Strong Collision Induced Spin-Lattice Relaxation for Tunneling NH_4-ion Systems in the Rotating Frame

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In order to calculate the rotating frame spin-lattice relaxation time $T_{1\varrho}$ for tunneling NH_4-ion systems at low temperature, a model of relaxation, which is available when $\gamma H_L \tau_r \gg 1$, is proposed, where H_L is the local dipolar field and τ_r the correlation time. The present model is useful especially in two cases: (1) when the NH_4-ion is relatively magnetically isolated and the assumption of a common spin temperature cannot be used. (2) when the level crossing of the NH_4-ion occurs in the rotating frame. In case (1), non-single exponential relaxation is predicted. In case (2), $T_{1\varrho}$ is shown to be proportional to τ_r, while the prediction of the weak collision theory is $T_{1\varrho} \propto \tau_r^{-1}$. The present model is compared with the strong collision theory of Slichter and Ailion.

Introduction

Quantum rotation of symmetrical molecular groups like the CH_3-group, NH_4^+ and methane manifest itself by a tunneling splitting of the ground torsional state. In nmr experiments of absorption spectra, the tunneling splitting gives rise to a reduction of the low temperature second moment [1–4]. Recent works relating to the exchange narrowing of proton spins of NH_4-ions are cited in reference [5].

The measurement of T_1, the spin-lattice relaxation time in the laboratory frame, has given useful information about the dynamical nature of the tunneling motion [6–9]. However, the treatment of T_1 is more difficult than that of the absorption spectra because the phonon system plays an important role. On the basis of Haupt's idea [10], Punkkinen [11] and Nijiman et al. [12] calculated T_1 of NH_4-ions undergoing quantum rotation. The measurement of $T_{1\varrho}$, the spin-lattice relaxation time in the rotating frame [13], is also a useful tool to investigate the tunneling motion [14, 15, 16].

The assumption of a common spin temperature leads to the following expressions for T_1 and $T_{1\varrho}$:

$$T_1^{-1} = C_1 \frac{\tau_r}{1 + (n\omega_0 \pm \Lambda_0)^2 \tau_r^2} + C_2 \frac{\tau_r}{1 + (n\omega_0)^2 \tau_r^2}, \quad (1)$$

$$T_{1\varrho}^{-1} = C_3 \frac{\tau_r}{1 + (2\omega_1 \pm \Lambda_0)^2 \tau_r^2} + C_4 \frac{\tau_r}{1 + 4\omega_1^2 \tau_r^2}, \quad (2)$$

where $\omega_0 = \gamma H_0$, $\omega_1 = \gamma H_1$ and $n = 1, 2$. H_0 and H_1 are the strengths of the external static and the rf field, respectively, Λ_0 is the tunneling frequency of the ground torsional state and τ_r the correlation time. Equations (1) and (2) predict that, when $\Lambda_0 \gg \omega_0$ (or $\Lambda_0 \gg \omega_1$), the temperature dependence of $T_1(T_{1\varrho})$ shows a minimum which is independent of the observed frequency $\omega_0(\omega_1)$. The very short relaxation time $T_1(T_{1\varrho})$ is also predicted when $\Lambda_0 = n\omega_0$ ($\Lambda_0 = 2\omega_1$). The predictions of (1) and (2) have been already verified by experiment [8, 9, 17, 18].

Since (1) and (2) are derived by using the non-adiabatic first-order perturbation theory with the zeroth-order wave functions, the applicability is limited by the following conditions: (a) The collisions between the molecule and phonon system must be frequent, i.e. $\gamma H_L \tau_r \ll 1$. (b) The strength of the magnetic field H_0 (or H_1) must be sufficiently larger than the local dipolar field H_L.

The aim of the present work is to present a model for tunneling NH_4-ion systems which is applicable to low temperatures, i.e. $\gamma H_L \tau_r \gg 1$. The model is based on the strong collision theory of relaxation. By using the assumption of a common spin temperature, Slichter and Ailion [19] developped a relaxation theory which is applicable for $\gamma H_L \tau_r \gg 1$ and $H_1 \lesssim H_L$. The SA theory however, cannot be ap-

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plied to relatively magnetically isolated NH_4-ions, because the assumption of a common spin temperature breaks down. Our model of $T_{1\varrho}$ may also be applicable to such magnetically dilute systems. It has the following features:

(1) When the level crossing of the NH_4-ion occurs in the rotating frame, it is predicted that $T_{1\varrho} \propto \tau_r$ (1), which is quite different from $T_{1\varrho} \propto \tau_r^{-1}$ (2).

(2) The model is applicable not only for $H_1 \lesssim H_L$, but also for $H_1 > H_L$.

(3) Non-single exponential relaxation is predicted when $\Lambda_0 \gg \omega_1$ or $\Lambda_0 \cong 2\omega_1$.

1. Preparation of the System in the Rotating Frame

1.1. Wave Functions and Energy Levels in the Rotating Frame

Consider magnetically weakly coupled NH_4-ions subjected to a strong magnetic field H_0. The Hamiltonian of the system can be written as

$$H = H_Z + H_R + H_D^0 + H_D^n + H_{RP} + H_P, \quad (3)$$

where the terms have the following meaning:

$$H_Z = -\gamma\hbar H_0 \sum_i I_{iz} \quad (i = 1-4)$$

is the Zeeman energy of the proton system. H_R is the torsional Hamiltonian of NH_4^+. H_D^0 and H_D^n are the secular and non-secular parts of the dipolar interaction among protons in the NH_4^+, respectively. The dipolar Hamiltonian connects the spin state with the torsional mode. H_{RP} is the interaction between the torsional and phonon systems.

According to the Pauli principle, the zero-th order wave functions of protons $|f_i^l\rangle$ are combinations of the product of the torsional function $|r_i^l\rangle$ and the spin function $|m_i\rangle$ which remain unchanged on even permutation of four protons, where $i = 1-16$ and l becomes 0 and 1 for the ground and first-exited torsional states, respectively. These combinations were given by Watton and Petch [3]. They are

$$|f_i^l\rangle = |r_i^l m_i\rangle = E_a{}^l E_{b0}, E_b{}^l E_{a0}, F_j{}^l F_{js} \quad (j = 1,2,3,\ s = 0, \pm 1) \quad \text{and}$$
$$A^l A_s (s = 0, \pm 1, \pm 2), \quad i = 1-16. \quad (4)$$

We assume that the tunneling frequencies Λ_0 and Λ_1 of the ground and first-exited torsional states are much smaller than the energy difference E_{01} between the ground and first-exited torsional states. This assumption is valid when the potential barrier for the reorientation of the NH_4-ion differs sufficiently from zero. For simplicity we deal with the case $\Lambda_0 \ll \omega_0$ ($\omega_0 = \gamma H_0$).

In thermal equilibrium with the lattice, the proton system of the NH_4-ion is written by the density matrix $\sigma^0 = \exp(-H_Z/kT_L)/16$, where the contribution from $H_R + H_D^0 + H_D^n$ in (3) is neglected. After the 90°-pulse, the Hamiltonian of the proton system in the rotating frame is

$$H_s = -\gamma\hbar H_1 \sum_{i=1}^{4} I_{iz} + H_R + H_d,$$
$$H_d = H_d{}^0 + H_d{}^n, \quad (5)$$

where a new set of axis is chosen in the rotating frame with z the axis along H_1 and x in the H_0H_1 plane. H_D^n in (3) is responsible for the spin-lattice relaxation similar in magnitude to the usual T_1, the spin-lattice relaxation time in the laboratory frame. We neglect this term in (5). $H_d{}^0$ and $H_d{}^n$ are the secular and non-secular parts ot the intramolecular dipolar interaction in the rotating frame [13].

When the absorption spectrum shows motional narrowing, i.e. $\gamma H_L \tau_r \ll 1$, the zero-th order wave function of (4) will be appropriate to represent the protons of the NH_4-ion. However, when the absorption spectrum shows the rigid lattice line shape, (4) is no more a good representation. We assume that the stationary state for $\gamma H_L \tau_r \gg 1$ is given by the eigen function of (5) as

$$\psi_i^l = \sum_{k=1}^{16} a_{ik}^l |f_k^l\rangle, \quad i = 1-16, \quad l = 0,1. \quad (6)$$

The energy level of $\psi_i{}^0$ in the ground torsional state is shown in Fig. 1 for $\Lambda_0 \gg \gamma H_1 \gg \gamma H_L$. As shown in the figure, the zero-th order dipolar shift of the F-states is of the order of γH_L, which is much larger than that of A- and E-states. The first-order dipolar shift is of the order of $(\gamma H_L)^2/\Lambda_0$ and not shown in the figure.

1.2. Transient Precession of Magnetization and Free Decay

Just after the 90°-pulse, the density matrix of the proton system may be written, neglecting the effect of the spin-lattice relaxation, as

$$\sigma(t) = \sigma_1 + \sigma_2(t), \quad (7)$$

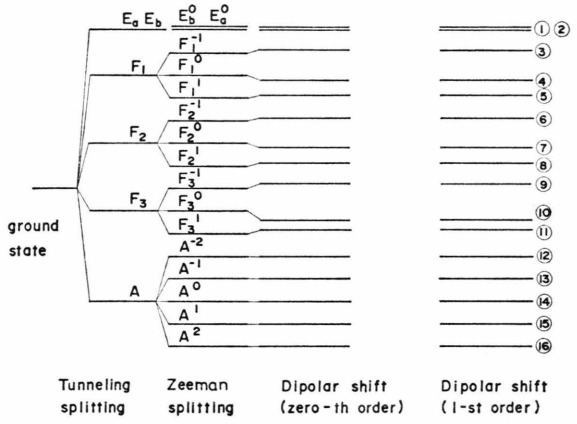

Fig. 1. Energy level scheme of NH_4-ion in the ground torsional state. The first order dipolar shift is not shown in the figure.

where σ_1 and $\sigma_2(t)$ are the diagonal and non-diagonal parts of $\sigma(t)$ with the use of (6), respectively. $\sigma_2(t)$ containes the time dependent terms with the factor $\alpha_{ij}\exp[-i(\varepsilon_i-\varepsilon_j)\,t/\hbar]$, where ε_i and ε_j are the energy of the ψ_i^0 and ψ_j^0 states, respectively. We can introduce the intermolecular dipole-dipole interaction, supposing that their effect is to give a certain width to the energy of the ψ_i^0 state. We have

$$\sigma_2(t)_{ij}=\alpha_{ij}\exp[-i(\varepsilon_i-\varepsilon_j)\,t/\hbar]\cdot\exp(-i\Delta t),\quad i\neq j, \tag{8}$$

where Δ is the width of the energy difference $|\varepsilon_i-\varepsilon_j|$. Assuming a Gaussian broadening function of Δ,

$$f(\Delta)=\exp(-\Delta^2/2\beta^2)/\sqrt{2\pi}\beta,$$

we have the average value of $\sigma_2(t)$ as

$$\langle\sigma_2(t)\rangle_{ij}=\alpha_{ij}\exp[-i(\varepsilon_i-\varepsilon_j)\,t/\hbar]\cdot\exp(-2\pi^2\beta^2t^2), \tag{9}$$

where β is the inter-molecular contribution to the second moment of the resonance line of the proton spins.

The time dependence of the magnetization M_t in the rotating frame is

$$M_t=\mathrm{Tr}(\sigma_1 M)+\mathrm{Tr}(\sigma_2(t)M), \tag{10}$$

where $M=\gamma\hbar\sum_{i=1}^{4}I_{iz}$. The second term of (10) gives rise to the transient precession of the magnetization after the 90°-pulse. Since the $\langle\sigma_2(t)\rangle_{ij}$ decay in the time $t\sim\beta^{-1}$, M_t reaches the equilibrium value $M_{teq}=\mathrm{Tr}(\sigma_1 M)$. Equation (9) shows that the component of M_t ossilates with the frequency $(\varepsilon_i-\varepsilon_j)/\hbar$, which depends on the tunneling frequency Δ_0. Then, as pointed by Nicol and Pinter [16], a measurement of M_t is useful to determine Δ_0. When $H_1=0$, M_t yields the free decay signal after the 90°-pulse. We get the usual absorption spectra by a Fourier transformation of M_t for $H_1=0$.

M_t and M_{teq} were calculated as a function of Δ_0 and H_1 as summerized in Figs. 2 and 3. As shown in Fig. 3, a magnetization loss due to the resonant matching of the Zeeman and torsional levels occurs. For example, the magnetization loss amounts to about 25% when $\Delta_{AF}/2\pi=250$ kHz, $\Delta_{AE}/2\pi=125$ kHz and $\gamma H_1/2\pi=125$ kHz, where Δ_{AF} and Δ_{AE} are the tunneling frequencies between A- and F-states, and A- and E-states, respectively.

Note the difference between the M_t calculated by Nicol et al. [16] and in the present study. M_t was calculated by Nicol et al. using second-order per-

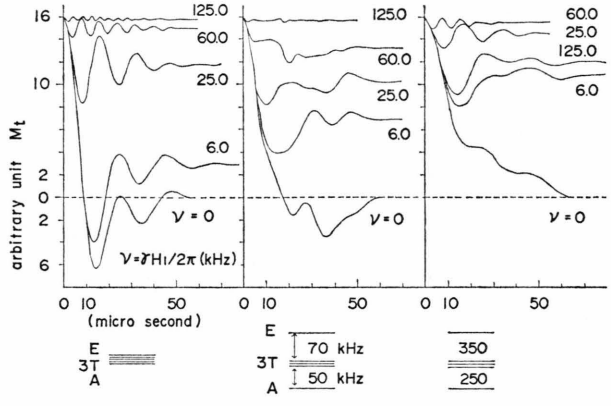

Fig. 2. Transient precession of the magnetization M_t calculated by using Eq. (10) for $(\theta,\varphi)=(90°,45°)$.

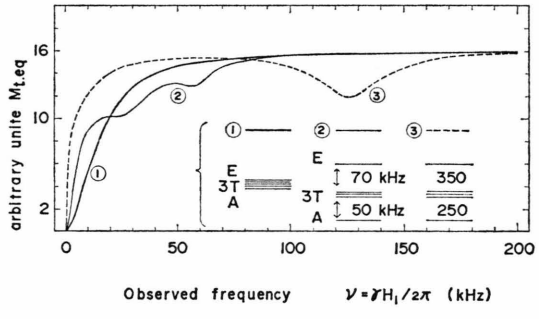

Fig. 3. Equilibrium value of the magnetization M_{teq} in the rotating frame which is calculated by using Eq. (10) as a function of H_1 for $(\theta,\varphi)=(90°,45°)$.

turbation theory on the basis that the zero-th order wave functions $|f_i^0\rangle$, by which $H_Z + H_R$ is diagonal, are the good quantum number. Therefore, their calculation is valid for values of H_1 larger than the local field in the rotating frame. In the present study on the other hand, the wave functions ψ_i^0, by which $H_Z + H_R + H_d^0 + H_d^n$ is diagonal, were adopted. Then, (10) is valid even if H_1 is smaller than H_L, and also when level crossing in the rotating frame occurs. However, (10) breaks down when the absorption spectrum shows motional narrowing.

2. Calculation of $T_{1\varrho}$. in the Rotating Frame

2.1. Transition Rates

After the decay of the transient precession of the magnetization, the equilibrium state of the system is written by the diagonal part σ_1. Then the system can be described by the population p_{0i} of the eigen state ψ_i^0. (The equilibrium state does not always mean thermal equilibrium.)

The total Hamiltonian of the system in the rotating frame is

$$H_\varrho = H_s + H_{RP} + H_P, \tag{11}$$

where H_s is given by (5). The spin-lattice relaxation is caused by the non-magnetic interaction H_{RP} between ψ_i^l states ($i = 1-16$, $l = 0, 1$). We may calculate the transition rate $W_{0a-1u}(W_{1u-0a})$ that the NH_4-ion in the ψ_a^0 state jumps to the ψ_u^1 state (and vice versa), and also $w_{0a-0b}(w_{0b-0a})$, the transition rate between two states in the ground torsional state. Since the transition rate by the direct process is proportional to $E^3 \exp(E/kT)$ [10], the transitions between the ground and first-exited torsional states are more dominant in the spin-lattice relaxation than those between the ground torsional states at the temperatures we are concerned with. Then, the spin-lattice relaxation is caused by the Orbach process [20]. The procedure to calculate $T_{1\varrho}$ is essentially the same as that to calculate T_1 by using the strong collision approach [21, 22], except that the non-exponential relaxation is dealt with in the present study.

The time dependence of the magnetization M_z (or the magnetic energy) of the NH_4-ion is presented in terms of the population p_{li} of the ψ_i^l state. We may derive a master equation (the so called the Pauli equation) for the population:

$$\dot{P}_{0a} = \sum_{j=1}^{16} W_{1j-0a} P_{1j} - \left(\sum_{i=1}^{16} W_{0a-1i}\right) P_{0a},$$

$$\dot{P}_{1u} = \sum_{s=1}^{16} W_{0s-1u} P_{0s} - \left(\sum_{v=1}^{16} W_{1u-0v}\right) P_{1u},$$

$$(a, u = 1-16), \tag{12}$$

where P_{0a} and P_{1u} are the deviations of the populations p_{0a} and p_{1u} from the thermal equilibrium values, respectively. In order to derive an available form of T_1 by the Orbach process among multiple levels, two models have been proposed [21], [22]. They are (A) the all-level model (B) the four-level model. In this section, we would like to calculate $T_{1\varrho}$ according to (A).

In the all-level model, the wave functions of the ground torsional state are given by ψ_i^0 in (6), while the states of the first-excited torsional level are approximated by $|f_i^1\rangle$ in (4). By taking into accounts of the fact that the population of the first-exited torsional state is Q times ($Q = \exp[-E_{01}/kT_L]$) smaller than that of the ground torsional state, the following transition rates are introduced:

$$W_{0a-1j-0b} = \frac{W_{1j-0a} W_{1j-0b}}{W_{1j-0a} + W_{1j-0b}} Q, \tag{13}$$

$$W_{1c-0i-1d} = \frac{W_{1c-0i} W_{1d-0i}}{W_{1c-0i} + W_{1d-0i}}, \tag{14}$$

where (13) is the transition rate that a molecule in the ψ_a^0 state goes into the ψ_b^0 state through the $|f_j^1\rangle$ state, and (14) is the rate that a molecule in the $|f_c^1\rangle$ state goes to the $|f_d^1\rangle$ state through the ψ_i^0 state.

By using (13) and (14), (12) may be approximated as

$$\dot{P}_{0k} = \sum_{b \neq k} W_{0b-0k} P_{0b} - \left(\sum_{a \neq k} W_{0k-0a}\right) P_{0k}, \quad k = 1-16, \tag{15}$$

$$\dot{P}_{1u} = \sum_{d \neq u} W_{1d-1u} P_{1d} - \left(\sum_{c \neq u} W_{1u-1c}\right) P_{1u}, \quad u = 1-16, \tag{16}$$

where

$$W_{0k-0a} = \sum_{j=1}^{16} W_{0k-1j-0a}$$

and

$$W_{1u-1c} = \sum_{i=1}^{16} W_{1u-0i-1c}.$$

In the all-level model, W_{0a-1u} is given by

$$W_{0a-1u} = |a_{au}^0|^2 W_{r_u{}^0-r_u{}^1}. \tag{17}$$

$W_{r_u{}^0-r_u{}^1}$ is the rate of the non-magnetic transition between the ground and first-exited torsional states with the same symmetry [10] and is similar in magnitude to $(\tau_r)^{-1}$.

$$W_{r_u{}^0-r_u{}^1} = k_u \exp(-E_{01}/kT_L), \quad u = 1-16. \tag{18}$$

According to the symmetry, to which $|r_u\rangle$ belongs, k_u will take different value in general. For simplicity, we assume that all k_u have the same values in the all-level model, i.e. $W_{r_u{}^0-r_u{}^1} = W_r$. Then, the transition rate W_{0a-0b} is given by

$$W_{0a-0b} = u_{ab} W_r, \tag{19}$$

where u_{ab} is a complicated function of ω_1, Λ_0 and the direction (θ, φ) of the external field H_0. We may evaluate u_{ab} by using (6): (i) When the energy separation of two states is larger than the local dipolar field, i.e. $|\varepsilon_a - \varepsilon_b|/\hbar > \gamma H_L$, we have

$$u_{ab} \sim (\hbar\gamma H_L)^2/(\varepsilon_a - \varepsilon_b)^2.$$

(ii) When the level crossing of NH_4-ion occurs (strictly speaking, when two levels are in anti crossing state), i.e. $|\varepsilon_a - \varepsilon_b|/\hbar \sim \gamma H_L$, we have $u_{ab} \sim 10^{-1} \sim 1$.

2.2. $T_{1\varrho}$ for Relatively Magnetically Isolated NH_4-ions

Let us consider the spin-exchange in NH_4-ions for $\Lambda_0 \gg \gamma H_L$. The inter-molecular dipolar interaction may be introduced in the calculation of $T_{1\varrho}$ supposing that its effect is partly to give the dipolar shift of the energy level of the $\psi_i{}^0$ state and partly to cause spin-exchange among NH_4-ions. $\psi_i{}^0$ is written as $\psi_i{}^0 = a|f_A^0\rangle + b|f_F^0\rangle + c|f_E^0\rangle$, where $|f_A^0\rangle$, $|f_F^0\rangle$ and $|f_E^0\rangle$ represent the zero-th order functions belonging to the A-, F- and E-states, respectively. Since the mixing between the A-, F- and E-spin states is very small for $\Lambda_0 \gg \gamma H_L$, it is convenient to represent $\psi_i{}^0$ by $|f_i{}^0\rangle$. The energy ε_i of $\psi_i{}^0$ may be also approximated by that of $E_i{}^0$ of the $|f_i{}^0\rangle$ state as

$$E_i{}^0 = \langle f_i{}^0 | H_Z + H_R + H_d{}^0 | f_i{}^0 \rangle. \tag{20}$$

As shown in Fig. 1 and (21), the zero-th order dipolar shift of A-spin is zero, while that of F-spin is of the order of H_L (the local field of the intra-molecular interaction H_L is about 5 Gauss). Therefore, spin-exchange between A- and F-spin by inter-molecular interaction does not occur as long as $\beta < \gamma H_L$, because this transition does not conserve energy [23]. Then, the assumption of a common spin temperature cannot be used even if $H_1 \lesssim H_L$, i.e. the treatment of SA [19] breaks down. In this section, a system where a common spin temperature is not established has been treated. In § 2.3, the relation of $T_{1\varrho}$ is given assuming a common spin temperature.

In the relatively magnetically isolated NH_4-ion system, the spin exchange among NH_4-ions is strongly restricted because $\beta < \gamma H_L$. The time dependence of $M_z(t)$ was computed by using (15) and (19). The results are plotted on a semilog scale in Figs. 4a—4c. The results in the figure may be summerized as follows. We consider the typical three cases.

i) When $\Lambda_0 \ll \gamma H_L$, the time dependence of $M_z(t)$ is single exponential (Figure 4a).

ii) When $\Lambda_0 \gg \gamma H_1$, $M_z(t)$ becomes strongly non-single exponential (Fig. 4c, $\nu = 20$ kHz, 50 kHz).

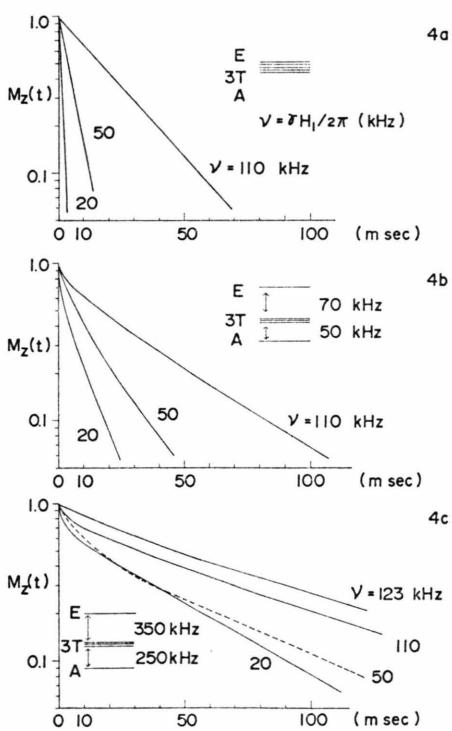

Fig. 4. Time dependence of the magnetization $M_z(t)$ in the rotating frame calculated by using Eq. (15) for $(\theta, \varphi) = (90°, 45°)$ and $W_r = 10^3$ sec^{-1}.

The magnetization $M_z(t)$ is decomposed into two species: the magnetization $M_A(t)$ of A-spins and $M_F(t)$ of F-spins. $M_E(t)$ of E-spins is almost zero and is not considered here. $M_A(t)$ relaxes slowly with the rate $k_1 \sim (\gamma^2 H_L^2/\Lambda_0^2) W_r$ and M_F fast with the rate $k_2 \sim (\gamma^2 H_L^2/4\omega_1^2) W_r$. We have

$$M_z(t) = M_A(0) \exp(-k_1 t) + M_F(0) \cdot \exp(-k_2 t), \quad (21)$$

where $M_A(0)$ and $M_F(0)$ are the initial values of $M_A(t)$ and $M_F(t)$, respectively. It is possible to determine Λ_0 by measurement of the longer relaxation time $T_1 = k_1^{-1}$ and shorter one $T_s = k_2^{-1}$ as $\Lambda_0 \sim 2\omega_1 \sqrt{T_1/T_s}$.

iii) When level crossing between A- and F-spins occurs, i.e. $\Lambda_0 \sim 2\omega_1$, $M_z(t)$ is also non-single exponential in general (Fig. 4c, $\nu = 110$ kHz, 123 kHz). We have

$$M_z(t) = M_A(0) \exp(-k_1 t) + M_F(0) \cdot \exp(-k_2 t) + M_{AF}(0) \exp(-k_3 t), \quad (22)$$

where $M_{AF}(0)$ is the initial value of the magnetization $M_{AF}(t)$ of mixed states of A- and F-spins at the level crossing. And also

$$k_1 \sim \{\gamma^2 H_L^2/(2\omega_1 + \Lambda_0)^2\} W_r,$$
$$k_2 \sim (\gamma^2 H_L^2/4\omega_1^2) W_r \quad \text{and} \quad k_3 \sim W_r.$$

Then, $M_{AF}(t)$ relaxes faster than $M_A(t)$ and $M_F(t)$. As shown in Fig. 4c, the rate of the initial decay of $M_z(t)$ is not largest when $2\omega_1 = \Lambda_0$, which is due to the fact that the magnetization $M_{AF}(0)$ of the mixted states of A- and F-spins is reduced at the level crossing.

2.3. *Expression for $T_{1\varrho}$ Assuming a Common Spin Temperature*

Consider the case where the inter-molecular distance is almost equal to the intra-molecular distance, i.e. $\beta \sim \gamma H_L$. It is possible to assume a common spin temperature because the spin exchange caused by the inter-molecular interaction conserves the spin energy. Gorter [24] derived the following expression for T_1 by assuming a common spin temperature:

$$1/T_1 = \frac{\sum_{m,n} W_{m-n}(E_m - E_n)^2}{2\sum_m E_m^2}. \quad (23)$$

We may derive a similar expression for $T_{1\varrho}$ by using the all-level model:

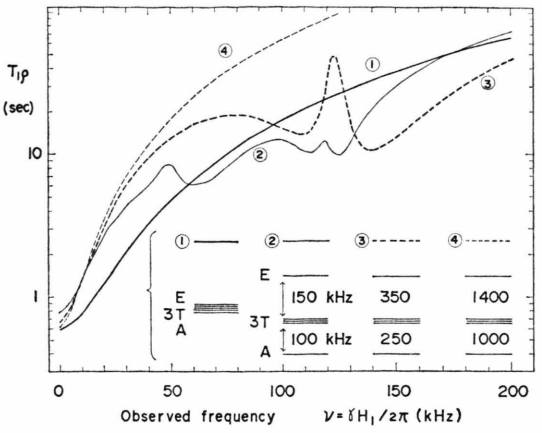

Fig. 5. H_1-dependence of $T_{1\varrho}$ calculated by using Eq. (24) for $(\theta, \varphi) = (90°, 45°)$ and $W_r = 1.0\ \text{sec}^{-1}$.

$$1/T_{1\varrho} = \frac{\sum_{i,j} W_{0i-0j}\{\varepsilon_i(Z,d) - \varepsilon_j(z,d)\}^2}{2\sum_i \varepsilon_i(z,d)^2}, \quad (24)$$

where $\varepsilon_i(z,d) = \langle \psi_i^0 | H_Z + H_d | \psi_i^0 \rangle$. The frequency dependence of $T_{1\varrho}$ was calculated by using (24). The results are summerized in Figure 5. As shown in the figure, the ω_1-dependence of $T_{1\varrho}$ does not always have a minimum value at the level crossing, i.e. $2\omega_1 = \Lambda_0$, which is, as stated before, due to the fact that the Zeeman energy of the ψ_i^0 state is reduced when $2\omega_1 \sim \Lambda_0$.

Equation (24) corresponds to the expression for $T_{1\varrho}$ which was derived by SA [19] using the strong collision theory. Equation (24) succeeds in introducing the tunneling frequency of the NH_4-ion. When $\Lambda_0 \ll \gamma H_L$ or $\Lambda_0 \gg \gamma H_L$, the spin energy $\varepsilon_i(z,d)$ can be defined without ambiguity and (24) is useful. However, (24) becomes ambiguous when $\Lambda_0 \sim \gamma H_L \sim \gamma H_1$, because the spin energy $\varepsilon_i(z,d)$ cannot be defined clearly due to the strong coupling between the spin and tunneling systems.

3. Summery and Discussion

At higher temperatures, where $\gamma H_L \tau_r \ll 1$, we obtain the following expression for the transition rate W_{ij} between two states $|f_i^0\rangle$ and $|f_j^0\rangle$:

$$W_{ij} = \frac{\gamma^4 \hbar^2}{r^6} \frac{\tau_{ij}}{1 + \{E_i(Z,R) - E_j(Z,R)\}^2 \tau_{ij}^2}, \quad (25)$$

where $E_i(Z,R) = \langle f_i^0 | H_Z + H_R | f_i^0 \rangle$ and τ_{ij} is the correlation time. The relaxation phenomena for

$\gamma H_L \tau_r \ll 1$ have been discussed [11], [15] by using (25). However, there exist some different aspects in relaxation phenomena between $\gamma H_L \tau_r \ll 1$ and $\gamma H_L \tau_r \gg 1$. It is worthwhile to point out the defect of (25) in applying it to low temperature i.e. $\gamma H_L \tau_{ij} \gg 1$. When the level crossing occurs or two degenerated states are considered, (25) yields $(\gamma^4 \hbar^2 / r^6) \tau_{ij}$, which is physically unreliable because W_{ij} becomes larger with decreasing temperature (Eq. (25) is correct for $\gamma H_L \tau_{ij} \ll 1$). In a recent work [25], T_1 of a tetrahedrally coordinated four-spin-1/2 system was discussed. Useful suggestions for the nmr study were given. However, the use of the Lorentz type spectral density in Ref. [25], to my view, leads to an incorrect result in the vicinity of the level crossing for $\gamma H_L \tau_r \gg 1$.

In the present study, a model of $T_{1\varrho}$, which is available when $\gamma H_L \tau_r \gg 1$, has been proposed for the tunneling NH_4-ion system. The transition rates were calculated on the basis of the Orbach process [20] and not of weak collision theory. When $|\varepsilon_i - \varepsilon_j|/\hbar < \gamma H_L$ in (19), we obtain $W_{0i-0j} = A W_r \sim A \tau_r^{-1}$, which is quite different from (25) with $E_i(Z, R) - E_j(Z, R) = 0$, where the coefficient A takes a value of $10^{-1} \sim 1$. When $|\varepsilon_i - \varepsilon_j|/\hbar \gg \gamma H_L$ (19) is almost equal to (25). The transition rate of (19) is always proportional to W_r and then decreases with decreasing temperature. The present model of $T_{1\varrho}$ is applicable to systems where the SA theory [19] breaks down. In compounds with relatively magnetically isolated NH_4-ions, the spin exchange, which is caused by the inter-molecular dipolar interaction, is less effective due to the dipolar shift of F-spins. Then, the relaxation for $\Lambda_0 \gg \gamma H_1$ becomes non-single exponential even if $H_1 \lesssim H_L$.

The tunneling motion of the CH_3-group also affects T_1 [9], [10]. The one dimensionality of the C_3-symmetry of the CH_3-group makes the mechanism of relaxation rather simple. When the tunneling frequency of the CH_3-group is much larger than the Larmor frequency and the intra-molecular dipolar interaction is considered, the magnetization decays with the rate $C(1/\Lambda_0^2)\tau_r^{-1}$ for $\gamma H_L \tau_r \gg 1$, where $C = \gamma^4 \hbar^2 / r^6$. However, in the case of the NH_4-ion, F-spins relax fast with the rate $C(1/\omega_0^2) \cdot \tau_r^{-1}$ (or $C(1/\omega_1^2)\tau_r^{-1}$) and A-spins slowly with the rate $C(1/\Lambda_0^2)\tau_r^{-1}$. The difference of the nature of relaxations between two species of molecules is caused by the symmetry to which the NH_4-ion (T-symmetry) and the CH_3-group (C_3) belong.

The all-level model, which was used in the calculation of $T_{1\varrho}$, was derived by using some assumptions and approximations. Then, for a final test of the present theory, it is necessary to measure $T_{1\varrho}$ especially in the vicinity of the level crossing.

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