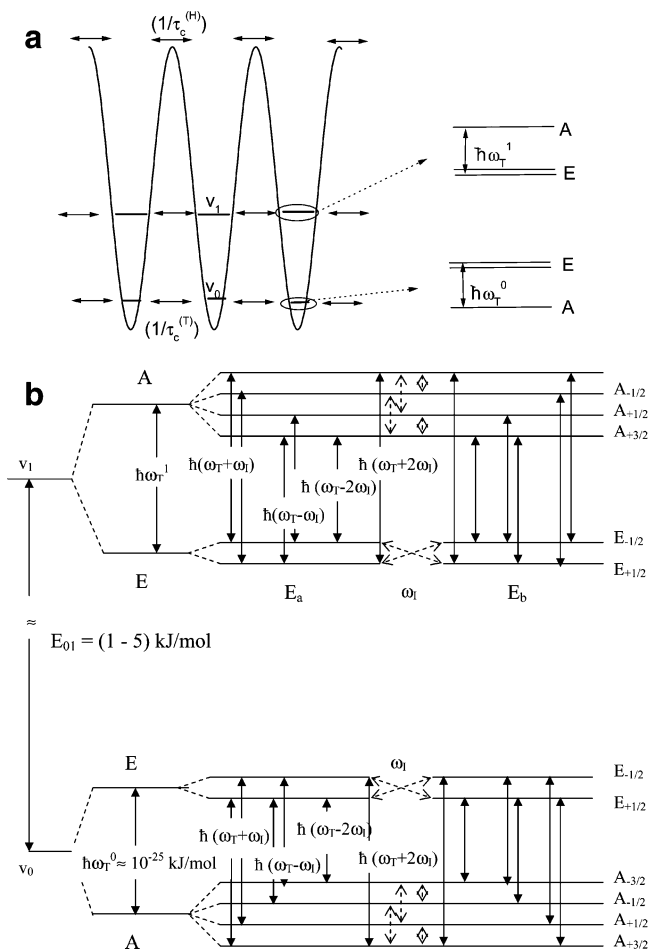


Figure 1. Schematic representation of the motion in the periodic triple potential well (a) and the energy-level scheme of the two lowest torsional states ν_0 and ν_1 of a methyl rotor in an applied magnetic field (b). $1/\tau_c^{(H)}$ and $1/\tau_c^{(T)}$ are the rate constant classical jumps across the barrier and tunneling jumps through the barrier. The ν_0 and ν_1 states exhibit a tunnel splitting (ω_r) into states with the symmetry A and E. The solid arrows indicate the allowed transitions, and the dashed arrows indicate the forbidden transitions $\hbar\omega_l$ and $\hbar 2\omega_l$.

determined by the correlation times $\tau_c^{(H)}$ and $\tau_c^{(T)}$ govern the proton NMR relaxation processes at low temperatures. The classical motion characterized by $\tau_c^{(H)}$ (Arrhenius dependence) takes place over the whole temperature range. The theoretical equations known in the literature used to study the methyl group dynamics will be discussed and compared with the equations given in the present paper.

The calculated spectral densities of the complex motion will be applied in the analysis of the experimental temperature dependencies of the proton spin–lattice relaxation time (T_1) of the CH_3COOK molecule. Protons in this molecule belong only to the methyl group, but this group is in the crystal lattice and cannot be treated as an isolated methyl group. This fact has been revealed in two different experimental temperature dependencies of T_1 for the same CH_3COOK polycrystalline substance.^{16,18}

2. The Model of Motion

The methyl group undergoes a complex stochastic motion (Figure 1a) made of two components, namely, the classical motion and the tunneling through the potential barrier. The correlation time of the classical (Arrhenius type), thermally

activated hindered rotation about the symmetry axis of the methyl group is

$$\tau_c^{(H)} = \tau_{c0}^{(H)} \exp(E_H/RT) \quad (2)$$

where the activation energy (E_H) equals the value of the hindering potential minus the value of the ground-state vibrational level. The value of E_H (potential barrier per one mole of particles) for the methyl group varies from very few to over a dozen kJ/mol. The preexponential factor $\tau_{c0}^{(H)}$ characterizes the rate of the motion. This value is in the range from 10^{-14} to 10^{-17} s.

According to classical mechanics, to overcome a potential barrier, the particles must have a kinetic energy greater than the height of the barrier. However, according to quantum mechanics, there is a possibility of overcoming a potential barrier by particles whose kinetic energy is lower than the barrier, by the process of tunneling.²⁸

Let us consider the motion of a particle in the field of forces with the rectangular barrier. The particle with the energy E is to overcome a potential barrier of height U_0 and width L from the side of area I (Figure 1). The height of the potential (U_0) is constant for x in the range ($0 < x < L$), so in the second area, II. $U_0 = 0$ for $x < 0$ (area I) and $x > L$ (area III) (Figure 1).

The solution of the problem of motion of particles through a potential barrier can be found in the following Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = E\psi \quad (3)$$

which also is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (4)$$

in areas I and III. Equation 4 changes into

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (E - U_0)\psi \quad (5)$$

in area II.

The general solutions of eqs 4 and 5 are

$$\psi = A_I e^{ikx} + B_I e^{-ikx} \quad (\text{for area I}) \quad (6)$$

$$\psi = A_{II} e^{\mu x} + B_{II} e^{-\mu x} \quad (\text{for area II}) \quad (7)$$

$$\psi = A_{III} e^{ikx} + B_{III} e^{-ikx} \quad (\text{for area III}) \quad (8)$$

where

$$k = \frac{1}{\hbar} \sqrt{2mE} \quad (9)$$

and

$$\mu = \frac{1}{\hbar} \sqrt{2m(U_0 - E)} \quad (10)$$

where m is the mass of the particle.

The amplitude of the wave in area III is equal to A_{III} , and this wave transmits through the barrier (U_0). However, the

quantity B_{III} describes the amplitude of the wave expanding in the negative direction of the x axis, too. $B_{\text{III}} = 0$ because the wave in this area does not propagate in the x direction. Two waves propagate in area I, the wave of amplitude A_1 (approaching wave) and the wave of amplitude B_1 (reflected wave). The ratio

$$D = \frac{|A_{\text{III}}|^2}{|A_1|^2} \quad (11)$$

can be interpreted as the ratio of an intensity of the stream of particles after jumps through the barrier (U_0) over an intensity of the stream of particles approaching the barrier (U_0). The value D can be also interpreted as a probability of the tunneling of the particles through the barrier (U_0). Frequently, the coefficient D is called the coefficient of transmittance or coefficient of transparency of the barrier.

The ratio

$$R = \frac{|B_1|^2}{|A_1|^2} \quad (12)$$

characterizes the probability of the reflection of the particle from the barrier (U_0) (coefficient of reflection). The sum of transmittance (D) and reflection (R) is equal to 1.

For a wide rectangular barrier ($\mu L \gg 1$), the following equation holds

$$D = D_0 e^{-2L/\hbar \sqrt{2m(U_0-E)}} \quad (13)$$

For the barriers that are more complicated in shape, the value of D obeys

$$D = D_0 e^{-2L/\hbar \int_{x_1}^{x_2} \sqrt{2m(U_0-E)} dx} \quad (14)$$

where x_1 and x_2 are the coefficients of the beginning and end of the barrier for a given value of E .

Importantly, the probability of the tunneling of the particle through the barrier decreases exponentially with the widening of the potential barrier and also with the increase in the square root of $(U_0 - E)$. This probability assumes reasonable values only in the microscopic world. It is equal to zero for the macroscopic objects (high value of L and big value of m).

$D = D_0$ when $E = U_0$. Also $D \approx D_0 e^{-(2L/\hbar)\sqrt{2m(U_0-E)}}$ when $E \ll U_0$. The value under the square root in eqs 13 and 14 is negative for $E > U_0$.

The energy

$$N_A E = C_p T \quad (15)$$

characterizes the thermal energy of the Avogadro number of particles, C_p is the molar specific heat, and T is temperature on the Kelvin scale. $E_H = N_A U_0$ (in joules per mole) (eq 2) concerns the potential barrier per 1 mol of particles. The value of $\exp[-\sqrt{(E_H - C_p T)}]$ equals 1 for $E_H = C_p T_{\text{tun}}$ (Figure 3). T_{tun} is the characteristic temperature at which this event take place. Above the temperature T_{tun} , the probability of tunneling is zero. The arrow in Figure 3 shows the temperature T_{tun} . The plot in Figure 3 reveals that the value of the coefficient D (probability of tunneling) significantly increases at temperatures below the

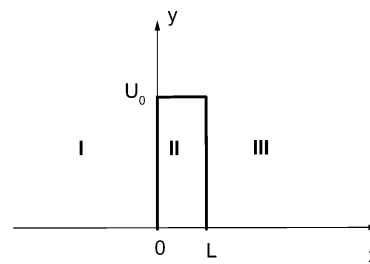


Figure 2. U_0 and L stand for the height and width of the potential barrier. The Roman numbers denote the area before, through, and after the potential barrier.

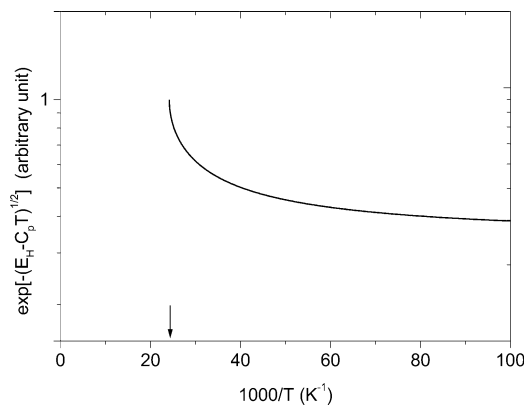


Figure 3. Illustration of the temperature dependence described by the equation $D = \exp(-\sqrt{(E_H - E)})$, where $E = C_p T$, $E_H = 5.03$ kJ/mol, and $C_p = 121.5$ J/mol. The arrow shows the temperature $T = E_H / C_p$ (41.4 K).

characteristic temperature when $C_p T_{\text{tun}} = E_H$. Interestingly, before cessation of the tunneling, the probability of tunneling increases. The rate constant of motion and the probability of motion have the same meaning. The correlation time characterizing a given motion is inversely proportional to the rate constant of a given motion. For the rotation about the C_3 axis in the triple equivalent minima potential, the rate constant (k_3) is related to the correlation time (τ_c) as follows:

$$\tau_c = \frac{1}{3k_3} \quad (16)$$

Therefore, eq 13 can be explicitly applied as the correlation time of tunneling:

$$\tau_c^{(T)} = \tau_0^{(T)} e^{B \sqrt{(E_H - C_p T)}} \quad (17)$$

where

$$\tau_{c0}^{(T)} = \frac{1}{3D_0} \quad (18)$$

and

$$B = \frac{2L}{\hbar} \sqrt{\frac{2m}{N_A}} \quad (19)$$

The value of B in eq 19 depends on the mass of the tunneling particle and on the width of the potential barrier. If the mass of the tunneling proton is $m = 1.67 \times 10^{-27}$ kg and the barrier width is $L = 1.78$ Å (proton-proton distance in methyl group), then the value of B is $0.25(\sqrt{J})^{-1}$. The preexponential factor $\tau_0^{(T)}$ (eq 17) characterizes the rate of the tunneling motion. This

value is known to be in the range from 10^{-6} s (deuterons) to 10^{-9} s (protons).

Usually,^{9–24} the correlation time of methyl group tunneling is assumed to follow the exponential temperature dependence as

$$\tau_c^{(T)} = \tau_{c0}^{(T)} \exp(E_{01}/RT) \quad (20)$$

The activation energy for the tunneling motion is found to be comparable with the value of E_{01} , the energy difference between the ground and the first excited torsional levels of the methyl group. Equation 20 has been assumed by intuition.

The character of the temperature dependence of the correlation time of $\tau_c^{(T)}$ following from eq 17 is different than that from eq 20. The correlation time given in eq 17 deviates into shorter values from the linear dependence $\ln(\tau_c^{(T)})$ versus $(1000/T)$ just before reaching of the temperature T_{tun} . Then, for $T > T_{\text{tun}}$, the probability of tunneling is zero.

The fact that the spectral density of tunneling motion is zero at high temperatures has been noted also for the tunneling of the hydrogen bonded proton in solids consisting of hydrogen bonded tautomers.²⁹

The stochastic molecular motions in the ground and first excited torsional states do not have the same rates. Therefore, the correlation times $\tau_c^{(T)}$ and $\tau_c^{(H)}$ for separate ν_0 and ν_1 states have to be defined separately. Assuming that eqs 2 and 17 define $(\tau_c^{(H)})_{\nu_0}$ and $(\tau_c^{(T)})_{\nu_0}$, the respective correlation times for ν_1 can be defined as

$$(\tau_c^{(H)})_{\nu_1} = \tau_{c0}^{(H)} \exp[(E_H - E_{01})/RT] \quad (21)$$

$$\left(\frac{1}{\tau_c^{(T)}}\right)_{\nu_1} = k' \left(\frac{1}{\tau_c^{(T)}}\right)_{\nu_0} \quad (22)$$

where $k' \gg 1$.

The value of $k' \gg 1$ indicates a faster rate of tunneling in the first excited torsional state than in the ground state. A value of ~ 30 for k' has been established for the rate $(\tau_c^{(T)})_{\nu_1}^{-1}$ of the proton transfer in the hydrogen bond.^{30–32}

3. Proton Spin–Lattice Relaxation Rate

The proton relaxation rate $(1/T_1)$ is governed by the stochastic molecular motions which introduces time dependence into the interaction Hamiltonian through modulation of the dipole–dipole interactions. Usually, the dipolar perturbation Hamiltonian is considered for a two-spin system. Since spins i and s belong to the molecule, which undergoes stochastic motions, the coordinates $(R_{is}, \nu_{is}, \varphi_{is})$ are random functions of time. R_{is} is the distance between spins i and s . ν_{is} and φ_{is} are the polar and azimuth angles, respectively, describing the orientation of the internuclear vector in the laboratory frame with the z axis in the direction of the external magnetic field (B_0). When the two spins belong to the same group in the molecule, the internuclear distance (R_{is}) becomes constant. The distance R_{is} between the spins belonging to different groups of the same molecule can change with changes in ν_{is} and φ_{is} because of the reorientation of one of the spins (Figure 4).

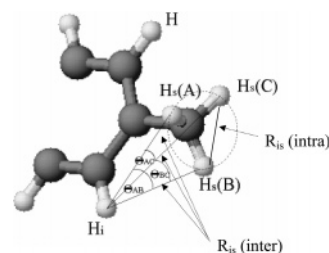


Figure 4. The $R_{is}(\text{inter})$ distance between the i th proton outside the methyl group and the s th proton belonging to this methyl group assumes the values $R_{is}(A)$, $R_{is}(B)$, and $R_{is}(C)$ when the methyl group undergoes C_3 hindered rotation. Θ_{AB}^{is} , Θ_{BC}^{is} , Θ_{AC}^{is} are the angles of the $R_{is}(\text{inter})$ jumps. The $R_{is}(\text{intra})$ distance referring to the dipolar interaction of two methyl protons becomes constant during the methyl group rotation.

The perturbation dipolar Hamiltonian $H_{is}'(t)$ contains the functions $F_{is}^0(t)$, $F_{is}^1(t)$, and $F_{is}^2(t)$ which are random in time:³³

$$F_{is}^0(t) = d_c^{is}(t)[3 \cos^2 \vartheta_{is}(t) - 1] \quad (23a)$$

$$F_{is}^1(t) = d_c^{is}(t) \sin \vartheta_{is}(t) \cos \vartheta_{is}(t) \exp(i\varphi_{is}(t)) \quad (23b)$$

$$F_{is}^2(t) = d_c^{is}(t) \sin^2 \vartheta_{is}(t) \exp(i2\varphi_{is}(t)) \quad (23c)$$

where $d_c^{is}(t) = \gamma_i \gamma_s \hbar R_{is}^{-3}(t)$ is the dipolar coupling constant.

The spin–lattice relaxation rate can be found by summing up the transition probabilities within the spin energy levels in a magnetic field. If the spin system can always be described by a spin temperature, then it is possible to use the general formula.³³

$$\frac{1}{T_1} = \frac{\sum_{mm'} w_{mm'} (E_m - E_{m'})^2}{\sum_m E_m^2} \quad (24)$$

The transition probability per unit time ($w_{mm'}$) from an initial state $|m\rangle$ to a final state $|m'\rangle$ can be written as

$$w_{mm'} = \frac{1}{\hbar^2} J_{mm'}(\omega_{mm'}) \quad (25)$$

where

$$J_{mm'}(\omega_{mm'}) = \int_{-\infty}^{+\infty} K_{mm'}(\tau) \exp(-i\omega_{mm'}\tau) d\tau \quad (26)$$

and

$$K_{mm'}(\tau) = \langle (\varphi_m | H_{is}'(t) | \varphi_{m'}) (\varphi_m | H_{is}'(t + \tau) | \varphi_{m'})^* \rangle \quad (27)$$

$K_{mm'}(\tau)$ are correlation functions of the matrix elements $(\varphi_m | H_{is}'(t) | \varphi_{m'})$, and $J_{mm'}(\omega_{mm'})$ are the spectral densities of these correlation functions. φ_m and $\varphi_{m'}$ are the eigenfunctions, which correspond to the states $|m\rangle$ and $|m'\rangle$. $H_{is}'(t)$ is the random part of the dipolar Hamiltonian (perturbation Hamiltonian).

Two types of dipolar interactions should be distinguished: the “intra” interactions within an isolated methyl group and the “inter” interactions with other protons of the molecule and with protons of different molecules (Figure 4).

The resulting equation for the spin–lattice relaxation in substances, in which each pair of homonuclear spins with the quantum number $1/2$ can be treated as an isolated two-spin

system (inter contribution, “*EE*” contribution), contains spectral densities at frequencies ω_1 and $2\omega_1$.³³

$$\left(\frac{1}{T_1}\right)_{EE}^{is} = \frac{3}{2}I(I+1)[J_{is}^1(\omega_1) + J_{is}^2(2\omega_1)] \quad (28)$$

$J_{is}^m(\omega_1)$ and $J_{is}^m(2\omega_1)$ are the spectral densities of the autocorrelation functions, that is,

$$J_{is}^m(\omega_1) = \int_{-\infty}^{\infty} \langle F_{is}^m(t) F_{is}^{m*}(t + \tau) \rangle \exp(-im\omega_1\tau) d\tau \quad (29)$$

where $m = 1$ or 2 and $F_{is}^m(t)$ are given in eqs 23b and c.

The $1/T_1$ relaxation for N number of spins in a molecule is determined by the sum of dipolar interactions.¹ If the i spins numbered 1, 2, or 3 belong to the methyl group and the s spins to another proton, then the resulting equation is

$$\left(\frac{1}{T_1}\right)_{EE} = \frac{3}{2}I(I+1)N^{-1} \sum_{i=1}^3 \sum_{s=4}^N [J_{is}^1(\omega_1) + J_{is}^2(2\omega_1)] \quad (30)$$

The values of $(T_1)_{EE}$ on the low-temperature side of the minimum depend on the resonance frequency (ω_1). $(T_1)_{EE}$ is long at minimum value due to the long proton–proton distances (longer than those inside a methyl group). This contribution to the relaxation rate can cause the appearance of a separate maximum of the relaxation rate when $\omega_T \gg \omega_1$. $(1/T_1)_{EE}$ can be calculated accurately only for protons belonging to the same molecule. Even the changes of the R_{is} (inter) (Figure 4) vector can be taken into account. However, when spin i belongs to the methyl group and spin s to the neighboring molecule (for example, to the protonated impurity), $(1/T_1)_{EE}$ can be estimated only when this maximum is well separated from the maximum of the intramolecular contribution $((1/T_1)_{AE})$.

The protons belonging to the CH_3 group under rotation in the triple symmetric potential cannot be treated as an isolated spin pair. The spin energy levels in a magnetic field for a purely 3-fold potential barrier of the CH_3 rotator and for the two lowest torsional states were calculated by Haupt.¹⁰ The motions (jumps over the barrier and jumps through the barrier) of methyl protons in a triple potential (Figure 1a) induce the transitions between the spin states marked in Figure 1b by solid line arrows. The spin–lattice relaxation of an isolated CH_3 group is determined only by $A \leftrightarrow E$ transitions. The symmetry conserving transitions $E_a \leftrightarrow E_b$ are forbidden by the spin selection rules and do not contribute to the spin relaxation of single methyl groups in compliance with Haupt’s¹⁰ finding. It should be emphasized that spin levels in a magnetic field (B_0) are known from the literature for the three protons of a rotating methyl group, while the probabilities of transitions between these levels are usually calculated for dipole–dipole interactions in the spin pairs. Therefore, the random functions used to calculate spectral densities belong to the two-spin perturbation Hamiltonian.

The resulting equation for the relaxation rate $(1/T_1)_{AE}$ (intra contribution, “*AE*” contribution) has been obtained by Haupt et al.^{10,11} The value $(1/T_1)_{AE}$ refers to the relaxation of two protons at the distance R_{is} (intra) (Figure 4).

If the methyl spin system can always be described by a spin temperature (which is a crude approximation in the present case), then the spin–lattice relaxation rate can be determined by summing up the transition probabilities (eq 24) within the manifold of levels, as illustrated in Figure 1b.

When given that spin i of a methyl group interacts with two s spins of another methyl group, the dipolar interactions sum up. For N —total number of spins in a molecule—where three spins numbered from 1 to 3 belong to a methyl group, the resulting equation is

$$\left(\frac{1}{T_1}\right)_{AE} = \frac{3}{4}I(I+1)N^{-1}$$

$$\sum_{i=1}^3 \sum_{s=1}^3 [J_{is}^1(\omega_1 + \omega_T) + J_{is}^1(\omega_1 - \omega_T) + J_{is}^2(2\omega_1 + \omega_T) + J_{is}^2(2\omega_1 - \omega_T)] \quad (31)$$

where ω_1 is the Larmor frequency and ω_T is the torsional tunneling splitting.

When $\omega_T = 0$, eq 31 is reduced to the well-known equation describing the relaxation of three moving spins in the molecule with N number of spins.

The contribution of $(1/T_1)_{AE}$ to the relaxation can be independent of the resonance frequency (ω_1) when $\omega_T \gg \omega_1$. $(T_1)_{AE}$ can be long at the minimum value because of a high value of ω_T . The methyl tunneling frequencies are typically in the range $100 \text{ GHz} \geq \omega_T/2\pi \geq 4 \text{ kHz}$.³⁴

The vibrational relaxation is much faster than the spin–lattice relaxation. It is reasonable to assume that all molecules occupy two torsional levels only.^{30–32} Therefore, the relaxation rate is

$$\frac{1}{T_1} = n_{v0} \left(\frac{1}{T_1}\right)_{(v0)} + n_{v1} \left(\frac{1}{T_1}\right)_{(v1)} \quad (32)$$

n_{v0} and n_{v1} are the fractions of molecules in the ground and first excited states, respectively. $(1/T_1)_{(v0)}$ and $(1/T_1)_{(v1)}$ are the relaxation rates of the molecules in the ground and first excited torsional states, respectively. The values of $(1/T_1)_{(v0)}$ and $(1/T_1)_{(v1)}$ are

$$\left(\frac{1}{T_1}\right)_{(v0)} = \left(\frac{1}{T_1}\right)_{AE(v0)} + \left(\frac{1}{T_1}\right)_{EE(v0)} \quad (33)$$

$$\left(\frac{1}{T_1}\right)_{(v1)} = \left(\frac{1}{T_1}\right)_{AE(v1)} + \left(\frac{1}{T_1}\right)_{EE(v1)} \quad (34)$$

where $(1/T_1)_{EE(v1)}$, $(1/T_1)_{EE(v0)}$, $(1/T_1)_{AE(v0)}$, and $(1/T_1)_{AE(v1)}$ are given by eqs 30 and 31 with the spectral densities corresponding to the motions at these levels.

4. Correlation Functions and Spectral Densities for the Complex Motion of the R_{is} Vector Undergoing Classical Hopping and Rotational Tunneling

A spin pair distanced by R_{is} at low temperatures can undergo stochastic jumps between three sites of potential energy minima through a barrier (rotational tunneling). In such a case, the tunneling accompanies the thermal jumps over the barrier. These two stochastic processes modulate the interaction Hamiltonian independently of each other. Each process has its own spectral density determined by a different correlation time (eqs 2 and 17).

If the random functions (eqs 23a–c) can be written as a product of functions, which are time dependent due to the separate reorientations, the correlation function for the complex

motion can be calculated as a product of two correlation functions.²⁷

$$F_{is}^m(t) = f_{(1)is}^m(t) f_{(2)is}^m(t) \quad (35)$$

$$\langle F_{is}^m(t) F_{is}^{m*}(t + \tau) \rangle = \langle f_{(1)is}^m(t) f_{(1)is}^{m*}(t + \tau) \rangle \langle f_{(2)is}^m(t) f_{(2)is}^{m*}(t + \tau) \rangle \quad (36)$$

The $F_{is}^m(t)$ function given in eqs 23a–c can be changed into the product of the two functions $f_{(1)is}^m(t)$ and $f_{(2)is}^m(t)$ in the following way:

$$f_{(1)is}^0(t) = d_c^{is}(t) (3 \cos^2[v_{is}(t)] - 1) \quad (37a)$$

$$f_{(2)is}^0(t) = r(t) \quad (37b)$$

$$f_{(1)is}^1(t) = d_c^{is}(t) \sin \vartheta_{is}(t) \cos \vartheta_{is}(t) \exp(i\varphi_{is}(t)) \quad (37c)$$

$$f_{(2)is}^1(t) = r(t) \quad (37d)$$

$$f_{(1)is}^2(t) = d_c^{is}(t) \sin^2 \vartheta_{is}(t) \exp(i2\varphi_{is}(t)) \quad (37e)$$

$$f_{(2)is}^2(t) = r(t) \quad (37f)$$

where $r(t) = 1$. The value of $r(t)$ is a unit vector coincident with \mathbf{R}_{is} , that is, $r(t) = (\mathbf{R}_{is}/|\mathbf{R}_{is}|)$ (see eqs 1 and 2 in ref 33 or eqs 58–63 in ref 34). The $r(t)$ value can also be time dependent if, for example, the proton pair distance changes due to jumping of one the protons (Figure 4).

Now, let us assume that the two spins i and s separated by R_{is} undergo jumps among the stable positions A, B, and C. Each site, A, B, or C, is defined by the appropriate minimum in the potential energy surface. The time dependence of $f_{(1)is}^m(t)$ is due to the classical jumps over the barrier, and the time dependence of $f_{(2)is}^m(t)$ is due to incoherent tunneling. The time required to perform a jump is considered negligible as compared with the residence time in each equilibrium position. Thus, at any time, a constant number of spin pairs can be found at sites A, B, or C. The random functions $f_{(a)is}^m(t)$, where $a = 1$ or 2, take one of the three discrete values $f_{(a)is}^m(\text{A})$, $f_{(a)is}^m(\text{B})$, or $f_{(a)is}^m(\text{C})$. There are nine cases to consider: if the nucleus s is in A at $t = 0$, it can be in A, B, or C at time t ; if in B and at $t = 0$, it may be in A, B, or C at time t ; and if in C and at $t = 0$, it may be in A, B, or C at time t . Thus, the autocorrelation functions $\langle F_{is}^m(t) F_{is}^{m*}(t + \tau) \rangle$ have nine terms in the following sums:

$$\langle f_{(a)is}^m(t) f_{(a)is}^{m*}(t + \tau) \rangle = \sum_{\Omega} \sum_{\Omega_0} \langle f_{(a)is}^m(\Omega) f_{(a)is}^{m*}(\Omega_0) \rangle P_{(a)}(\Omega, t + \tau | \Omega_0, t) P_{(a)}(\Omega_0) \quad (38)$$

where Ω stands for the state A, B, or C at time $(t + \tau)$ and Ω_0 stands for A, B, or C at time t . $P_{(a)}(\Omega, t + \tau | \Omega_0, t)$ is the probability of finding $f_{(a)is}^m(t)$ in the state Ω at time $t + \tau$, after being in the state Ω_0 at time t . $P_{(a)}(\Omega_0)$ is the initial probability of finding $f_{(a)is}^m(t)$ in the state Ω_0 at time t . Three $P_{(a)}(\Omega_0)$ probabilities and nine $P_{(a)}(\Omega, t + \tau | \Omega_0, t)$ probabilities are

obtained by solving the set of differential equations. For the jumps between three equivalent sites, the equations are

$$P_{(a)}(\text{A}) = P_{(a)}(\text{B}) = P_{(a)}(\text{C}) = 1/3 \quad (39)$$

$$P_{(a)}(\text{A}, t + \tau | \text{A}, t) = P_{(a)}(\text{B}, t + \tau | \text{B}, t) = P_{(a)}(\text{C}, t + \tau | \text{C}, t) = (1/3) [1 + 2 \exp(-|\tau|/\tau_{c(a)})] \quad (40)$$

$$P_{(a)}(\text{B}, t + \tau | \text{A}, t) = P_{(a)}(\text{C}, t + \tau | \text{A}, t) = P_{(a)}(\text{A}, t + \tau | \text{B}, t) = P_{(a)}(\text{C}, t + \tau | \text{B}, t) = P_{(a)}(\text{A}, t + \tau | \text{C}, t) = P_{(a)}(\text{B}, t + \tau | \text{C}, t) = (1/3) [1 - \exp(-|\tau|/\tau_{c(a)})] \quad (41)$$

where $\tau_{c(a)} = \tau_c^{(H)}$ or $\tau_{c(a)} = \tau_c^{(T)}$.

The expressions for the separate conditional probabilities (eqs 39–41) if the motion takes place in triple nonequivalent potential are different than those for the motion in triple equivalent potential. A shift of the T_1 minimum to higher temperatures and an increase in the minimum T_1 value is expected (see, for example, the appendix in refs 26 and 38–40). This effect should be, however, insignificant if the inequivalence of the potential barriers is very small (for example, $\Delta E = 0.04$ kJ/mol).

Substituting eqs 39–41 into eq 38 and next into eq 36 we arrive at

$$\langle F_{is}^m(t) F_{is}^{m*}(t + \tau) \rangle = \left[C_{1(1)is}^m + C_{2(1)is}^m \exp\left(-\frac{|\tau|}{\tau_c^{(H)}}\right) \right] \left[C_{1(2)is}^m + C_{2(2)is}^m \exp\left(-\frac{|\tau|}{\tau_c^{(T)}}\right) \right] \quad (42)$$

where

$$C_{1(1)is}^m = (1/9) [f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{A}) + f_{(1)is}^m(\text{B}) f_{(1)is}^{m*}(\text{B}) + f_{(1)is}^m(\text{C}) f_{(1)is}^{m*}(\text{C}) + 2f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{B}) + 2f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{C}) + 2f_{(1)is}^m(\text{B}) f_{(1)is}^{m*}(\text{C})] \quad (43)$$

$$C_{2(1)is}^m = (1/9) [2f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{A}) + 2f_{(1)is}^m(\text{B}) f_{(1)is}^{m*}(\text{B}) + 2f_{(1)is}^m(\text{C}) f_{(1)is}^{m*}(\text{C}) - 2f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{B}) - 2f_{(1)is}^m(\text{A}) f_{(1)is}^{m*}(\text{C}) - 2f_{(1)is}^m(\text{B}) f_{(1)is}^{m*}(\text{C})] \quad (44)$$

$$C_{1(2)is}^m = (1/9) [f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{A}) + f_{(2)is}^m(\text{B}) f_{(2)is}^{m*}(\text{B}) + f_{(2)is}^m(\text{C}) f_{(2)is}^{m*}(\text{C}) + 2f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{B}) + 2f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{C}) + 2f_{(2)is}^m(\text{B}) f_{(2)is}^{m*}(\text{C})] \quad (45)$$

$$C_{2(2)is}^m = (1/9) [2f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{A}) + 2f_{(2)is}^m(\text{B}) f_{(2)is}^{m*}(\text{B}) + 2f_{(2)is}^m(\text{C}) f_{(2)is}^{m*}(\text{C}) - 2f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{B}) - 2f_{(2)is}^m(\text{A}) f_{(2)is}^{m*}(\text{C}) - 2f_{(2)is}^m(\text{B}) f_{(2)is}^{m*}(\text{C})] \quad (46)$$

As in the polycrystalline material, particular spin pairs can assume arbitrary angles, v_{is} and φ_{is} ; the calculations of $\langle f_{(1)is}^m(\Omega) f_{(1)is}^{m*}(\Omega_0) \rangle$ were performed for the mean values $(3 \cos^2 v_{is} - 1)^2 = 4/5$ ($S_0 = 4/5$), $[\sin v_{is} \cos v_{is} \exp(i\varphi_{is})]^2 =$

$2/_{15}$ ($S_1 = 2/_{15}$), and $[\sin^2 v_{is} \exp(2i\varphi_{is})]^2 = 8/_{15}$ ($S_2 = 8/_{15}$). Therefore, after spatial averaging, the isotropic averages are found to be

$$\langle f_{(1)is}^m(\Omega) f_{(1)is}^{m*}(\Omega_0) \rangle = S_m d_c^{is}(\Omega) d_c^{is}(\Omega_0) P_2(\cos \Theta_{\Omega\Omega_0}) \quad (47)$$

$$\langle f_{(2)is}^m(\Omega) f_{(2)is}^{m*}(\Omega_0) \rangle = \frac{d_c^{is}(\Omega)}{d_c^{is}(\Omega_0)} P_2(\cos \Theta_{\Omega\Omega_0}) \quad (48)$$

where $m = 0, 1$, or 2 and Ω_0 and $\Omega = A, B$, or C , respectively, $d_c^{is}(\Omega_0) = \gamma_i \gamma_s \hbar R_{is}^{-3}(\Omega_0)$, $d_c^{is}(\Omega) = \gamma_i \gamma_s \hbar R_{is}^{-3}(\Omega)$, $P_2(\cos \Theta_{\Omega\Omega_0}) = 0.5(3 \cos^2 \Theta_{\Omega\Omega_0} - 1)$ denotes the Legendre polynomial, and $\Theta_{\Omega\Omega_0}$ is the angle between $R_{is}(\Omega_0)$ and $R_{is}(\Omega)$. $\Theta_{\Omega\Omega_0} = \Theta_3 = 120^\circ$ for the proton–proton vector in the methyl group.

Since the value of the dipolar coupling constant can be changed when only one spin jumps, it can be noticed that the value $f_{(2)is}^m(A) = 1$ while the values $f_{(2)is}^m(B) = d_c^{is}(B)/d_c^{is}(A)$ and $f_{(2)is}^m(C) = d_c^{is}(C)/d_c^{is}(A)$.

Substituting eqs 47 and 48 into eqs 43–46, the following equations are obtained:

$$C_{1(1)is}^m = S_m C_1^{is} \quad (49)$$

$$C_{2(1)is}^m = S_m C_2^{is} \quad (50)$$

$$C_{1(2)is}^m = C_1^{is} / d_c^{is}(A)^2 \quad (51)$$

$$C_{2(2)is}^m = C_2^{is} / d_c^{is}(A)^2 \quad (52)$$

where

$$C_1^{is} = (1/9)[d_c^{is}(A)]^2 + d_c^{is}(B)^2 + d_c^{is}(C)^2 + d_c^{is}(A)d_c^{is}(B)(3 \cos^2 \Theta_{AB}^{is} - 1) + d_c^{is}(A)d_c^{is}(C)(3 \cos^2 \Theta_{AC}^{is} - 1) + d_c^{is}(B)d_c^{is}(C)(3 \cos^2 \Theta_{BC}^{is} - 1) \quad (53)$$

$$C_2^{is} = (1/9)[2d_c^{is}(A)]^2 + 2d_c^{is}(B)^2 + 2d_c^{is}(C)^2 - d_c^{is}(A)d_c^{is}(B)(3 \cos^2 \Theta_{AB}^{is} - 1) - d_c^{is}(A)d_c^{is}(C)(3 \cos^2 \Theta_{AC}^{is} - 1) - d_c^{is}(B)d_c^{is}(C)(3 \cos^2 \Theta_{BC}^{is} - 1) \quad (54)$$

Therefore, the total correlation functions of the random functions $F_{is}^m(t)$ for the classical motion and rotational tunneling are

$$\langle F_{is}^m(t) F_{is}^{m*}(t + \tau) \rangle = S_m [d_c^{is}(A)]^{-2} \left[C_1^{is} + C_2^{is} \exp\left(-\frac{|\tau|}{\tau_c^{(H)}}\right) \right] \left[C_1^{is} + C_2^{is} \exp\left(-\frac{|\tau|}{\tau_c^{(T)}}\right) \right] \quad (55)$$

where C_1^{is} , C_2^{is} , $\tau_c^{(H)}$, and $\tau_c^{(T)}$ are given by eqs 53, 54, 2, and 17, respectively.

The respective spectral densities, which are the results of the Fourier transform of the correlation functions, are

$$J_{is}^m(\omega) = S_m [d_c^{is}(A)]^{-2} \int_{-\infty}^{\infty} \left[C_1^{is} + C_2^{is} \exp\left(-\frac{|\tau|}{\tau_c^{(H)}}\right) \right] \left[C_1^{is} + C_2^{is} \exp\left(-\frac{|\tau|}{\tau_c^{(T)}}\right) \right] \exp(-i\omega\tau) d\tau = S_m [d_c^{is}(A)]^{-2} \left[C_1^{is} C_2^{is} \frac{2\tau_c^{(H)}}{1 + (\omega\tau_c^{(H)})^2} + C_1^{is} C_2^{is} \frac{2\tau_c^{(T)}}{1 + (\omega\tau_c^{(T)})^2} + (C_2^{is})^2 \frac{2\tau_c^{(TH)}}{1 + (\omega\tau_c^{(TH)})^2} \right] \quad (56)$$

where

$$\frac{1}{\tau_c^{(TH)}} = \frac{1}{\tau_c^{(H)}} + \frac{1}{\tau_c^{(T)}} \quad (57)$$

Equation 56 allows a calculation of the spectral density for the frequencies $\omega = n\omega_1$, where $n = 1$ or 2 , as well as for the frequencies $\omega = (\omega_T \pm m\omega_1)$. Therefore, the spectral densities given in eq 56 should be applied in the calculations of $(1/T_1)_{EE}$ (eq 30) as well as in $(1/T_1)_{AE}$ (eq 31).

When d_c^{is} and $\tau_c^{(H)}$ in eq 56 are related to the reorientation R_{is} vector, where spin i belongs to the methyl group and spin s to another group in the molecule, let us denote these values as $d_c^{is}(\text{inter})$. The value of $d_c^{is}(\text{inter})$ can be variable [$R_{is}(A) \neq R_{is}(B) \neq R_{is}(C)$], as shown in Figure 4. Equations 53 and 54 allow for such a case. The values of $R_{is}(A)$, $R_{is}(B)$, and $R_{is}(C)$ can be unknown only in the case when spin s belongs to the neighboring molecule or to the protonated impurity in the sample. Usually, in such cases, $J^m(n\omega_1)$ is calculated on the basis of the value of $J^m(n\omega_1)$ with $R_{is}(A) = R_{is}(B) = R_{is}(C) = R_{is} = 1.78 \text{ \AA}$ (H–H distance between two protons in a methyl group) by multiplication by X_2 . The value of X_2 is expected to be much less than 1.

If $d_c^{is}(A) = d_c^{is}(B) = d_c^{is}(C) = d_c^{is}$, then $\Theta_{AB}^{is} = \Theta_{AC}^{is} = \Theta_{BC}^{is} = \Theta_3^{is}$ for the proton–proton vector inside the methyl group. Let us denote $d_c^{is}(\text{intra})$ in eq 56 as the values related to the reorientation of the R_{is} vector where both spins belong to the same methyl group.

If $R_{is}(A) = R_{is}(B) = R_{is}(C)$, $\Theta_{AB}^{is} = \Theta_{AC}^{is} = \Theta_{BC}^{is} = \Theta_3^{is}$, and $\tau_c^{(T)} = \infty$, the spectral density given in eq 56 is reduced to

$$J_{is}^m(\omega) = S_m (d_c^{is})^2 \sin^2 \Theta_3^{is} \frac{2\tau_c^{(H)}}{1 + (\omega\tau_c^{(H)})^2} \quad (58)$$

which is a well-known expression for the spectral density of the classical motion of a two-spin system at a constant value of the distance R_{is} undergoing the 3-fold hindered rotation.

If $\tau_c^{(H)} \rightarrow \infty$, eq 56 is reduced to the equation:

$$J_{is}^m(\omega) = S_m (d_c^{is})^2 \sin^2 \Theta_3^{is} \frac{2\tau_c^{(T)}}{1 + (\omega\tau_c^{(T)})^2} \quad (59)$$

Equation 59 gives the values of spectral density of tunneling jumps. Such a spectral density never exists alone. This accompanies the spectral density of classical motion.³⁶ The classical motion exists at liquid helium temperatures, but the values of spectral densities of this motion are infinitesimal if

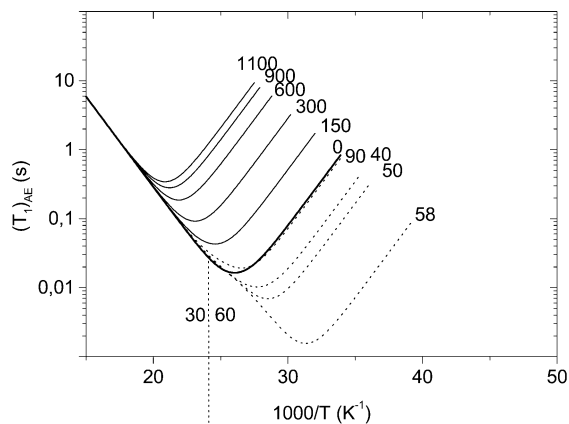


Figure 5. $(T_1)_{AE}$ ($\omega_l = 2\pi \times 30$ MHz) of an isolated methyl group (eqs 31 and 56) versus $(1000/T)$ for different values of $\omega_T = 2\pi \times \nu_T$, where ν_T in units of megahertz are 0, 30, 40, 50, 58, 60, 90, 150, 300, 600, 900, and 1100. The plots for the values $0 < \omega_T < 3\omega_l$ are marked by dashed lines, while these for $\omega_T > 3\omega_l$ are marked by solid lines. The assumed motion parameters are $E_H = 5.03$ kJ/mol, $\tau_0^{(H)} = 5 \times 10^{-16}$ s, $R_{is} = 1.78$ Å, and $\Theta_3^s = 120^\circ$.

ω_l is high. Therefore, that is why often the classical motion is not detected in experiments at low temperatures.

Thus, when the motions characterized by the correlation times $\tau_c^{(H)}$ and $\tau_c^{(T)}$ separately modulate the interaction Hamiltonian of the methyl group, the spectral densities of these motions are given by eqs 58 and 59. A different situation appears when both motions, which are independent, modulate the interaction Hamiltonian simultaneously. Then, the total spectral density is given by eq 56.

When $\omega_T \gg \omega_l$, the T_1 method is convenient for estimation of the values of ω_T from the experiment. Then, the $(1/T_1)_{AE}$ and $(1/T_1)_{EE}$ maximums appear separately in the temperature plots. The maximum $(1/T_1)_{AE}$ appears at higher temperatures than the maximum of $(1/T_1)_{EE}$. Moreover, the maximum $(1/T_1)_{AE}$ is not resonance frequency dependent, while $(1/T_1)_{EE}$ depends on the value of ω_l on the low-temperature side of the maximum.

The small tunnel splitting, that is, $\omega_T \leq \omega_l$, makes the high-temperature maximums (due to classical motion) of $(1/T_1)_{AE}$ and $(1/T_1)_{EE}$ appear at the same temperature, and both are frequency dependent. Usually, for such a case, the value of $(1/T_1)_{AE}$ is higher than $(1/T_1)_{EE}$ because $R_{is}(\text{intra}) < R_{is}(\text{inter})$. Thus, the dominating relaxation mechanism is $(1/T_1)_{AE}$. The values of $(T_1)_{AE}$ at the minimum which is due to classical motion decrease with increasing ω_T when $0 < \omega_T < 2\omega_l$. Then, these undergo an increase (Figure 5). This is interesting to note that the temperature plot of $(T_1)_{AE}$ for $\omega_T = 3\omega_l$ is almost identical to the plot for $\omega_T = 0$. T_1 is no longer frequency dependent for $\omega_T = \omega_l$ and $\omega_T = 2\omega_l$. This unusual temperature dependence of $(T_1)_{AE}$ is visible in Figure 5 for $\omega_T = (2\pi \times 30)$ and $(2\pi \times 60)$ MHz. Therefore, it can be concluded that the sensitivity of the NMR relaxation method in the determination of $\omega_T < 3\omega_l$ is low. The indicator for the low tunnel splitting values of the methyl group can be the frequency dependence of the high-temperature minimum of T_1 from the low-temperature side.

5. Interpretation of the Experimental Data in Terms of the Theory Proposed

Potassium Acetate (CH_3COOK). The experimental results of the spin–lattice relaxation time measurements (T_1) (15, 30, and 52 MHz) for CH_3COOK obtained by Koksals et al.¹⁶ have been plotted as a function of $1000/T$ in Figure 6. The spin–

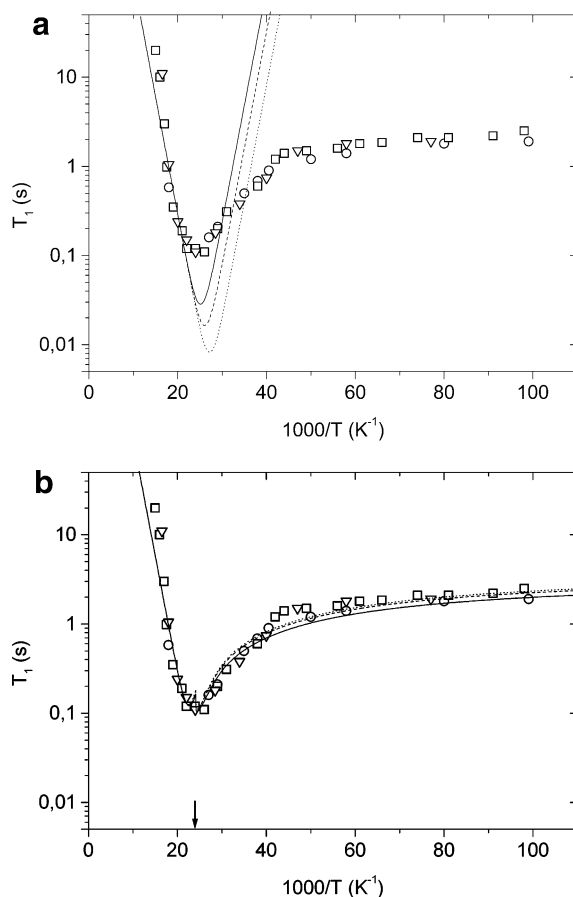


Figure 6. Temperature dependencies of the proton spin–lattice relaxation time for CH_3COOK at 15, 30, and 52 MHz¹⁶ marked by circles, squares, and triangles, respectively. The theoretical curves are marked by the following lines: solid, 52 MHz; dashed, 30 MHz; and dotted, 15 MHz. The best-fit parameters are listed in Table 1. Theoretical curves were computed using the well-known equation for the case of a classical C_3 methyl group rotation (a). The lines in part b represent the best fit of eqs 31 and 56 to the data. The arrow shows the temperature $T_{\text{urn}} = E_H/C_p$ (41 K).

lattice relaxation time is independent of the Larmor frequency in a wide temperature regime (a similar temperature dependence of T_1 has been reported for the compounds $(\text{CH}_3\text{COO})_2\text{Ba}$, $(\text{CH}_3\text{COO})_2\text{Cd}$, and $(\text{CH}_3\text{COO})_2\text{Ca}$). The authors¹⁶ interpreted their results in terms of a single correlation time of the tunneling process at low temperatures, a single correlation time of thermally activated jumps at high temperatures, and an effective correlation time which is described by eq 1 for temperatures between 70 and 56 K. The activation energy obtained from the slope of T_1 versus $1000/T$ for $25 \text{ K}^{-1} < 1000/T < 50 \text{ K}^{-1}$ is identified by E_{01} , the energy difference between the ground and first excited torsional states of the CH_3 rotator. The change in the slope of the T_1 plot below temperatures of 25 K ($1000/T = 50 \text{ K}^{-1}$) was interpreted in terms of the activation energy of molecules that occupy the ground-state level only. The activation energy of the tunneling process turns out to be $\hbar\omega_T^0$, that corresponding to the ground-state tunnel splitting. The interpretation proposed in the present paper involves the change in the low-temperatures slope of T_1 as a result of the character of the temperature dependence of the correlation time of tunneling according to eq 17.

The single potassium acetate molecule has protons in the methyl group only. The temperature dependencies of T_1 cannot be interpreted in terms of the C_3 classical motion of the methyl group (Figure 6a). The weak frequency dependence of T_1 versus

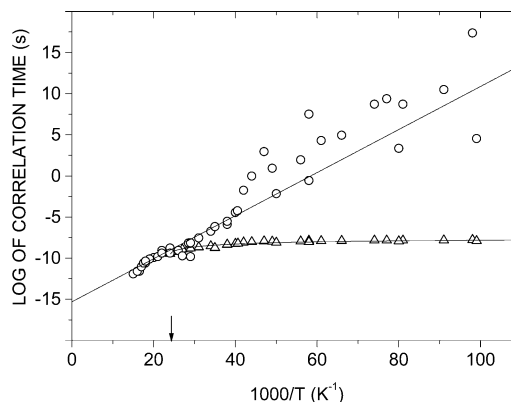
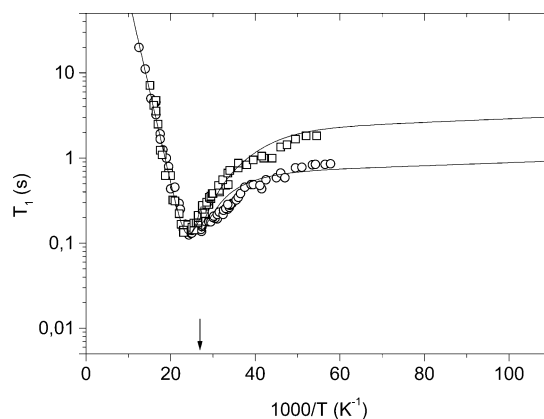
TABLE 1: Molar Specific Heat and Motional Parameters Obtained from the T_1 Measurements of Authors^{16,18} and the Theory Presented in This Paper

compound (experiment)	CH ₃ COOK ¹⁶	CH ₃ COOK ¹⁸
C_p (J/K/mol)	121.5 ± 10	114 ± 10
$[\tau_0^{(H)}]_{v0}$ (10^{-15} s)	0.5 ± 1	2 ± 1
$[\tau_0^{(T)}]_{v0}$ (10^{-10} s)	3 ± 1	3 ± 1
$B(\sqrt{J})^{-1}$	0.08 ± 0.02	0.08 ± 0.02
E_H (kJ/mol)	5.0 ± 0.5	4.2 ± 0.5
ω_T^0 (2π MHz)	400 ± 50	350 ± 50

$1000/T$ indicates that only the $(1/T_1)_{AE}$ term governs the proton relaxation process in the CH₃COOK molecule and the observed T_1 temperature dependence corresponds to the resonance frequency approximately equal to ω_T ($\omega_T \approx (\omega_T \pm \omega_1) \approx (\omega_T \pm 2\omega_1)$) which points to $\omega_T \gg \omega_1$. The best fit of eqs 31 and 56 to the experimental data is shown in Figure 6b. The fitting parameters ($\tau_0^{(H)}$)_{v0}, ($\tau_0^{(T)}$)_{v0}, E_H , C_p , B , and ω_T^0 are listed in Table 1. The value of the proton–proton distance in the methyl group and the angle of the R_{is} jump were taken from the literature ($R_{is} = 1.78$ Å and $\Theta_3^{is} = 120^\circ$). In the high-temperature range, the only one mechanism is the classical motion leading to the spin–lattice relaxation. The left side slope of the T_1 minimum in Figure 6b determines the activation energy (E_H) (Table 1). Therefore, the other estimated values are $T_{\text{tun}} = 41$ K and $C_p = 121.5$ J/K/mol. The arrow in Figure 6b shows the temperature T_{tun} . Above the temperature $T_{\text{tun}} = 41.4$ K ($1000/T \approx 24.2$ K⁻¹), only the correlation time ($\tau_c^{(H)}$)_{v0}, corresponding to the activation energy (E_H), affects the value of T_1 . Below the temperature T_{tun} , the dominant mechanism of the relaxation is rotational tunneling. The special character of the temperature dependence of ($\tau_c^{(T)}$)_{v0} causes the change in the low-temperature slope of T_1 . This change reflects the increase of the probability of tunneling motion before reaching the temperature T_{tun} . The molar specific heat equals 119.3 J/K/mol⁴¹ or 109.4 J/K/mol according to ref 42. The agreement between the molar specific heat of CH₃COOK obtained from the T_1 temperature dependence and this value published in the literature is very good. The value of B equals $0.08(\sqrt{J})^{-1}$. This value is about 4 times lower than that estimated from eq 19 for the rectangular barrier at the width $L = 1.78$ Å. This result seems to be a reasonable average value for the Maxwell distribution of the kinetic energy of the particles.

No differences between the theoretical plots $1/T_1 = n_{v0}(1/T_1)_{v0}$ and $1/T_1 = n_{v0}(1/T_1)_{v0} + n_{v1}(1/T_1)_{v1}$ have been observed. This fact can be interpreted as being due to either a small population of molecules at the first excited vibration level or a high rate $(1/\tau_c^{(T)})_{v1}$ relative to the $(n\omega_1 \pm \omega_1^{\pm})$ frequencies considered. The population of molecules at the first excited vibration level at low temperatures is very small, for example, at $1000/T = 30$ K⁻¹, $n_{v1} = 0.044n_{v0}$. Therefore, the motion of molecules in the ground-state torsional level plays a dominant role in the proton relaxation process of the methyl group below the temperature T_{tun} .

The experimental and theoretical temperature dependencies of the correlation times are presented in Figure 7. These plots differ from the Arrhenius diagrams, usually presented in the literature, showing the temperature dependence of a single correlation time (eq 1). The correlation time ($\tau_c^{(T)}$)_{v0} (eq 17) exists up to the characteristic temperature T_{tun} , which is shown by the arrow. Just below T_{tun} , ($\tau_c^{(T)}$)_{v0} undergoes shortening which reflects the process of the increase of the probability of tunneling. This shortening is less visible on the logarithmic scale in Figure 7.

**Figure 7.** Proton correlation times ($\tau_c^{(H)}$)_{v0} (circles) and ($\tau_c^{(T)}$)_{v0} (triangles) of CH₃COOK as a function of $1000/T$ (K⁻¹). The points and lines refer to the experimental and theoretical correlation times, respectively. The motional parameters used in the calculations are taken from Table 1. The arrow shows the temperature $T_{\text{tun}} = E_H/C_p$ (41 K).**Figure 8.** Experimental points of proton $1/T_1$ for CH₃COOK (15 and 30 MHz) obtained by the authors¹⁸ marked by circles and squares, respectively. The theoretical curves of the best fit (the solid lines) were calculated using (eqs 30–34) together with eq 56. The best-fit parameter is $X_2 = 0.01$, and the others are listed in Table 1. The arrow shows the temperature $T_{\text{tun}} = E_H/C_p$ (37 K).

In contrast to the experimental results obtained by Koksal et al.,¹⁶ the data reported by Montjoie et al.¹⁸ show a clear frequency dependence on the low-temperature side of the $1/T_1$ ($1000/T$) maximum. These differences in the results of measurements of T_1 for the same material can be explained in light of the presented theory.

The frequency dependence of $1/T_1$ versus $1000/T$ at low temperatures for the CH₃COOK molecule obtained by Montjoie et al.¹⁸ (circles, 15 MHz; triangles, –30 MHz in Figure 8) has to be due to the $(1/T_1)_{EE}$ contribution to the spin–lattice relaxation. The CH₃COOK molecule does not have more protons than those in the methyl group; therefore, if such frequency dependence is observed, it has to originate from the intermolecular dipole–dipole interactions. The intermolecular interactions seem to be those between CH₃COOK and the protonated impurity (i.e., H₂O or CH₃COOH). The exact calculations of $(1/T_1)_{EE}$ (eq 30) are impossible in the case considered; therefore, eqs 28 and 56 with $R_{is} = 1.78$ Å and the X_2 factor as the best-fit parameter (as is described in the comment below eq 56) have been substituted into eq 32. The X_2 value obtained from this fit is small, 0.01. It can indicate that either the number of the s spins at a reasonable distance from spin i belonging to the CH₃COOK molecule is low or that the distances in these spin pairs are much greater than the proton–proton distance in the methyl group ($R_{is} = 1.78$ Å).

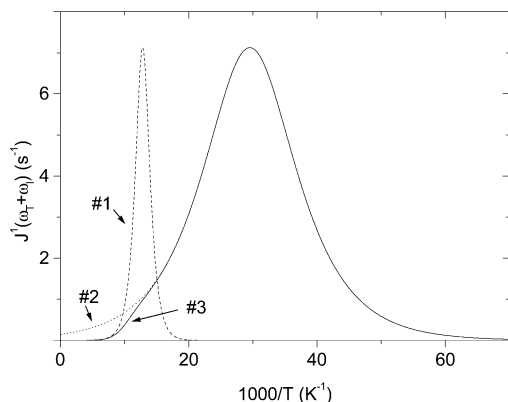


Figure 9. Temperature dependencies of the spectral densities $J^1(\omega_T + \omega_l)$ according to eqs 60 and 1, solid line #3; spectral density of classical motion (eqs 58 and 2), dashed line #1; and spectral density of tunneling (eq 59 and 20), dotted line #2. $\omega_l = 2\pi \times 30$ MHz, $\omega_T = 2\pi \times 10$ MHz, $\tau_c^{(H)} = 10^{-14}$ s, $\tau_0^{(T)} = 4 \times 10^{-11}$ s, $E_H = 8.4$ kJ/mol, $E_T = 1.3$ kJ/mol, $R_{is} = 1.78$ Å, and $\Theta_3^{is} = 120^\circ$.

Therefore, it can be concluded that a different-from-zero value of $(1/T_1)_{EE}$ testifies to the presence of an impurity with proton-containing molecules in the sample. Thus, the differences in the results of measurements of T_1 presented in Figures 6 and 8 are due to the different purities of the material studied. The contribution of $(1/T_1)_{EE}$ would not occur for the CH_3COOK substance free from impurities.

6. Other Models of the Correlation Function and Spectral Density

The equation for the spectral density of the R_{is} vector that undergoes single classical motion is well established in terms of time dependent perturbation theory

$$J_{is}^m(\omega) = S_m C_2^{is} \frac{2\tau_c^{(H)}}{1 + (\omega\tau_c^{(H)})^2} \quad (60)$$

The value of C_2^{is} depends on the model of motion. $C_2^{is} = (d_2^{is})^2$ for isotropic motion, and it equals $(d_2^{is})^2 \sin^2 \Theta_3^{is}$ for the C_3 reorientation in the triple equivalent potential (as this is written in eq 58). Also, $C_2^{is} = (d_2^{is})^2 0.75 \sin^2 \Theta_{AB}^{is}$ for jumps in double potential between equal potential minima A and B. The constant value of the R_{is} vector is assumed in eq 60 for C_2^{is} (which is not generally true for the R_{is} distance between a moving spin and a spin which does not participate in motion).

In a number of papers,^{9–24} the total correlation time (τ_c^{total}) (eq 1), representing the classical motion and rotational tunneling, has been used instead of τ_c^H in eq 60. In these papers, it is assumed that the spectral density of classical and tunneling jumps contribute to spin–lattice relaxation at high and low temperatures, respectively, and that the classical motion evolves smoothly from the tunneling motion over an intermediate temperature region.

Exemplary temperature dependence of spectral density for the C_3 rotation according to eq 60 (where $\tau_c^{(H)} = \tau_c^{\text{total}}$) is given in Figure 9 by solid line #3. Dashed lines #1 and #2 represent the spectral densities of the classical motion (eqs 58 and 2) and the motion related to tunneling (eqs 59 and 20), respectively. In the high-temperature region, solid line #3 does not follow dashed line #1, which represents the spectral density of the classical motion. Also, it is impossible to estimate from Figure 9 the intermediate temperature regime where classical motion

smoothly evolves to tunneling motion. Therefore, this approach to the spectral density seems unconvincing.

Conclusions

The equations are derived for the autocorrelation functions of the random functions of the dipolar Hamiltonian and for its spectral densities for three independent stochastic motions, that is, classical jumps over the potential barrier (correlation time $\tau_c^{(H)}$, Arrhenius formula) and tunneling jumps through the potential barrier (correlation time $\tau_c^{(T)}$, Schrödinger formula). The calculations carried out on the basis of these equations lead to the following conclusions:

- (1) The correlation functions related to the rotational tunneling equals zero at high temperatures at which $C_p T > E_H$, where C_p is the molar specific heat and E_H is the molar potential barrier.
- (2) Classical hopping between three equilibrium sites and the linear relation $\ln[(\tau_c^{(H)})_{\omega_0}]$ versus $1000/T$ can be detected even at very low temperatures, when low enough resonance frequencies are applied for T_1 measurement.
- (3) A small amount of water impurity in a sample generates the $(1/T_1)_{EE}$ contribution to the proton relaxation rate $(1/T_1)$ of the CH_3COOK molecule and changes the character of the temperature dependence of $1/T_1$.

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