Nuclear Magnetic Relaxation in the Presence of Quadrupole Nuclei

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Nuclear magnetic relaxation formulae are given for dipolar nuclei interacting with quadrupolar nuclei. The following cases are distinguished: High- and low-field case with respect to the quadrupole energy levels and, on the other hand, quasi rigid lattices and tumbling lattices with respect to molecular motions.

As examples of these cases, the proton T_1-dispersion of polyvinylchloride (quasi rigid lattice) and of protein solutions (tumbling lattice) are discussed and compared with theory. It is shown that the influence of the interaction with quadrupole nuclei is normally not negligible.

PVC shows a quadrupolar dip below room temperature as an especially remarkable consequence of the interaction with chlorine. An oscillator model is discussed in order to explain the molecular motion at low temperatures.

Proteins contain imino-groups acting as relaxation centers and mediating the contact to the aqueous solvent via hydrogen bonds. These relaxation centers can explain the low absolute values of the longitudinal relaxation times in protein solutions. Furthermore, several effects in such systems, reported previously, can easily be interpreted on the basis of the presented formalism.

1. Introduction

The energy levels of quadrupole nuclei are often much stronglier perturbed than pure dipole nuclei. This is due to the fact that the perturbing fields, "seen" by the quadrupole nuclei, are either the total externally applied magnetic field (in the so-called low-field case) or the electric field gradient (in the high-field case). These fields are more effective by orders of magnitude than, for instance, the dipolar fields arising from neighbouring dipole nuclei. Therefore, quadrupole nuclei normally relax extremely fast. In mixed systems of quadrupole and pure dipole nuclei an exchange of Zeeman energy from the pure dipole to the quadrupole subsystems can occur, leading to severe effects on the relaxation behaviour of the pure dipole nuclei [1, 2].

It is well known that the relaxation rates of pure dipole nuclei can be enhanced by the interaction with quadrupole nuclei. A discussion concerning systems describable with spin temperatures can be found in Reference [3]. Nevertheless, no practicable theoretical approach has been developed so far. In this paper, a description of various cases of the relaxation enhancement of pure dipole nuclei by quadrupole nuclei will be discussed. The consequences on the frequency and temperature dependence of the relaxation times will be described.

2. Theory

We consider an ensemble consisting of pure dipole nuclei (spin $I=1/2$) and quadrupole nuclei (spin $S \geqq 1$). In most cases the I-spins will be relaxed by the dipolar interaction to surrounding nuclear dipoles. The S-spins, however, are exposed to additional interactions causing a more effective relaxation mechanism. The relevant field for this mechanism is either the external magnetic field or the electric field gradients within the molecules. Both fields are principally able to cause splittings of the energy levels of the quadrupole nucleus. The field, being less effective in this sense, can be considered as perturbation to the other one. In any case, a perturbation of this type will be orders of magnitude stronger than the dipolar interaction. Thus, the S-spins are usually relaxed so fast that they practically stay in equilibrium during any relaxation experiment performed with the I-spins. Thus, the system can be described by simple Bloch equations instead of a system of equations [4].

$$\mathrm{d}\langle I_z\rangle/\mathrm{d}t = -(1/T_1)\,(\langle I_z\rangle - I_0)\,, \qquad (1\,\mathrm{a})$$

$$\mathrm{d}\langle I_x\rangle/\mathrm{d}t = -\langle I_x\rangle/T_2\,. \qquad (1\,\mathrm{b})$$

In other words, we can expect exponential relaxation curves, except for solids where Eq. (1 b) is invalid.

In the following we shall use relaxation formulae which are only valid within some general restrictions. The usual method is to sum up the contributions of all spin-pairs. It is assumed that these spin-

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pairs move uncorrelatedly[5]. This condition is, however, not very stringent as shown in Reference[6]. The transverse relaxation times T_2 are only defined in the motional narrowing case. So all relaxation formulae for T_2 given below are only valid in the absence of any secular dipolar broadening. Furthermore, it is assumed that the quantum effects of the lattice play no essential role, i. e. the formulae are valid only at temperatures well above zero.

Below we shall distinguish between "isotropic" and "anisotropic" molecular motions. This distinction concerns a time scale of the order of the relaxation times of the I-spins. Thus, an anisotropic motion is assumed when a spin-spin vector does not reach a certain range of the space angle in this time scale, relevant for the relaxation process. Whether a motion is considered to be anisotropic or not therefore depends on the speed of the diverse components of the total motion. A quite obvious example for anisotropic motions are polymers in the solid state, while polymer melts often show isotropic behaviour according to the special definition given above. The latter case implies that the averages of the spatial functions $F^{(i)}$, defined below, vanish. It should be mentioned that Solomon's perturbation theoretical T_1-theory (4) is principally not restricted to isotropic motions. Merely some slight modifications will be necessary.

In the subsequent treatment we have to deal with the quite unusual fact of fluctuating resonance frequencies ω_S. The question arises how to define the unperturbed Hamiltonian and the perturbation of an I-S pair. We'll discuss this problem by introducing an average "**a**" to be taken over all interaction states reached within the mean life-time of the I-spins, i. e. during the relaxation times:

$$\hbar H = \hbar \langle H_0 \rangle_a + \hbar H_1 .$$

In the limits of very slow ("quasi-rigid lattice") and very fast ("tumbling lattice") over-all-motions of the molecules these averages can be evaluated.

Furthermore we will apply an average "**b**" in the following formulae concerning any heterogeneity of the system with respect to molecular orientation, isotopical effects, electric field gradients and resonance transitions. It should be noted, that this average is only allowed for rapid material or spin-diffusional exchange between the diverse subsystems compared with the relaxation times. Otherwise one would expect nonexponential total relaxation curves composed of the relaxation curves of the individual subsystems[7].

The total rates $1/T_1$ and $1/T_2$ in Eq. (1) are composed of two parts originating from "homo" and "hetero" interactions

$$1/T_{1,2} = 1/T_{1,2}^{\mathrm{l}} + 1/T_{1,2}^{\mathrm{u}} \tag{2}$$

provided that rapid material and/or spin-diffusional exchange occurs throughout the system. $1/T_{1,2}^{\mathrm{l}}$ are the rates the I-spins experience by dipolar interaction with other I-spins, $1/T_{1,2}^{\mathrm{u}}$ are the rates caused by dipolar interaction with the S-spins. (Scalar interaction via indirect coupling is negligible under normal conditions.) For the interaction with like spins $I = 1/2$ it holds then

$$1/T_1{}^{\mathrm{l}} = \langle \tfrac{9}{8} \gamma_{\mathrm{I}}{}^4 \hbar^2 \sum_{\text{pairs}} \{ L^{(1)} \tilde{J}(\omega_{\mathrm{I}}) + L^{(2)} \tilde{J}(2\,\omega_{\mathrm{I}}) \} \rangle_{\mathrm{b}} \tag{3 a}$$

and

$$1/T_2{}^{\mathrm{l}} = \langle \tfrac{9}{32} \gamma_{\mathrm{I}}{}^4 \hbar^2 \sum_{\text{pairs}} \{ L^{(0)} \tilde{J}(0) + 10\,L^{(1)} \tilde{J}(\omega_{\mathrm{I}}) + L^{(2)} \tilde{J}(2\,\omega_{\mathrm{I}}) \} \rangle_{\mathrm{b}} \tag{3 b}$$

with the squared interaction amplitudes

$$L^{(i)} = \langle |F^{(i)}|^2 \rangle_{\mathrm{a}} - |\langle F^{(i)} \rangle_{\mathrm{a}}|^2 \quad (i = 0, 1, 2) .$$

The $F^{(i)}$ are more or less random functions of the relative positions

$$\begin{aligned} F^{(0)} &= (1 - 3\cos^2\Theta)/r^3 , \\ F^{(1)} &= (\sin\Theta \cos\Theta\, e^{-i\Phi})/r^3 , \\ F^{(2)} &= (\sin^2\Theta\, e^{-2i\Phi})/r^3 \end{aligned} \tag{3 c}$$

(r, Φ, Θ are spherical co-ordinates of the spin-spin-vector).

The averages "**a**" have to be taken over all interaction states reached within a period of the order of the relaxation times of the I-spins. The average "**b**" concerns possibly heterogeneous samples, for instance powders of microcrystallites, each of them underlying anisotropic molecular motions. The functions $L^{(i)}$ are given in Ref.[4] for isotropic motions, where $\langle F^{(i)} \rangle_{\mathrm{a}}$ vanishes. For Poisson processes we can write for the intensity functions

$$\tilde{J}(\omega) = 2\,\tau_c/(1 + \omega^2 \tau_c{}^2) . \tag{4}$$

The relaxation rates caused by unlike spins $S \geqq 1$ require some further discussion, which we shall divide into several special cases.

2.1. High-field Case

The high-field case is defined by the following condition for the splittings in the magnetic field and in the pure electric field gradient

$$\hbar\,\omega_S{}^{\mathrm{Z}} \gg \hbar\,\omega_S{}^{\mathrm{Q}}$$

($\omega_S{}^Z$ and $\omega_S{}^Q$ are the Larmor-frequencies of the S-spins to be expected in pure magnetic fields and pure electric field gradients, respectively). This case is simplified by the fact that both types of spins orient along the magnetic field.

Thus we have to modify the well known relaxation formulae for unlike spins (4) only slightly:

$$\frac{1}{T_1{}^{\mathrm{u}}} = \langle \gamma_I{}^2 \gamma_S{}^2 \hbar^2 S(S+1) \sum_{\text{pairs}} \{ \tfrac{1}{12} L^{(0)} \tilde{J}(\omega_I - \langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{2} L^{(1)} \tilde{J}(\omega_I) + \tfrac{3}{4} L^{(2)} \tilde{J}(\omega_I + \langle \omega_S \rangle_{\mathrm{a}}) \} \rangle_{\mathrm{b}} \tag{5 a}$$

and

$$\frac{1}{T_2{}^{\mathrm{u}}} = \langle \gamma_I{}^2 \gamma_S{}^2 \hbar^2 S(S+1) \sum_{\text{pairs}} \{ \tfrac{1}{6} L^{(0)} \tilde{J}(0) + \tfrac{1}{24} L^{(0)} \tilde{J}(\omega_I - \langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{4} L^{(1)} \tilde{J}(\omega_I) + \tfrac{3}{2} L^{(1)} \tilde{J}(\langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{8} L^{(2)} \tilde{J}(\omega_I + \langle \omega_S \rangle_{\mathrm{a}}) \} \rangle_{\mathrm{b}} . \tag{5 b}$$

The functions $L^{(i)}$ are the same as in Equation (3). In contrast to the relaxation by like spins the spin flip fluctuation of an interaction partner, namely the S-spins, can determine itself the intensity function in some very, special cases (Compare e. g. References [8, 9]).

Equations (5) contain two averages which have to be explained. At first we have to deal with the fact that the set of high-field resonance frequencies of the S-spins ω_S depend on the angle ε of the relative orientation of the magnetic field and the electric field gradient as given in Ref. [5], p. 233, i. e. these frequencies are time dependent due to molecular motion. Thus we have to take the average of the set of transition frequencies ω_S over a period of the order of the relaxation times of the I-spins. We indicate this average by an index "a". In the case of anisotropic motions a distribution of molecular orientations could lead to a distribution of subsystems with different relaxation times. Assuming rapid material or spin-diffusional exchange between all subsystems allows to perform the average "**b**" for the resultant relaxation rates. An example could be the powder average necessary with poly-crystalline or amorphous material. Furthermore, the average "b" includes the different resonance frequencies ω_S according to the magnetic quantum numbers (Ref. [5], p. 233). In the case of isotopical and electric field gradient distributions the average "**b**" includes all different quadrupole transition frequencies resulting thereof in addition.

For rapid isotropic motion compared with the relaxation times we can write

$$\langle \omega_S \rangle_{\mathrm{a}} \approx \omega_S{}^Z = \gamma_S B_0$$

and omit the average "**b**", provided that all molecular orientations are reached with the same probability within the relaxation times and there is only one species of isotopes.

The high-field formulae thus depend on two Larmor frequencies ω_I and $\omega_S{}^Z$ which both depend linearly on the external magnetic field. Therefore we expect no peculiar effect in the field-dependence of the relaxation times in contrast to the following case.

2.2. Low-field Case

The situation becomes more complicated in the low-field case, defined by

$$\hbar\, \omega_S{}^Z \ll \hbar\, \omega_S{}^Q .$$

Here we have to deal with the fact that the I-spins orient along the magnetic field, while the S-spins are directed along the electric field gradient, i. e. a generally different direction. This means that the usual analysis of the dipolar Hamiltonian [10] has to be modified.

2.2.1. *Dipolar Hamiltonian:*

The dipolar Hamiltonian is given by

$$\hbar\, H_1 = \frac{\hbar^2 \gamma_I \gamma_S}{r_{IS}^3} \left\{ \boldsymbol{I} \cdot \boldsymbol{S} - 3\, \frac{(\boldsymbol{I} \cdot \boldsymbol{r}_{IS})(\boldsymbol{S} \cdot \boldsymbol{r}_{IS})}{r_{IS}^2} \right\} . \tag{6}$$

In order to analyze the scalar products into expressions containing the operators $I^{\pm}$ and $S^{\pm}$ we introduce two systems of reference as shown in Figure 1. The z-axis of the I-system is directed along the external magnetic field, and the spin-spin vector $\boldsymbol{r}_{IS}$ is given in this system by the spherical co-ordinates r_{IS}, Φ_I, Θ_I. The S-spins are oriented along the symmetry axis of the electric field gradient (FGT-axis), which acts therefore as the Z'-axis of the S-system. The spherical co-ordinates of $\boldsymbol{r}_{IS}$ in this

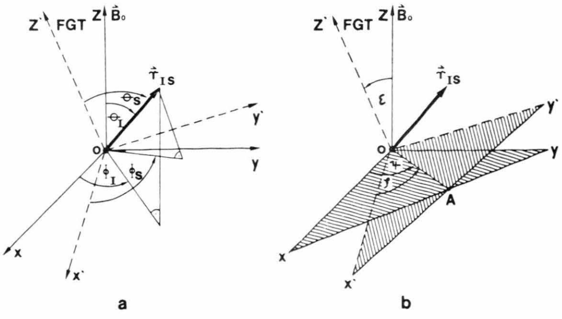

Fig. 1. a) Spherical co-ordinates of the distance vector $\boldsymbol{r}_{IS}$ in both systems of reference; b) Eulerian angles for Equation [9].

system are r_{IS}, Φ_S, Θ_S. Notice that the S-system is fixed to the molecule containing the S-spin and producing the electric field-gradient. Thus, we have to consider the motion of this frame of reference with respect to the laboratory system (I-system). The spatial orientation of the molecular system can be defined by the Eulerian angles ε, ψ, ξ (Fig. 1), allowing to transform cartesian co-ordinates between both systems[11].

Our aim is now to achieve an expression for the dipolar Hamiltonian in the form

$$\hbar H_1 = \hbar^2 \gamma_I \gamma_S \sum_{i,j=-1}^{1} A_{ij} \tag{7}$$

where $A_{ij} = E^{(i,j)} O^{(i,j)}$.

The functions $E^{(i,j)}$ concern the spatial parts while the spin operators, causing the transitions, are abbreviated by the quantities $O^{(i,j)}$.

Equation (6) can be written in the more appropriate form

$$\begin{aligned}\hbar H_1 = \hbar^2 \gamma_I \gamma_S \frac{1}{r_{IS}^3} [\mathbf{I} \cdot \mathbf{S} - 3 \{ I_z \cos \Theta_I + \tfrac{1}{2} \sin \Theta_I \\ \cdot (I^+ \exp\{-i \Phi_I\} + I^- \exp\{i \Phi_I\})\} \\ \cdot \{ S_{z'} \cos \Theta_S + \tfrac{1}{2} \sin \Theta_S \\ \cdot (S^+ \exp\{-i \Phi_S\} + S^- \exp\{i \Phi_S\})\}] .\end{aligned} \tag{8}$$

The problem is now that the operators acting on the I- and S-spins, respectively, are defined in different systems of reference. We therefore transform the scalar product

$$\mathbf{I} \cdot \mathbf{S} = I_x S_x + I_y S_y + I_z S_z$$

by the aid of the transformation equations

$$\mathbf{S} = R(\varepsilon, \psi, \xi) \mathbf{S}' \tag{9}$$

where the transformation matrix R depends on the Eulerian angles[11] (p. 289). Remembering that the transverse spin components can be replaced by terms of the form

$$I_x = \tfrac{1}{2}(I^+ + I^-), \quad I_y = \frac{1}{2i}(I^+ - I^-) \tag{10}$$

allows to express Eq. (8) in an analogous manner as the Hamiltonian for a single system of Ref.[5] (p. 289). We find for the components of Equation (7)

$$E^{(0,0)} = \frac{1}{r_{IS}^3} [n_3 - 3 \cos \Theta_I \cos \Theta_S],$$

$$\begin{aligned}E^{(-1,+1)} = \frac{1}{r_{IS}^3} [-l_1 - m_2 - i(m_1 - l_2) \\ + 3 \sin \Theta_I \sin \Theta_S \exp\{-i(\Phi_S - \Phi_I\}];\end{aligned}$$

$$\begin{aligned}E^{(0,+1)} = \frac{1}{r_{IS}^3} \Big[-\frac{1}{3} l_3 + \frac{i}{3} m_3 \\ + \sin \Theta_I \cos \Theta_S \exp\{-i \Phi_I\} \Big],\end{aligned}$$

$$\begin{aligned}E^{(+1,0)} = \frac{1}{r_{IS}^3} \Big[-\frac{1}{3} n_1 + \frac{i}{3} n_2 \\ + \sin \Theta_S \cos \Theta_I \exp\{-i \Phi_S\} \Big],\end{aligned} \tag{11 a}$$

$$\begin{aligned}E^{(+1,+1)} = \frac{1}{r_{IS}^3} \Big[-\frac{1}{3} l_1 + \frac{m_2}{3} + \frac{i}{3}(l_2 + m_1) \\ + \sin \Theta_I \sin \Theta_S \exp\{-i(\Phi_I + \Phi_S)\} \Big]\end{aligned}$$

with

$$\begin{aligned}l_1 &= \cos\psi \cos\xi - \cos\varepsilon \sin\psi \sin\xi, \\ l_2 &= -\cos\psi \sin\xi - \cos\varepsilon \sin\psi \cos\xi, \\ l_3 &= \sin\varepsilon \sin\psi;\end{aligned}$$

$$\begin{aligned}m_1 &= \sin\psi \cos\xi + \cos\varepsilon \cos\psi \sin\xi, \\ m_2 &= -\sin\psi \sin\xi + \cos\varepsilon \cos\psi \cos\xi, \\ m_3 &= -\sin\varepsilon \cos\psi;\end{aligned}$$

$$\begin{aligned}n_1 &= \sin\varepsilon, \sin\xi, \\ n_2 &= \sin\varepsilon \cos\xi, \\ n_3 &= \cos\varepsilon,\end{aligned}$$

and

$$\begin{aligned}O^{(0,0)} &= \tfrac{1}{2} I_z S_{z'}, & O^{(-1,+1)} &= -\tfrac{1}{4} I^- S^+, \\ O^{(0,+1)} &= -\tfrac{3}{2} S_{z'} I^+, & O^{(+1,0)} &= -\tfrac{3}{2} I_z S^+, \\ O^{(+1,+1)} &= -\tfrac{3}{4} I^+ S^+,\end{aligned} \tag{11 b}$$

where
$$S^+ = S_{x'} + i S_{y'}, \quad S^- = S_{x'} - i S_{y'}.$$

The functions for the opposite transitions are given by

$$E^{(-i,-j)} = E^{(i,j)*}. \tag{11 c}$$

Notice that the functions $E^{(i,j)}$ approach the functions $F^{(i)}$ [Eq. (3 c)] in the limit of a single system of reference, i. e. for ε, ψ, $\xi \to 0$ which means $\Theta_S \to \Theta_I$ and $\Phi_S \to \Phi_I$.

In this limit it holds

$$\begin{aligned}F^{(0)} &= E^{(0,0)} = E^{(-1,+1)}, \\ F^{(1)} &= E^{(0,+1)} = E^{(+1,0)}, \\ F^{(2)} &= E^{(+1,+1)}\end{aligned} \tag{12}$$

as it must be. Furthermore Eq. (7) is symmetrical with respect to the exchange of I and S.

The expressions in Eq. (11) contain co-ordinates which are not independent of each other. Thus a reduction of variables can and should be performed to leave a set of independent quantities. Firstly, we may choose for some of the variables fixed values.

In the following, we use $\xi = 0$ leading to a considerable simplification of the expressions given above. Furthermore, relations between the diverse co-ordinates can be derived. By the use of spherical trigonometry we obtain according to Fig. 2 (with $\alpha = 90° - \Phi_S$).

$$\cos \Theta_I = \cos \varepsilon \cos \Theta_S + \sin \varepsilon \sin \Theta_S \sin \Phi_S \,. \qquad (13\,\mathrm{a})$$

A further relation according to Fig. 3 can be derived by considering the hatched triangles. Expressing x by quantities of each triangle yields an equation which can finally be written in a form

$$\cos \alpha = \sin \Theta_S / \sqrt{1 - \cos^2 \varepsilon \cos^2 \Theta_S} \qquad (14\,\mathrm{a})$$

where α can be obtained from the spherical triangle in Figure 3 b. The diverse averages which have to be calculated of Eq. (11 a) can thus be obtained with the independent variables ε, ψ (defining the orientation of the FGT-axis) and Φ_S, Θ_S, r_{IS} (defining the orientation of $\boldsymbol{r}_{IS}$), where ξ has been chosen to be zero. A further simplification can be achieved by omitting intermolecular interactions. For more or less rigid molecules, intramolecular spin-spin vectors can be considered to have fixed values Φ_S and Θ_S. Φ_S can then be chosen to be zero while the value of Θ_S is given by the molecular structure.

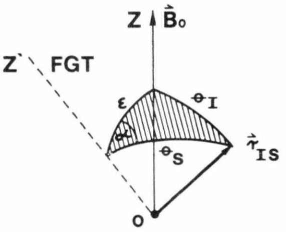

Fig. 2. Spherical triangle for the derivation of Equation [13].

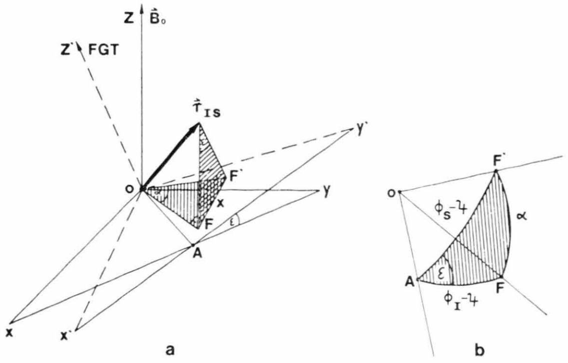

Fig. 3. Derivation of Equation [14].

The reduction formulae are then

$$\cos \Theta_I = \cos \varepsilon \cos \Theta_S \qquad (13\,\mathrm{b})$$

and (with $\alpha = \psi - \Phi_I$)

$$\cos(\psi - \Phi_I) = \sin \Theta_S / \sqrt{1 - \cos^2 \varepsilon \cos^2 \Theta_S} \,. \qquad (14\,\mathrm{b})$$

2.2.2. General Relaxation Rates:

Following Solomon's theory we obtain

$$\frac{1}{T_1^{\mathrm{u}}} = \langle \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \sum_{\mathrm{pairs}} \{ \tfrac{1}{12} K^{(+1,-1)} \cdot \tilde{J}(\omega_I - \langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{2} K^{(0,-1)} \tilde{J}(\omega_I) + \tfrac{3}{4} K^{(-1,-1)} \tilde{J}(\omega_I + \langle \omega_S \rangle_{\mathrm{a}} \} \rangle_{\mathrm{b}} \qquad (15\,\mathrm{a})$$

and

$$\frac{1}{T_2^{\mathrm{u}}} = \langle \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \sum_{\mathrm{pairs}} \{ \tfrac{1}{6} K^{(0,0)} \tilde{J}(0) + \tfrac{1}{24} K^{(+1,-1)} \tilde{J}(\omega_I - \langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{4} K^{(0,-1)} \tilde{J}(\omega_I) + \tfrac{3}{2} K^{(-1,0)} \tilde{J}(\langle \omega_S \rangle_{\mathrm{a}}) + \tfrac{3}{8} K^{(-1,-1)} \tilde{J}(\omega_I + \langle \omega_S \rangle_{\mathrm{a}}) \} \rangle_{\mathrm{b}} \qquad (15\,\mathrm{b})$$

with the square interaction amplitudes

$$K^{(i,j)} = \langle | E^{(i,j)} |^2 \rangle_{\mathrm{a}} - | \langle E^{(i,j)} \rangle_{\mathrm{a}} |^2 \,.$$

The set of resonance frequencies ω_S of the S-spins again includes functions of the angle ε, as given in Ref. [12] (p. 10). The averages "**a**" have to be taken over all orientations of the electric field gradient and of the vectors $\boldsymbol{r}_{IS}$, reached within the mean life time of the I-spins, i. e. during the relaxation times of this spin species. Differently oriented subphases in the case of anisotropic motions, the diverse types of transitions of the S-spins, isotopical distributions of the quadrupole nuclei and distributions of the electric field-gradient finally require the average "**b**".

The problem is now to perform these averages. We distinguish two limiting cases allowing this calculation.

2.2.3. Quasi Rigid Lattice:

We define this case by the requirement of quasi-stationary angles ε. This quasi-stationarity is reached under the condition that all relevant molecular motions, i.e. those occurring within a time scale shorter than the relaxation times, don't touch the angle ε or have sufficiently small amplitudes to keep the angle ε nearly constant. As mentioned above no transverse relaxation time is defined for this case. In order to treat the longitudinal relaxation rate we have to calculate the averages in Equation (15 a).

According to the quasi-stationarity of the angle ε we can write for the set of the transition frequencies of the S-spins

$$\langle\omega_S\rangle_{\mathrm{a}} \approx \omega_S = \omega_S(\varepsilon)\ . \tag{16}$$

The average "**a**" within the functions $K^{(i,j)}$ [Eq. (15)] requires the knowledge of the type of molecular motion, and we shall assume one special case below.

As a consequence of the flip-flop term $\tilde{J}(\omega_I - \omega_S)$ in Eq. (15 a), we expect a dip in the dispersion of T_1^{u} in the present case. This quadrupolar dip is due to the completely different magnetic field dependence of ω_I and ω_S, causing a level crossing effect. In Ref. [1] this dip has been verified experimentally for solid PVC. We shall shortly discuss this case in Section 3.1. For the moment we want to evaluate Eq. (15 a) in the quasi-rigid lattice case for one special type of motion.

The Oscillator Model:

We consider an oscillation of $\boldsymbol{r}_{IS}$ essentially keeping all angles and consequently also ω_S constant. This assumption should be a sufficient approximation for many types of vibrations, because the absolute value of $\boldsymbol{r}_{IS}$ influences the functions $E^{(i,j)}$ in the highest power of all co-ordinates. In the subsequent discussion of the problem we assume furthermore that the electric field gradient is rotationally symmetric ($\eta = 0$).

The angular terms in Eq. (15 a) are then essentially not affected by the average "**a**" and can therefore be treated as proportionality factors $C^{(i,j)}$, leading to

$$K^{(i,j)} = C^{(i,j)}\left[\left\langle\frac{1}{r_{IS}^6}\right\rangle_{\mathrm{a}} - \left\langle\frac{1}{r_{IS}^3}\right\rangle_{\mathrm{a}}^2\right] \tag{17}$$

with

$$C^{(i,j)} = |E^{(i,j)}\, r_{IS}^3|^2\,. \tag{18}$$

Assuming at first that the vibration amplitudes are excited stochastically, but that the value of r_{IS} averaged over a vibration period is constant for all amplitudes, as expected for harmonic potentials [13], allows to use the "oscillator model" given in Reference [14]. The intensity functions in Eq. (15 a) then turn out to be constant in the usual limit $\omega_0 \gg \omega$, where ω_0 is the vibration frequency:

$$\tilde{J}_{OS} \approx \frac{\tau_{\mathrm{c}}}{1 + \omega_0^2\,\tau_{\mathrm{c}}^2} = \text{const}\,. \tag{19}$$

τ_{c} is the correlation time for the fluctuation of the vibration amplitude. This means that no magnetic field dependence and no quadrupolar dip could be expected in contrast to the experimental finding [1].

Therefore we refine the model by assuming the more realistic situation that namely the alteration of the type or the amplitude of the now anharmonic vibration causes a change in the value of r_{IS} averaged over a period.

The absolute value of r_{IS} can be analyzed into

$$r_{IS}(t) = \langle r_{IS}\rangle_{\mathrm{a}} + \Delta(t) + a(t) \tag{20}$$

where $\Delta(t)$ is the momentaneous deviation of r_{IS}, averaged over a period of vibration, from the long time average $\langle r_{IS}\rangle_{\mathrm{a}}$ and $a(t)$ is the periodic elongation of the momentaneous type of vibration.

The normalized correlation function can be written under the assumption mentioned above

$$\tilde{G}(\tau) = \langle r_{IS}\rangle_{\mathrm{a}}^6 \left\langle \frac{1}{r_{IS}^3(0)\, r_{IS}^3(\tau)} \right\rangle_{\mathrm{a}}. \tag{21}$$

In linear approximation we obtain

$$\begin{aligned}\tilde{G}(\tau) &\approx \left\langle \left[1 - 3\,\frac{[\Delta(0) + a(0)]}{\langle r_{IS}\rangle_{\mathrm{a}}}\right] \cdot \left[1 - 3\,\frac{[\Delta(\tau) + a(\tau)]}{\langle r_{IS}\rangle_{\mathrm{a}}}\right]\right\rangle_{\mathrm{a}} \\ &= 1 + \frac{9}{\langle r_{IS}\rangle_{\mathrm{a}}^2}\left[\langle \Delta(0)\,\Delta(\tau)\rangle_{\mathrm{a}} + \langle a(0)\, a(\tau)\rangle_{\mathrm{a}}\right].\end{aligned} \tag{22}$$

Here we have taken advantage of the fact that the quantities Δ and a are uncorrelated. Because constant terms don't affect Fourier transforms at finite frequencies, we consider the reduced correlation function

$$\tilde{G}_{\mathrm{red}}(\tau) = \tilde{G}(\tau) - \tilde{G}(\infty) = 9(\tilde{G}_\Delta + \tilde{G}_{\mathrm{a}}) \tag{23}$$

with

$$\tilde{G}_\Delta = \langle\tilde{\Delta}(0)\,\tilde{\Delta}(\tau)\rangle_{\mathrm{a}}\,, \tag{24}$$

$$\tilde{G}_{\mathrm{a}} = \langle\tilde{a}(0)\,\tilde{a}(\tau)\rangle_{\mathrm{a}}\,, \tag{25}$$

and

$$\tilde{\Delta} = \frac{\Delta}{\langle r_{IS}\rangle_{\mathrm{a}}}\,, \tag{26}$$

$$\tilde{a} = \frac{a}{\langle r_{IS}\rangle_{\mathrm{a}}}\,. \tag{27}$$

In the time scale relevant for NMR experiments, i. e. in the range 10^{-11} sec $< \tau < 10^{-4}$ sec we may neglect $\tilde{G}_{\mathrm{a}}$. Therefore

$$\tilde{G}_{\mathrm{red}}(\tau) \approx 9\,\tilde{G}_\Delta\,. \tag{28}$$

The stochastic excitation of different vibration amplitudes must be considered to be a Poisson-process. Thus

$$\tilde{G}_{\mathrm{red}}(\tau) = 9\langle\tilde{\Delta}^2\rangle_{\mathrm{a}} \exp\{-\tau/\tau_{\mathrm{c}}\} \tag{29}$$

with τ_c the mean lifetime of a definite type of vibration. The intensity function finally turns out to be

$$\tilde{J}_{0S}(\omega) = B_1 \frac{2\tau_c}{1+\omega^2\tau_c^2} \qquad (30)$$

with

$$B_1 = 9\langle\tilde{\Delta}^2\rangle_a . \qquad (31)$$

We have now a field dependent intensity function which can account for the quadrupolar dip, experimentally observed in the quasi-rigid lattice case[1].

The final relaxation formula can be derived from Eqs. (15 a), (17), (18), and (30) with the aid of Eqs. (13 b) and (14 b) by performing the powder average as far as analytically possible:

$$\begin{aligned}\frac{1}{T_1^{\,u}} = \Big\langle \gamma_I^2\gamma_S^2\hbar^2 S(S+1)\, 9\, \frac{\langle\Delta^2\rangle_a}{\langle r_{IS}\rangle^6} &\cdot\Big\{\frac{1}{12}\langle C^{(+1,-1)}\rangle \frac{2\tau_c}{1+(\omega_I-\omega_S)^2\tau_c^2} \\ &+\frac{3}{2}\langle C^{(0,-1)}\rangle\frac{2\tau_c}{1+\omega_I^2\tau_c^2} \\ &+\frac{3}{4}\langle C^{(-1,-1)}\rangle\frac{2\tau_c}{1+(\omega_I+\omega_S)^2\tau_c^2}\Big\}\Big\rangle_\varepsilon\end{aligned} \qquad (32)$$

with[12]

$$\omega_S = \omega_S^{\,Q} \pm \left[\frac{3\pm f}{2}\right]\gamma_S B_0 \cos\varepsilon ,$$

$$f = (1+4\tan^2\varepsilon)^{1/2}$$

and the partial averages

$$\langle C^{(+1,-1)}\rangle = (1+\cos\varepsilon)^2 - 6\cos\varepsilon\sin^2\Theta_S ,$$

$$\langle C^{(0,-1)}\rangle = \tfrac{1}{9}\sin^2\varepsilon + \tfrac{2}{3}\cos^2\Theta_S(1-\sin^2\varepsilon) ,$$

$$\langle C^{(-1,-1)}\rangle = \tfrac{1}{9}(1-\cos\varepsilon)^2 + \tfrac{2}{3}\sin^2\Theta_S\cos\varepsilon .$$

The final powder average concerning ε has to be calculated numerically.

2.2.4. *Tumbling Lattice:*

We assume that molecular motion reaches a high degree of isotropy within a time scale of the order of the relaxation times. This situation is realized for instance in liquids. The condition for the correlation time of rotational diffusion is then $\tau_c \ll T_2^{\,u}$. In this case the averages "a" can easily be performed. Keeping the spherical co-ordinates of $\boldsymbol{r}_{IS}$ in the molecular system of reference constant and averaging over all independent variables yields for intramolecular interactions by the aid of Eqs. (11), (13), (14), and (15)

$$\begin{aligned}\langle\omega_S\rangle_a &= \omega_S^{\,Q} ,\\ K^{(0,0)} &= \left(\frac{1}{3}+\cos^2\Theta_S\right)\frac{1}{r_{IS}^6} ,\\ K^{(+1,-1)} &= \frac{4}{3}\frac{1}{r_{IS}^6} ,\\ K^{(0,-1)} &= \left(\frac{2}{27}+\frac{2}{9}\cos^2\Theta_S\right)\frac{1}{r_{IS}^6} ,\\ K^{(-1,0)} &\approx \frac{1}{3}\sin^2\Theta_S\cos^2\Theta_S\frac{1}{r_{IS}^6} ,\\ K^{(-1,-1)} &= \frac{4}{27}\frac{1}{r_{IS}^6} .\end{aligned} \qquad (33)$$

The angle Θ_S is determined by the structure of the molecules and the charge distribution on them.

The question might arise, why the $K^{(i,j)}$-functions deviate from the mean square interaction amplitudes for isotropic rotation in the high-field case. The reason can be found in the fact that the spin orientations remain constant during the tumbling of $\boldsymbol{r}_{IS}$ in the high-field case while in the low-field case a tumbling of the **S**-orientation occurs (Figure 4).

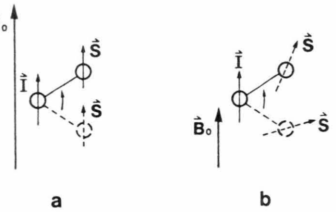

Fig. 4. Orientation of S in a tumbling molecule. a) High-field case; b) Low-field case.

For isotropic rotation we may use Debye shaped intensity functions[4] leading to

$$\begin{aligned}\frac{1}{T_1^{\,u}} = \frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{r_{IS}^6}\Big\langle\sum_{\text{pairs}}\Big\{&\frac{1}{9}\frac{2\tau_c}{1+(\omega_I-\omega_S^{\,Q})^2\tau_c^2} \\ &+\left(\frac{1}{9}+\frac{1}{3}\cos^2\Theta_S\right)\frac{2\tau_c}{1+\omega_I^2\tau_c^2}+\frac{1}{9}\frac{2\tau_c}{1+(\omega_I+\omega_S^{\,Q})^2\tau_c^2}\Big\}\Big\rangle_b\end{aligned} \qquad (34\text{ a})$$

and

$$\frac{1}{T_2{}^{\mathrm{u}}}=\frac{\gamma_I{}^2\,\gamma_S{}^2\,\hbar^2\,S(S+1)}{r_{IS}^6}\left\langle\sum_{\text{pairs}}\left\{\left(\frac{1}{18}+\frac{1}{6}\cos^2\Theta_S\right)2\,\tau_{\mathrm{c}}+\frac{1}{18}\,\frac{2\,\tau_{\mathrm{c}}}{1+(\omega_I-\omega_S{}^{\mathrm{Q}})^2\,\tau_{\mathrm{c}}{}^2}\right.\right.$$
$$\left.\left.+\left(\frac{1}{18}+\frac{1}{6}\cos^2\Theta_S\right)\frac{2\,\tau_{\mathrm{c}}}{1+\omega_I{}^2\,\tau_{\mathrm{c}}{}^2}+\frac{1}{2}\sin^2\Theta_S\cos^2\Theta_S\,\frac{2\,\tau_{\mathrm{c}}}{1+\omega_S{}^{\mathrm{Q}2}\,\tau_{\mathrm{c}}{}^2}+\frac{1}{18}\,\frac{2\,\tau_{\mathrm{c}}}{1+(\omega_I{}^2+\omega_S{}^{\mathrm{Q}})^2\,\tau_{\mathrm{c}}{}^2}\right\}\right\rangle_{\mathrm{b}}. \quad (34\,\mathrm{b})$$

The average "b" will only be necessary in the rapid exchange case if isotopical and/or electric field gradient distributions occur. These formulae show that a principally different relaxation behaviour, compared with the high-field case [Eq. (5)] cannot be expected for rapid molecular tumbling. As an application of this case we shall briefly discuss protein solutions containing N^{14}-H two-spin ensembles (Section 3.2.).

3. Discussion of Practical Cases

The purpose of this section is to give experimental evidence of the importance of the interaction with quadrupole nuclei. We don't want to present a final theoretical description of all details of the investigated systems. This would be beyond the scope of this paper and would require a more sophisticated study of the special properties of the diverse examples. Instead of this we discuss the principal aspects and leave special treatments to forthcoming papers.

3.1. Solid PVC (Cl^{35} and Cl^{37})

Chlorine compounds are good examples for the lowfield case at magnetic fields below $2\,T$(1). We tentatively apply the oscillator model discussed in Section 2.2.3. to experimental data of powdery solid PVC (1). The assumption of a quasi-rigid lattice should be justified the more the lower the temperature, where all defect motions [15] are frozen in. The

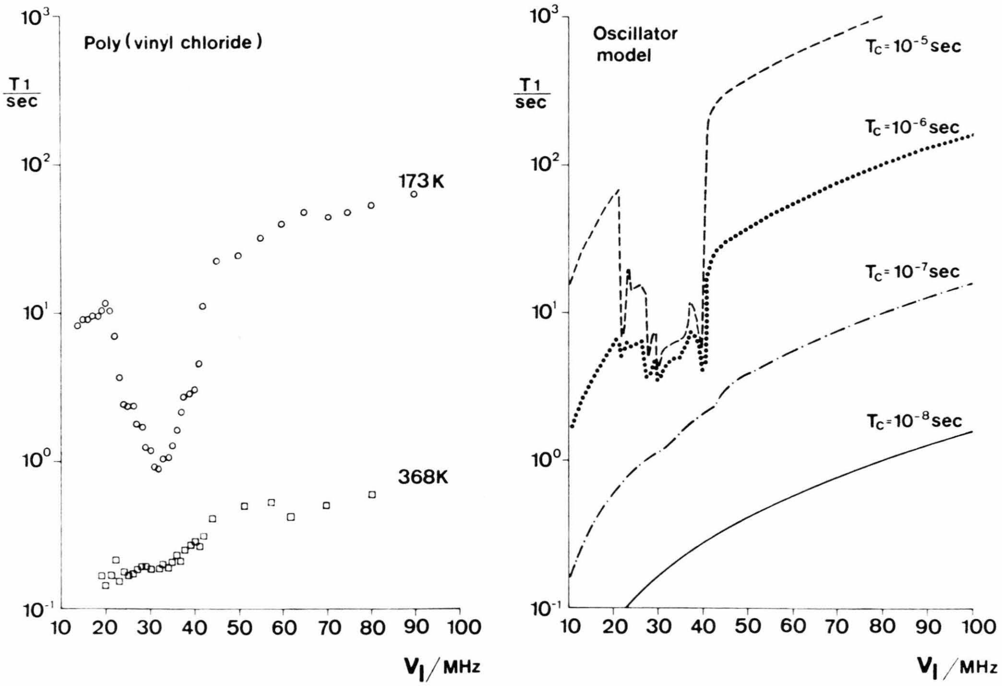

Fig. 5. Comparison of experimental data taken from Ref. [1] of powdery Poly (vinyl chloride) with theory. The dispersion of the theoretical relaxation times is calculated for a set of different correlation times in the oscillator model according to Equation [35]. The following data have been used in addition to those given in the text:

$r_{II}=1.7\cdot10^{-8}$ cm, $r_{IS}=2.0\cdot10^{-8}$ cm. $\langle\tilde{\Delta}^2\rangle_{\mathrm{a}}=10^{-2}$, $\omega_S{}^{\mathrm{Q}}(\mathrm{Cl}^{35})=32.5$ MHz, $\omega_S{}^{\mathrm{Q}}(\mathrm{Cl}^{37})=25.6$ MHz, $\Theta_S=30°$.

The simultaneous interaction of the reference nuclei with several protons has been taken into account by a factor 3.

experimental data are compared with theoretical curves in Fig. 5, where we have used Eq. (32) for the [CHCl]-groups and Eq. (3) for the [CH_2]-groups. The resulting rate is given as the weighted average of the two partial rates. Intergroup interactions have been globally taken into account by a factor 3 in the two-spin relaxation rates. The angle Θ_S has been assumed to have the fixed value 30°, given by the geometry of a CHCl-group. The rate $1/T_1{}^{\mathrm{u}}$ [Eq. (32)] must be averaged in addition according to the distribution of the chlorine isotopes. All other data are given in the legend of Figure 5.

The resulting proton relaxation rate can be derived from Eqs. (3) and (32) in the form

$$\frac{1}{T_1{}^{\mathrm{u}}}=3\sum_{j=1}^{2} a_j\Biggl[\left(C_1+\frac{13}{36}C_2\right)\tilde{J}(\omega_I)+4\,C_1\,\tilde{J}(2\,\omega_I) + C_2\sum_{i=1}^{4}\int_0^{\pi}\left\{\frac{1}{96}\langle C^{(+1,-1)}\rangle\,\tilde{J}(\omega_I-\omega_S{}^{(i,j)}) + \frac{3}{32}\langle C^{(-1,-1)}\rangle\,\tilde{J}(\omega_I+\omega_S{}^{(i,j)})\right\}\sin\varepsilon\,\mathrm{d}\varepsilon\Biggr] \tag{35}$$

with

$$C_1=\frac{9}{10}\gamma_I{}^4\,\frac{\langle\tilde{\Delta}^2\rangle_{\mathrm{a}}}{\langle r_{II}\rangle^6}\hbar^2\,,$$

$$C_2=\frac{45}{4}\gamma_I{}^2\,\gamma_S{}^{(j)^2}\frac{\langle\tilde{\Delta}^2\rangle_{\mathrm{a}}}{\langle r_{IS}\rangle^6}\hbar^2\,;$$

$\omega_S{}^{(i,j)}$ can have eight values: four transition frequencies as given in Eq. (32) for the two isotopes Cl^{35} ($a_1=75.5\%$) and Cl^{37} ($a_2=24.5\%$) with different values for $\omega_S{}^{\mathrm{Q}}$ and γ_S. The j-sum yields the isotopical average, the i-sum concerns the different transition frequencies. The integral in Eq. (35) must be evaluated numerically.

Figure 5 shows that the qualitative behaviour of this example can quite well be understood with the theory given above. A quantitative description needs, however, several refinements which are not available in a straight-forward way at the present state of the art. Therefore, we leave the comparison as presented in Fig. 5 and discuss the reasons for the deviations between theory and experimental data.

Two dispersion regions can be distinguished: the level-crossing region (quadrupolar dip), influenced by the secular flip-flop term, and the non-secular dispersion region. The quadrupolar dip was found to be smoother than predicted by the theoretical curve for $\tau_c \geqq 10^{-6}$ sec. Two reasons could be responsible for this fact: If there is any distribution of the electric field gradients throughout the sample, the frequencies $\omega_S{}^{\mathrm{Q}}$ would be smeared over a corresponding range. Thus a less structured dip should be expected.

The same effect can be reached by assuming shorter correlation times causing less steep flanks of the dip. The problem is then that the depth of the dip and the absolute values in the non-secular region don't fit together with this simple Debyean intensity function. This difficulty can however be overcome by the assumption of a more complicated situation with respect to the intensity functions. Probably, one has to consider a distribution of correlation times due to the heterogeneity of the sample: As most polymers, PVC consists of crystalline and amorphous parts, showing different types of molecular motions. Thus the quadrupolar dip should be influenced by the slow motions while the non-secular region is dominated by the fast components. Furthermore, the slopes and the absolute values of the non-secular dispersion regions could be better described in this way.

From this discussion it becomes clear that more experimental information from different methods must be incorporated in any further approach of the theory. We leave this task for a later work specialized on PVC.

3.2. Protein Solutions (N^{14})

We have chosen protein solutions for a further application of the presented theory because these systems contain N^{14} as quadrupole nuclei and are expected to be an example of the tumbling lattice case (Section 2.2.4).

The quadrupole frequencies $\omega_S{}^{\mathrm{Q}}$ of nitrogen are often not high enough to ensure the low-field case in usual magnetic fields [18]. So we have to deal with both the high- and the low-field case in the magnetic field range of usual relaxation dispersion experiments [16, 17]. Fortunately the relaxation formulae become quite similar for both cases in the limit of a rapidly tumbling lattice [Eq. (5) and (34)], which prevents any dramatic change in the transition region. It was found that the high- and low-field formulae deviate in the limit of high frequencies less than 5%.

Proteins consist of a variety of amino acids having different quadrupole frequencies [18–20]. Furthermore, different mobilities within different proton phases occur [21]. So we have to deal with a rather complex situation, which is not very inviting for a comparison of the theory with experiments. Nevertheless, we want to treat tentatively a very simple model situation because a lot of experimental data is available for these systems [17, 21–24]. A more specific discussion is in preparation.

We start from our previous suggestion [21] that there are relaxation sinks within the protein molecules, dominating the relaxation behaviour of the whole system via exchange processes provided that the protein concentration is high enough [21, 25]. The imino-groups are considered to be one essential type of relaxation sinks being very effective because they are donators in hydrogen bonds within the hydration shell of the protein molecules. We assume an ensemble of imino-groups having a certain distribution of quadrupole frequencies $g(\omega_S^Q)$ but common correlation times τ_c (determined by the rotational diffusion and/or by the hydrogen exchange of the imino-groups). For $\Theta_S = 0$, we obtain from Eq. (34 a) for the longitudinal relaxation rate at low fields

$$\frac{1}{T_1^{u}} = \frac{4}{9}\,\frac{\gamma_I^2\,\gamma_S^2\,\hbar^2}{r_{IS}^6}\left[\frac{4\,\tau_c}{1+\omega_I^2\,\tau_c^2} + \int_0^\infty g(\omega_S^Q)\left\{\frac{\tau_c}{1+(\omega_I-\omega_S^Q)^2\,\tau_c^2} + \frac{\tau_c}{1+(\omega_I+\omega_S^Q)^2\,\tau_c^2}\right\} d\omega_S^Q\right]. \qquad (36)$$

In this first approach we omit any detailed consideration of the actual quadrupole frequencies and assume a normal distribution

$$g(\omega_S^Q) = \frac{1}{\sigma\sqrt{2\pi}}\,\exp\{-[(\omega_S^Q - \langle\omega_S^Q\rangle)^2]/2\,\sigma^2\} \qquad (37)$$

with $\sigma = (\langle\omega_S^{Q^2}\rangle - \langle\omega_S^Q\rangle^2)^{1/2}$. This distribution prevents the appearance of the quadrupolar dip. In the tumbling lattice case the dip is rather narrow and can therefore be smeared out even with a moderate width of the ω_S^Q-distribution.

In a first approximation we can distinguish two proton phases:

a) protons underlying rapid material exchange such as water and NH-protons,

b) protons permanently bound to the protein molecules (within the time scale of the relaxation times).

The latter phase forms a rather heterogeneous ensemble according to the special amino acid composition and the spatial structure of the protein [26].

The question is now to which extent cross-relaxation influences the longitudinal relaxation times to be expected for instance in the exchangeable proton phase, which is normally measured if the nmr signals are recorded with a narrow band spectrometer. Attempts to take cross-relaxation into account have been made in Ref. [27] and [28]. In this paper, however, we want to omit the discussion of this point and give the longitudinal relaxation times of the exchangeable protons to be expected without the influence of cross-relaxation as an estimate of the maximum relaxation capacity of this phase.

Examples are aqueous serum albumin solutions. From Ref. [26] we conclude that a serum albumin molecule contains about 4140 protons. 742 of them are bound to nitrogen. Taking globally the enhancement caused by the simultaneous interaction of the nitrogen with several protons into account by a factor 3, the longitudinal relaxation times of an isolated phase of exchangeable protons can be estimated for a given concentration of the solution, assuming $r_{IS} = 10^{-8}$ cm and assuming the rapid exchange formula for all NH-protons

$$\frac{1}{T_1^{\,ex}} = \frac{C_1}{T_1^{\,NH}} + \frac{1-C_1}{T_1^{\,H_2O}}\,. \qquad (38)$$

Figure 6 shows, the result for a solution with 28.1% protein at 0° C, i. e. $C_1 = 11.4\%$ and $T_1^{H_2O} = 1.6$ sec.

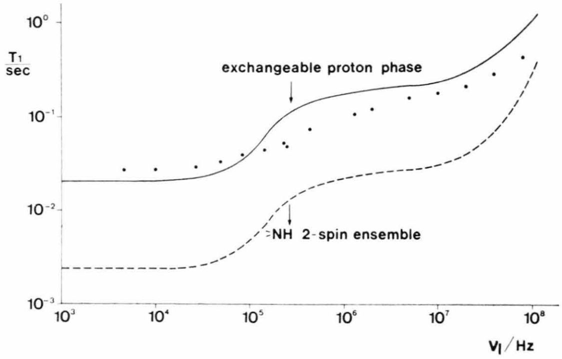

Fig. 6. Dispersion of the longitudinal relaxation times of isolated imino-groups and of the exchangeable proton-phase [Eq. (38)] in an aqueous protein solution. The experimental data (●, 28.1% serum albumin solution at 0 °C) are taken from Ref. [21]. The following theoretical data have been used in addition to those given in the text:

$\sigma = 6.6 \times 10^6$ rad/sec,
$\langle\omega_S^Q\rangle = 8.8 \times 10^6$ rad/sec,
$\tau_{C_1} = 1.8 \times 10^{-6}$ sec,
$\tau_{C_2} = 5.0 \times 10^{-9}$ sec.

Inter-pair contributions have been taken into account by a factor 3. Cross relaxation effects to the bound proton phase have so far not been taken into account, though their influence can be essential. This comparison shows, however, that imino-groups are principally able to determine the relaxation behaviour of such systems.

Hereby, we have assumed for simplicity that the correlation function for the NH-interaction consists of merely two components: a rapid component decaying with $\tau_c = 5 \cdot 10^{-9}$ sec leaving a "Restkorrelation" of 4% which finally decays to zero with a decay time $\tau_c = 1.8 \cdot 10^{-6}$ sec. Whether these components are due to protons of different mobility and/or to an anisotropic motion of all protons[15] cannot be distinguished at the present state of the art.

Though the cross-relaxation effects between both phases are so far not included, we can state that the NH-groups are able to relax the whole system to a considerable degree. Furthermore, the action of imino-groups as relaxation sinks explains easily some experimental facts reported previously.

Total or partial deuteration of the solvent causes simultaneously a reduction of the number of relaxation centers. Thus the isolated phase of the remaining exchangeable protons shows virtually the same relaxation times (apart from the effect of a small change of the viscosity upon deuteration)[21]. On the other hand, the relaxation capacity of the exchangeable protons is effectively weakened causing a lower cross-relaxation rate to the bound protons. In cases where the bound protons are strongly relaxed via cross-relaxation and spin diffusion an elongation of the longitudinal relaxation times occurs as recently observed by Edzes and Samulski[27]. These authors concluded from their measurements that the relaxation centers are located within the water phase, i.e., in our words, within the exchangeable proton phase. This statement is in agreement with our previous result that the relaxation capacity of the bound protons, found in fully deuterated solvents, is not able to account for the short relaxation times in undeuterated solvents[21].

4. Conclusions

The usual relaxation formulae are often not applicable to samples containing quadrupole nuclei. The modifield theory is principally able to describe these situations. It should be mentioned that this formalism can easily be extended to electron paramagnetic compounds with strong zero field splitting[29]. This case is quite equivalent to the low-field case discussed above.

The modified oscillator model explains the occurence of the quadrupolar dip in solid PVC. Here we have assumed the quasi rigid lattice case. The other extreme is the rapid tumbling of the lattice as realized for instance in protein solutions. The relaxation rates in highly concentrated solutions at low fields are influenced by the $N^{14}H$-interaction.

At the first sight one might fear that the effects discussed above merely prevent any simply interpretable relaxation behaviour and are of no further use. On the other hand quite specific investigations of the interaction with the quadrupole nuclei become possible, offering new types of experiments.

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