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NUCLEAR SPIN – LATTICE RELAXATION AND COMPLEX MOTION OF MACROMOLECULES IN SOLUTION

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ABSTRACT

The NMR spectral densities of a complex motion consisting of combination of anisotropic overall motion and internal motion have been derived. Two approximations of the equations derived for the cases of slow, $J_{slow}(\omega)$, and fast, $J_{fast}(\omega)$, internal motions are presented. These equations imply that reduction in spectral density of overall motion can be observed if the maxima of internal and overall motions spectral densities versus temperature are well separated, so for the fast internal motion. Slow intramolecular motion influences the values of spectral densities of the overall motion if one of the two spins performs a motion as for example a proton in double minimum of the ^{15}N -H.....N hydrogen bond. The analysis presented reveals small differences between the temperature dependencies of spectral densities of the isotropic and anisotropic overall motions. The theory is illustrated by the ^{13}C protonated carbon spin-lattice relaxation of α -cyclodextrin macromolecule, using the expected motional parameters: $D_{||}/D_{\perp} \approx 5$ at room temperature and for a fast or slow internal motion.

1. Introduction

NMR spin-lattice relaxation processes are usually governed by stochastic molecular motions, which modulate the interaction Hamiltonian. For a dipolar nuclei ($I = 1/2$) the interaction Hamiltonian describes the interaction between two spins, a distance R_{is} apart. The stochastic motion causes random changes in the magnitude and orientation of the internuclear vector R_{is} . If a molecular motion of R_{is} consists of two or more constituent motions, it is referred to as a complex motion. The theory of nuclear spin-lattice relaxation in the solid state upon the complex motion consisting of combination of two site and three site jumps in symmetric and asymmetric local environment has been presented in Reference 1. The purpose of the present paper is to analyse the derived expressions of spectral density for complex motion consisting of combination of anisotropic overall motion and internal motion. The approximations for the case of spectral densities of slow, $J_{slow}(\omega)$, and fast, $J_{fast}(\omega)$, internal motions are analysed. Such a complex motion is realized in the liquid state where the internal motion is masked by the global motion of molecule (overall motion). The internal motion can be jumps in double and triple potential (hindered rotation) as well as diffusional in the character axial rotation. The spectral density of a complex motion of fast internal motion accompanying the isotropic overall motion is well known from the Lipari and Szabo “model - free approach” [2,3].

This paper proves that the reduction in the spectral density of the overall motion is observed if the maxima of the internal motion and the overall motion spectral densities versus temperature are well separated, so for the fast internal motion only. The expressions for the spectral densities of complex motion are identical for the slow internal motion or no slow internal motion.

The analysis presented in this paper reveals also small differences between the temperature dependencies of spectral density of complex motion for isotropic and anisotropic overall motions.

2. Correlation and spectral density functions

The NMR relaxation of protonated ^{13}C or ^{15}N is usually caused by dipole – dipole interaction with the directly bonded proton spins. The experimental transverse and longitudinal relaxation rates and NOE's can be expressed in terms of the spectral density functions which are the single-sided Fourier transform of the time dependent autocorrelation functions $G(\tau)$ of the random functions $F^m(t)$ in the perturbation dipolar Hamiltonian [4]. $G(\tau) = \langle F^m(t) F^{m*}(t+\tau) \rangle$ is designed a correlation function of a stationary random process; since the correlation function $G(\tau)$ is independent of the reference time “t” and is both a real and even function of τ . $G(\tau)$ then describes the time scale for decay of inherent motional order in the system. $G(\tau)$ decays toward zero. Information on the dynamical processes is dependent on the existence of $G(\tau)$. Fourier transformation achieves the transition between time and frequency domains. In this way the frequency spectrum of the molecular motions $J(\omega)$ is obtained from the autocorrelation functions $\langle F^m(t) F^{m*}(t+\tau) \rangle$. The imaginary part of the spectral density, commonly associated with a "dynamic" frequency shift, generally has been considered negligible [5]. The Fourier transform of the autocorrelation function is

$$J^m(\omega) = \int_{-\infty}^{\infty} \langle F^m(t) F^{m*}(t+\tau) \rangle \exp(-i\omega\tau) d\tau \quad (1)$$

where $m = 0, 1, 2$ and

$$F^0(t) = d_{is}(t)[3\cos^2\vartheta(t) - 1], \quad (2a)$$

$$F^1(t) = d_{is}(t)\sin\vartheta(t)\cos\vartheta(t)\exp[i\varphi(t)], \quad (2b)$$

$$F^2(t) = d_{is}(t) \sin^2 \vartheta(t) \exp[i2\varphi(t)]. \quad (2c)$$

The dipolar coupling constant $d_{is}(t)$ in Equations (2a) to (2c) is $\gamma_i \gamma_s \hbar R_{is}^{-3}(t)$. The symbol R_{is} is the distance between spins (i) and (s); $\vartheta(t)$ and $\varphi(t)$ 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 . Thermal motion in the physical system makes the values R_{is} , ϑ and φ time dependent. For the models of the jumps between two or three equilibrium sites, the function $F^m(t)$ takes discrete values $F^m(1)$, $F^m(2)$, $F^m(3)$. Thus the autocorrelation function in Equation (1) can be replaced by a sum of four or nine terms according to the definition equation [6].

$$\langle F^m(t) F^{m*}(t + \tau) \rangle = \sum_{\Omega} \sum_{\Omega_0} \langle F^m(\Omega_0) F^{m*}(\Omega) \rangle P(\Omega, \tau | \Omega_0, 0) P(\Omega_0) \quad (3)$$

where Ω stands for the state (1), (2) or (3) at time τ and Ω_0 stands for (1), (2) or (3) at $t = 0$.

$P(\Omega, \tau | \Omega_0, 0)$ is the conditional probability of finding R_{is} in the state Ω at time τ , after being in the state Ω_0 at time $t = 0$ and $P(\Omega_0)$ is the probability of finding the R_{is} in the state Ω_0 at time $t = 0$.

Correlation functions for the model two non-equivalent - (1), (2) and three equivalent - (1), (2), (3) sites jumps equals [1, 7 – 15]

$$\begin{aligned} \langle F^m(t) F^{m*}(t + \tau) \rangle = & \frac{a}{(a+1)^2} \{ a \langle F^m(1) F^{m*}(1) \rangle + \frac{1}{a} \langle F^m(2) F^{m*}(2) \rangle + 2 \langle F^m(1) F^{m*}(2) \rangle + \\ & [\langle F^m(1) F^{m*}(1) \rangle + \langle F^m(2) F^{m*}(2) \rangle - 2 \langle F^m(1) F^{m*}(2) \rangle] \exp(-\frac{|\tau|}{\tau_{(2)}}) \} \end{aligned} \quad (4)$$

$$\begin{aligned}
\langle F^m(t)F^{m*}(t+\tau) \rangle = & \frac{1}{9} \{ \langle F^m(1)F^{m*}(1) \rangle + \langle F^m(2)F^{m*}(2) \rangle + \langle F^m(3)F^{m*}(3) \rangle + \\
& 2 \langle F^m(1)F^{m*}(2) \rangle + 2 \langle F^m(1)F^{m*}(3) \rangle + \langle F^m(2)F^{m*}(3) \rangle + \\
& 2 [\langle F^m(1)F^{m*}(1) \rangle + \langle F^m(2)F^{m*}(2) \rangle + \langle F^m(3)F^{m*}(3) \rangle - \\
& \langle F^m(1)F^{m*}(2) \rangle - \langle F^m(1)F^{m*}(3) \rangle - \langle F^m(2)F^{m*}(3) \rangle] \exp(-\frac{|\tau|}{\tau_{(3)}}) \}
\end{aligned} \tag{5}$$

where $\tau_{(n)}$ ($n = 2, 3$) are the correlation times of given reorientation

$$a = \frac{p_{(1)}}{p_{(2)}} = \frac{K_{12}}{K_{21}} = \exp(\Delta E / RT) \tag{6}$$

The ΔE is the energy difference between the potential minima at these sites (when $\Delta E = 0$ then $a = 1$), K_{12} and K_{21} are equilibrium constants, $p_{(1)}$ and $p_{(2)}$ are the fractions of molecules at (1) and (2) sites ($p_{(1)} + p_{(2)} = 1$).

The correlation functions (Equations (4) and (5)) do not vanish in infinity but converge to a non-zero constant. Therefore, their Fourier transforms are divergent unless the distribution theory is invoked, then the Fourier transform of a constant is Dirac's delta function.

The isotropic ensemble averages (powdered solids or liquids) of the random function products are necessary for further calculations of correlation functions:

$$\langle F^m(X)F^{m*}(Y) \rangle = K^m d_{is}(X) d_{is}(Y) P_2(\cos \Theta_{XY}) \tag{7}$$

where $X = (1), (2), (3)$, $Y = (1), (2), (3)$, K^m equals $4/5, 2/15, 8/15$ for $m = 0, 1, 2$ respectively,

$P_2(\cos \Theta_{XY}) = \frac{1}{2}(3\cos^2 \Theta_{XY} - 1)$ denotes the Legendre polynomial for the angle Θ_{XY} . Θ_{XY} is the

angle between the $\mathbf{R}_{is}$ vectors at the separate equilibrium sites.

$J(\omega)$ is a maximum at $\omega = 0$, is approximately constant over the range of correlation time $\tau_{2(3)}$, and falls off with increasing frequency as $\omega \rightarrow 1/\tau_{2(3)}$.

2.1 Internal motion, C_n

Literature provides several experimental and theoretical reports on molecular reorientations described in terms of stochastic jumps between potential minima (equilibrium sites) separated by potential energy barriers [1, 7 – 26]. The time required for a jump is considered negligible when compared with the residence time at each equilibrium position. Thus, at any time molecules are distributed between equilibrium sites and their constant fraction can be found at n sites where $n = 1, 2, 3, \dots$. For asymmetric local environments (inequivalent potential minima), some positions are metastable and thus characterised with shorter residence times and higher values of potential minima. In these models of molecular reorientation one considers hopping between two ($n = 2$) or three ($n = 3$) equal or unequal potential energy minima (Fig 1). Such a reorientation model was applied to study hindered rotation of a molecular group (for example CH_3 or NH_3) [1, 10, 19, 26] or side chains in macromolecules and conformational motions (jumps between two or three conformations [10, 17, 18], butterfly-like fashion motion [25], ring puckering [22], proton transfer in a hydrogen bonded system [7, 8, 14, 15]). The probabilities of hopping over potential barrier are proportional to the barrier heights (classical hopping, Arrhenius law). Relaxation rates appear very sensitive to the change not only in the reorientation of R_{is} vector but also in its length. Simultaneous changes in the orientation and length of the R_{is} vector in the motion can take place when only one of the two spins $1/2$ involved in the dipole-dipole interaction performs a motion as in the ^{15}N -H dipole-dipole system bonded through a hydrogen bond like ex. $^{15}\text{N}\text{-H}\cdots\text{O} \leftrightarrow ^{15}\text{N}\cdots\text{H}\text{-O}$.

The correlation functions and spectral densities of hopping among two, (1) and (2), or three, (1), (2) and (3), equilibrium sites calculated from Equations (4 – 7) are

$$\langle F_{is}^m(t) F_{is}^{m*}(t+\tau) \rangle = K^m [S_{1(n)} + S_{2(n)} \exp(-\frac{|\tau|}{\tau_{(n)}})] \quad (8)$$

$$J_{is}^m(\omega) = K^m J(\omega) \quad (9)$$

and

$$J(\omega) = S_{2(n)} \frac{2\tau_{(n)}}{1 + \omega^2 \tau_{(n)}^2} \quad (10)$$

where $n = 2, 3$ and $K^m = 4/5, 2/15$ and $8/15$ for the $m = 0, 1, 2$ respectively,

The correlation time $\tau_{(n)}$ of given reorientation follows the Arrhenius temperature dependence

$$\tau_{(n)} = \tau_0^n \exp\left(\frac{E_n}{RT}\right) \quad (11)$$

and τ_0^n and E_n are the preexponential factor and the activation energy.

The $S_{1(2)}$ and $S_{2(2)}$ coefficients for a motion between two sites of unequal energy are

$$S_{1(2)} = \frac{a}{(a+1)^2} [a d_{is}^{(1)2} + \frac{1}{a} d_{is}^{(2)2} + d_{is}^{(1)} d_{is}^{(2)} (3 \cos^2 \Theta_2 - 1)] \quad (12)$$

$$S_{2(2)} = \frac{a}{(a+1)^2} [d_{is}^{(1)2} + d_{is}^{(2)2} - d_{is}^{(1)} d_{is}^{(2)} (3 \cos^2 \Theta_2 - 1)] \quad (13)$$

The symbols d_{is} (1) and d_{is} (2) stand for the dipolar coupling constant at (1) and (2) positions respectively and Θ_2 is the angle between two positions of R_{is} vector.

The $S_{1(3)}$ and $S_{2(3)}$ coefficients for the motion in which R_{is} vector does not change its length, ($d_{is}(1) = d_{is}(2) = d_{is}(3) = d_{is}$) between three sites of equal energy distanced by the Θ_3 angle (Fig 1) are

$$S_{1(3)} = d_{is}^2 \cos^2 \Theta_3 \quad (14)$$

$$S_{2(3)} = d_{is}^2 \sin^2 \Theta_3 \quad (15)$$

The single-axial rotation can be also of diffusional (small angle jumps) character [28 – 30]. The differences in the temperature dependencies of spectral densities of both types of single-axial motions – diffusional and hindered, C_3 , for the same motion parameters are very small. Therefore, Equation (8) can be applied generally for the single axial rotation of R_{is} vector.

For three inequivalent minima ($\rho_{(1)} \neq \rho_{(2)} \neq \rho_{(3)}$) the expressions for spectral densities get much complex [10, 14, 31, 32].

2.2 Anisotropic overall rotation, C_{aniso} .

A model describing the motion of a rigid symmetrical top molecule with the rotational diffusion coefficients $D_{xx} = D_{yy} = D_{\perp}$, $D_{zz} = D_{\parallel}$ has been presented by Woessner [28, 29], Huntress [33], Hubbard [34] and Canet [35]. The relaxation of rigid anisotropic molecules undergoing rotational Brownian diffusion is governed by the five exponential correlation function which is reduced to a three-exponential form for the axially symmetric top molecules:

$$\langle F_{is}^m(t) F_{is}^{m*}(t+\tau) \rangle = K^m d_{is}^2 [A \exp(-|\tau|/\tau_a) + B \exp(-|\tau|/\tau_b) + C \exp(-|\tau|/\tau_c)] \quad (16)$$

and

$$J(\omega) = d_{is}^2 \left(A \frac{2\tau_a}{1 + \omega^2 \tau_a^2} + B \frac{2\tau_b}{1 + \omega^2 \tau_b^2} + C \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right) \quad (17)$$

$$\tau_a = (6D_{\perp})^{-1} \quad (18)$$

$$\tau_b = (5D_{\perp} + D_{\parallel})^{-1} \quad (19)$$

$$\tau_c = (4D_{\perp} + 2D_{\parallel})^{-1} \quad (20)$$

$$A = \frac{1}{4} (3\cos^2 \alpha_{is} - 1)^2 \quad (21)$$

$$B = \frac{3}{4} \sin^2 (2\alpha_{is}) \quad (22)$$

$$C = \frac{3}{4} \sin^4 (\alpha_{is}) \quad (23)$$

α_{is} is the angle between the R_{is} vector and the symmetry axis of the molecule. The main values of the rotational diffusion tensor (coefficients of rotational diffusion) $D_{xx} = D_{yy} = D_{\perp}$ and $D_{zz} = D_{\parallel}$ follow the Arrhenius temperature dependence:

$$D_{\parallel} = D_{0\parallel} \exp\left(-\frac{E_{\parallel}}{RT}\right) \quad (24)$$

$$D_{\perp} = D_{0\perp} \exp\left(-\frac{E_{\perp}}{RT}\right) \quad (25)$$

where $D_{0\parallel}$ and $D_{0\perp}$ are preexponential factors, $E_{\parallel}$ and $E_{\perp}$ are activation energies.

The spectral density of anisotropic motion differs from that of isotropic motion as the character of the temperature dependence of the spectral density of C_{aniso} depends on the α_{is} angle (the angle between R_{is} and the main axis of the molecule). When overall motion is significantly anisotropic ($D_{\parallel} \gg D_{\perp}$) the corresponding higher temperature minimum of spectral density can be split into the two separate minima. Then the T_1 minimum due to the faster rotation (characterized by $D_{\parallel}$) appears at lower temperatures than that due to the slower motion (characterized by $D_{\perp}$) and this latter one is made shallower by the faster motion (this effect is similar to that caused by the fast internal motion).

Equations (24) and (25) for the rotational diffusion coefficient can differ in the pre-exponential factor and activation energies. If the activation energies for $D_{\perp}$ and $D_{\parallel}$ are the same as for example in Reference. 36, the motion anisotropy is determined by the values of the pre-exponential factors $D_{0\perp}$ and $D_{0\parallel}$. Then the temperature dependence of relaxation times for anisotropic motion has a minimum of the same value as that of the isotropic motion but a little shifted towards lower temperatures. In such a situation it seems impossible to specify whether the motion is isotropic or anisotropic.

2.3 Complex motion, $(C_{aniso} + C_n)$.

Molecules in liquids undergo a complex motion; i. e. the overall motion of the whole molecule accompanies the internal motions. The complex motion of a spin pair belonging to a methyl group jumping between three equivalent potential minima and subjected to isotropic rotational diffusion was first considered by Woessner [28 – 30] and next by Wallach [37] and also by Dellwo and Wand [26]. The expression for the spectral density of the complex motion ($C_{aniso} + C_n$) composed of the anisotropic (type symmetrical top) overall motion, C_{aniso} , and the internal motion (diffusional in character) has been derived by Woessner [30].

The fundamental claim of Woessner: “Although the two types of motion are independent, their contributions to relaxation are not. If the interaction Hamiltonian is modulated by series of independent stochastic processes, the total correlation function of a complex motion should be calculated” is the basis of the calculations of the total correlation function of complex motion. If the random functions 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:

$$F^m(t) = f_{(1)}^m(t) f_{(2)}^m(t) \quad (26)$$

$$\langle F^m(t) F^{m*}(t + \tau) \rangle = \langle f_{(1)}^m(t) f_{(1)}^{m*}(t + \tau) \rangle \langle f_{(2)}^m(t) f_{(2)}^{m*}(t + \tau) \rangle \quad (27)$$

The $F^m(t)$ random functions given in Equations (2a) to (2c) can be simply changed into the product of the two functions $f_{(1)}^m(t)$ and $f_{(2)}^m(t)$ by assuming $f_{(1)}^m(t) = F^m(t)$ and introducing the unit vector

$r(t)$ coincident with R_{is} vector, that is $r(t) = \frac{\overrightarrow{R_{is}(t)}}{|R_{is}|} = 1$. With a view to expressing the $F_m(t)$

as products of two functions $f_{(1)}^m(t)$ and $f_{(2)}^m(t)$ we write

$$f_{(1)}^0(t) = d_{is}(t)(1 - 3\cos^2 \nu(t)) \quad (28a)$$

$$f_{(2)}^0(t) = r(t) \quad (28b)$$

$$f_{(1)}^1(t) = d_{is}(t) \sin \nu(t) \cos \nu(t) \exp[i\varphi(t)] \quad (28c)$$

$$f_{(2)}^1(t) = r(t) \quad (28d)$$

$$f_{(1)}^2(t) = d_{is}(t) \sin^2 \nu(t) \exp[2i\varphi(t)] \quad (28e)$$

$$f_{(2)}^2(t) = r(t) \quad (28f)$$

The $r(t)$ value can also be time dependent if, for example, the proton pair distances change due to jumping or tunnelling along the hydrogen bond of one proton. Then the unit vector, $r(t)$, changes its length.

The correlation function and the spectral density of the complex motion ($C_{aniso} + C_n$) can be easily derived in the same way as the spectral density of ($C_{iso} + C_n$). The relevant equation is presented in paper [38].

$$\begin{aligned} \langle F_{is}^m(t) F_{is}^{m*}(t+\tau) \rangle &= K^m [S_{1(n)} + S_{2(n)} \exp(-\frac{|\tau|}{r_{(n)}})] \\ [A \exp(-|\tau|/\tau_a) + B \exp(-|\tau|/\tau_b) + C \exp(-|\tau|/\tau_c)] \end{aligned} \quad (29)$$

and

$$J(\omega) = S_{1(n)} \left(A \frac{2\tau_a}{1 + \omega^2 \tau_a^2} + B \frac{2\tau_b}{1 + \omega^2 \tau_b^2} + C \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right) + S_{2(n)} \left(A \frac{2\tau_{an}}{1 + \omega^2 \tau_{an}^2} + B \frac{2\tau_{bn}}{1 + \omega^2 \tau_{bn}^2} + C \frac{2\tau_{cn}}{1 + \omega^2 \tau_{cn}^2} \right) \quad (30)$$

When the motion is isotropic, then $\tau_a = \tau_b = \tau_c$, $A + B + C = 1$ and the spectral density given in

Equation (30) is reduced to

$$J(\omega) = S_{1(n)} \frac{2\tau_a}{1 + \omega^2 \tau_a^2} + S_{2(n)} \frac{2\tau_{an}}{1 + \omega^2 \tau_{an}^2} \quad (31)$$

where

$$\frac{1}{\tau_{an}} = \frac{1}{\tau_a} + \frac{1}{\tau(n)} \quad (32)$$

$$\frac{1}{\tau_{bn}} = \frac{1}{\tau_b} + \frac{1}{\tau(n)} \quad (33)$$

$$\frac{1}{\tau_{cn}} = \frac{1}{\tau_c} + \frac{1}{\tau(n)} \quad (34)$$

When $d_{is}(1) = d_{is}(2) = d_{is}(3) = d_{is}$ (as for the protonated carbon-13) the

$$S_{1(n)} = d_{is}^2 S^2 \text{ and } S_{2(n)} = d_{is}^2 (1 - S^2). \text{ The } S^2 = \cos^2 \Theta_3 \text{ for } n = 3 \text{ or } S^2 = \left(1 - \frac{3a \sin^2 \Theta_2}{(a+1)^2}\right) \text{ for } n = 2.$$

The well defined value of S^2 for the two site jumps and hindered rotation assumes free value 0.25

$< S^2 < 1$ in the Lipari and Szabo “model – free approach” [2, 3]. This S^2 parameter is called usually as “order parameter”.

If a R_{is} vector performs a complex motion, two T_1 minima should be observed, corresponding to the slower (overall) and faster (internal) components. The T_1 relaxation minimum corresponding to the overall motion (higher temperatures) is made shallower by internal motion and does not reflect the minimum associated with such a motion in the absence of the internal motion. Moreover this minimum can be split into two sub minima for the high anisotropy of the overall ($D_{||} \gg D_{\perp}$).

2.4 Complex motion consisting of fast or slow internal and anisotropic overall motion

Spectral density expressed by Equation (30) can be approximated for the fast and slow internal motion. For the fast internal motion ($\tau_{(n)} < \tau_a, \tau_b, \tau_c$), Equation (30) is reduced to

$$J_{fast}(\omega) = S_{1(n)} \left(A \frac{2\tau_a}{1 + \omega^2 \tau_a^2} + B \frac{2\tau_b}{1 + \omega^2 \tau_b^2} + C \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right) \quad (35)$$

We can see that the fast internal motion reduces the spectral density of the overall motion by the $S_{1(n)}$ coefficient. This coefficient describes the memory of the low-temperature fast motion.

The slow internal motion ($\tau_{(n)} > \tau_a, \tau_b, \tau_c$) influences the spectral density of overall motion only when $d_{is}(1) \neq d_{is}(2)$ which means that the interproton distance changes during motion. The length of the R_{is} vector is time dependent when only one proton undergoes proton transfer as in the ^{15}N -H dipole-dipole system bonded through a hydrogen bond.

Then Equation (30) is reduced to

$$J_{slow}(\omega) = (S_{1(2)} + S_{2(2)}) \left(A \frac{2\tau_a}{1 + \omega^2 \tau_a^2} + B \frac{2\tau_b}{1 + \omega^2 \tau_b^2} + C \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right) \quad (36)$$

where

$$S_{1(2)} + S_{2(2)} = p_{(1)} d_{is}(1)^2 + p_{(2)} d_{is}(2)^2 \quad (37)$$

When $d_{is}(1) = d_{is}(2) = d_{is}$ then $S_{1(2)} + S_{2(2)} = d_{is}^2$ also $S_{1(3)} + S_{2(3)} = d_{is}^2$ and the slow internal motion has no influence on the values of the spectral density of the overall motion. In such a case the slow internal motion and the lack of internal motion lead to the same equation (Equation (13)) expressing the spectral density for the single overall motion¹.

3. Illustrative examples

α -Cyclodextrins macromolecules in solutions

The ^{13}C relaxation rates of the ring carbon atoms at the room temperature, measured under conditions of proton decoupling, were analysed in References 39 and 40. The observed relaxation rate is almost completely dominated by the dipolar C-H interaction. The overall motion of these macromolecules was assumed to be represented by axially symmetric rotational diffusion tensor with D_x and D_y equal and denoted by $D_{\perp}$ while the distinct D_z component is denoted by $D_{\parallel}$. The internal dynamics (interconversion between conformers) was assumed either very slow or very fast in comparison to the overall molecular reorientation.

¹ The equations for the spectral density of complex motion reproduced by the model of symmetric top with fast and slow internal motion have been presented recently [39]. These equations are different than our Equations (35) and (36). The equation in Reference 39 for $J_{fast}(\omega)$ describes the spectral density of overall anisotropic motion only, while that for $J_{slow}(\omega)$ does not apply to the ^{13}C relaxation because the distance C-H is not changed during the internal motion.

To illustrate the temperature dependencies of T_1 relaxation time of ^{13}C atom obtained employing Equation (30) for the spectral densities, we chose a complex motion composed of the overall motion characterised by the isotropic correlation time ($D_{||} = D_{\perp}$) of an order of nanoseconds at room temperature [40] and an internal motion that could be either fast or slow. The fast internal motion (Fig 2a) is characterised by the correlation time of an order of picoseconds and the slow internal motion (Fig 2b) by a correlation time of an order of nanoseconds at room temperature. To facilitate a comparison of the isotropic and anisotropic (overall) motions, the value of $D_{||}$ was chosen so that at room temperature $\frac{D_{||}}{D_{\perp}} \approx 5$ and $D_{\perp} = \frac{1}{6\tau_{iso}}$, where τ_{iso} is the correlation time of isotropic motion. Such anisotropy is expected for the α -cyclodextrin overall [39].

As follows from Fig. 2a, the relaxation time T_1 shows two well separated minima in the temperature scale. The spectral density function of the fast internal motion has a maximum in low temperatures and the overall motion has a maximum in high temperatures. The T_1 time in the range of high temperatures is much longer than that expected when no internal motion would take place as the spectral density $J_{fast}(\omega)$ (Equation (35)) is reduced by a factor of $S_{1(3)}$ (Equation (14)). Also we can see in Fig 2a, in the high temperature regime, some small differences between the temperature plots for anisotropic and isotropic overall motions.

The temperature dependence of ^{13}C T_1 relaxation time for the slow internal motion is illustrated in Fig 2b. The same anisotropy of the overall motion ($\frac{D_{||}}{D_{\perp}} \approx 5$ at room temperature) as in Fig 2a was assumed. The maximum of the spectral density of the internal motion is superimposed on the maximum of the spectral density of the overall motion, which makes very small differences in T_1 dependencies for the situations with and without the internal motion. Moreover, similarly as for the fast intramolecular motion, the differences in the T_1 temperature dependencies for the isotropic and anisotropic overall motions are very small.

The correlation times applied to analyse of the fast and slow internal motions are presented in Fig. 2c.

Conclusions

The reduction in the ^{13}C spin-lattice relaxation rate of the overall motion is observed only if the maxima of the internal motion and the overall motion spectral densities versus temperature are well separated, so for the fast internal motion. The expressions for the spectral densities derived for the presence and the absence of slow internal motion are identical if the dipolar coupling constant d_{is} is constant value.

The anisotropy of the overall macromolecule motion ($D_{\parallel} / D_{\perp} \approx 5$) cannot be inferred from the ^{13}C relaxation rates because of small differences between temperature dependencies of spectral densities for the complex motion consisting of isotropic and anisotropic overall motions.

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Figure captions

Fig 1

Diagram illustrating the motion of R_{is} vector between two and three sites and the appropriate potential energy pictures.

Fig. 2

The illustration of the heteronuclear ^{13}C $T_1(\omega_s = 2\pi \times 75.43 \text{ MHz}, \omega_i = 2\pi \times 300 \text{ MHz})$ temperature dependence due to complex motion. The complex motion ($C_3 + C_{aniso}$) – solid line and ($C_3 + C_{iso}$) – open squares. The case where the internal motion is absent is represented by dashed line (anisotropic overall) and solid squares (isotropic overall). The motional parameters are: $R_{is} = 0.109$

nm, $\alpha_{is} = 70^\circ$, $\Theta_3 = 109.4^\circ$, $\tau_{iso} = 1 \cdot 10^{-16} \exp(\frac{4523}{T})$, $D_\perp = \frac{1}{6\tau_{iso}}$, $D_\parallel = 1.67 \cdot 10^{15} \exp(-\frac{1507}{T})$,

$\tau_{(3)} = 1 \cdot 10^{-14} \exp(\frac{1507}{T})$ (a, fast internal motion), $\tau_{(3)} = 1 \cdot 10^{-14} \exp(\frac{3015}{T})$ (b, slow internal

motion). The correlation times of the fast and slow internal motions and isotropic motion are illustrated in (c). The arrow indicates the room temperature.

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Fig 1

Fig 2a

Fig. 2b

Fig. 2c