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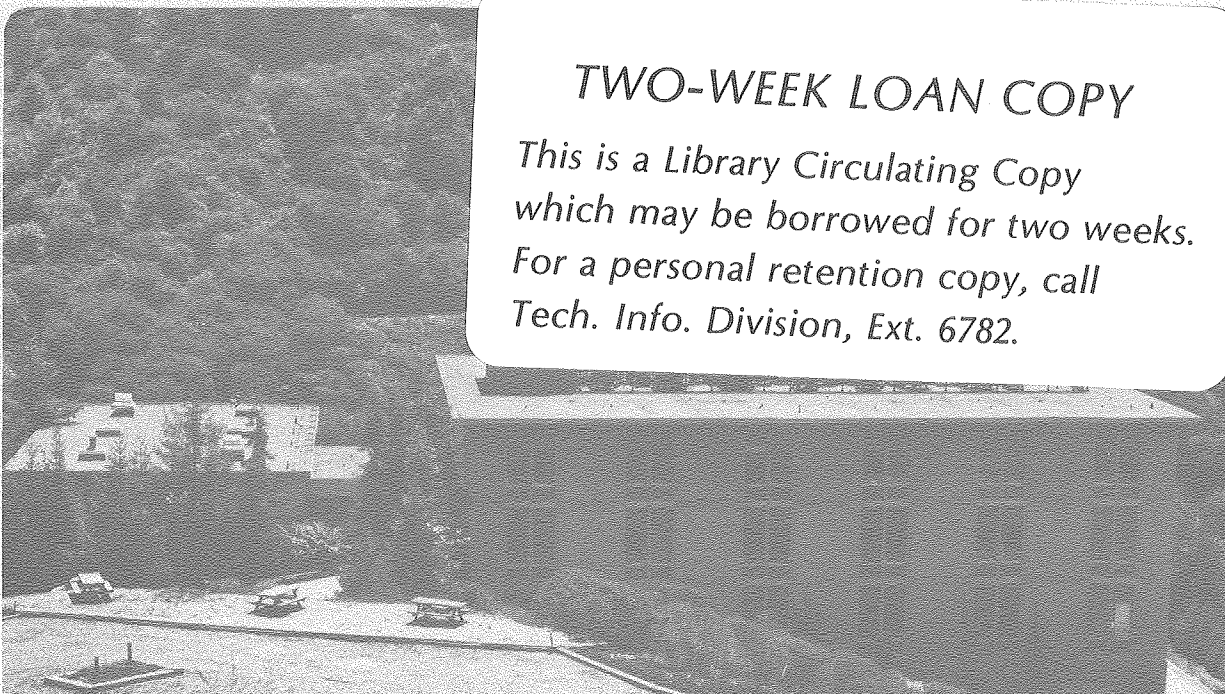
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SPIN-LATTICE RELAXATION OF REORIENTING OR TUNNELING
DEUTERATED METHYL GROUPS

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ABSTRACT

The spin-lattice relaxation of deuterated methyl groups, which is exponential at high temperatures, becomes non-exponential at low temperatures as evidence of the coupling between the Zeeman and tunneling systems. The dominant relaxation is considered to be the quadrupole interaction. Experimental results at liquid nitrogen and liquid helium temperatures support the theoretical model.

I. INTRODUCTION

The relaxation mechanism of reorienting or tunneling methyl groups in solids has been under intensive investigation [1-14]. The non-exponential nature of spin lattice relaxation [1,8,13] and the Haupt effect [6] of thermally induced dipolar polarization can be explained as a result of the dynamical couplings among Zeeman, dipolar, tunneling and the rotational polarization systems. At high temperatures the non-zero couplings are only between the Zeeman and rotational polarization systems and between the dipolar and tunneling systems, respectively.

In this paper the system of deuterated methyl (CD_3) groups in solids is studied. Some interesting new features arise due to the deuterium quadrupole coupling. In a manner analogous to the CH_3 case [11], let us assume that the relevant quasi-constants of the motion are the Zeeman, quadrupole, tunneling and rotational polarization systems. The dipolar reservoir is negligibly small in the CD_3 case. It is assumed in particular that the fluctuation of quadrupole coupling of the deuterons by random reorientation or tunneling of the methyl group is the dominant relaxation mechanism. We shall derive the relaxation equations for the above subsystems and see which subsystems are mutually coupled by relaxation. The full calculation is given in Section II. Here we mention the main findings. For random reorientation at high temperatures (i.e. $\gtrsim 77^\circ\text{K}$) Zeeman, quadrupole, tunneling and the rotation polarization systems are predicted to be uncoupled, in contrast to the CH_3 case. As a result the Zeeman spin lattice relaxation is expected to be exponential. For tunnelling CD_3 groups at low temperatures ($\ll 77^\circ\text{K}$) the Zeeman and tunneling systems are coupled and consequently, the Zeeman spin lattice

relaxation is predicted to become non-exponential. The experiments we have done to test the calculations consist of measuring the Zeeman spin lattice relaxation of dilute toluene, with the methyl group deuterated, at liquid nitrogen and liquid helium temperatures. The experimental results are discussed in Section III. We mention here that indeed the relaxation is exponential at liquid nitrogen temperature and becomes non-exponential at liquid helium temperature, thus verifying the unique expectations for CD_3 relaxation.

II. THEORY

Consider a CD_3 group with geometrical parameters shown in Figure 1. Unlike the system of methyl protons, the dominant relaxation mechanism of deuterated methyl groups is caused by the fluctuation of quadrupole coupling through random rotation of the reorienting or tunneling methyl groups. The much less efficient relaxation process due to fluctuating dipolar interactions may be neglected. The Hamiltonian of the rotating methyl deuterons in high field consists of a Zeeman term (H_Z), tunneling term (H_t), the time-averaged truncated quadrupole interaction (\bar{H}_Q) and its fluctuating nonsecular part ($H_1(t)$) responsible for relaxation:

$$H = H_Z + H_t + H_Q + \bar{H}_1(t).$$

The energy level diagram with the classification of irreducible representations of the C_3 group is shown in Figure 2. The truncated quadrupole interaction \bar{H}_Q , averaged over the random rotation is reduced by a factor of $P_2(\cos \theta)$

$$\bar{H}_Q = \frac{\omega_Q}{3} P_2(\cos \theta) P_2(\cos \beta) T_A^{(0)}$$

where $T_{\mu}^{(m)}$ is the component of symmetry-adapted tensor operator of second rank [15] and $\mu=A, E^a, E^b$ are the irreducible representations of the C_3 group [16],

$$T_{\mu}^{(m)} = T_1^{(m)} + \lambda T_2^{(m)} + \lambda^* T_3^{(m)} \quad \text{with } \mu=A, E^a \text{ or } E^b$$

for $\lambda=1, \epsilon$ or ϵ^* , $\epsilon = \exp(i2\pi/3)$ and $T_i^{(0)} = 3I_{iz}^2 - I(I+1)$, $i = 1, 2, 3$.

Here the tensor components $T_{\mu}^{(+1)}$ and $T_{\mu}^{(+2)}$ are generated from $T_{\mu}^{(0)}$ by commutation relation [15]

$$[(I_{\pm}, T_{\mu}^{(m)})] = \sqrt{I(I+1) - m(m\pm 1)} T_{\mu}^{(m\pm 1)}$$

As shown in Figure 1, β is the angle between the C_3 axis and the magnetic field and θ is the angle between the C_3 axis and the principle axis of the electric field gradient tensor.

The fluctuating term $H_1(t)$ can be expressed as a product of the symmetry-adapted tensor operators and spatial functions,

$$H_1(t) = \sum_{\mu=E^a, E^b} \sum_{m=-2}^2 \frac{\omega_Q}{3} T_{\mu}^{(m)} (F_{\mu}^{(m)}(t))^+$$

where $F_{E^a}^{(0)} = -\frac{3}{8} e^{2i\phi} \sin^2 \theta \sin^2 \beta - \frac{3}{8} i e^{i\phi} \sin 2\theta \sin 2\beta$

$$F_{E^a}^{(+1)} = -\frac{\sqrt{6}}{8} i e^{2i\phi} \sin^2 \theta \sin \beta (+1 + \cos \beta) + \frac{\sqrt{6}}{8} e^{i\phi} \sin 2\theta (\cos 2\beta + \cos \beta)$$

$$F_{E^a}^{(+2)} = \frac{\sqrt{6}}{16} e^{2i\phi} \sin^2 \theta (1 + \cos \beta)^2 - \frac{\sqrt{6}}{8} i e^{i\phi} \sin 2\theta \sin \beta (+1 + \cos \beta)$$

and $F_{E^b}^{(m)} = (-1)^m (F_{E^a}^{(-m)})^*$

The angle ϕ fluctuates randomly by fast rotation of the methyl group about the C_3 axis.

The correlation functions $G_{\mu}^{(m)}(t)$ are assumed to decay exponentially and to be characterized by a single correlation time τ_c ,

$$\left(\frac{\omega_0}{3}\right)^2 F_{\mu}^{(m)}(t) F_{\mu}^{(m^*)}(t+\tau) = \delta_{mm} G_{\mu}^{(m)}(0) \exp(-t/\tau_c).$$

They are evaluated as tabulated in Table 1.

For spin-lattice relaxation only the evolution of the diagonal part ρ_D of the density matrix is relevant [17]. Based on the Symmetry Restricted Spin Diffusion (SRSD) model [13] we assume that there are four degrees of freedom characterizing the quasiequilibrium during the relaxation process. In the high spin temperature assumption one may decompose ρ_D into a set of four traceless and mutually orthonormal operators and the unit operator with their corresponding Lagrange multipliers α_k ,

$$\rho_D \sim 1 + \alpha_1 O_1 + \alpha_2 O_2 + \alpha_3 O_3 + \alpha_4 O_4.$$

O_1 , O_2 , O_3 and O_4 defined below correspond to Zeeman, tunneling, quadrupole and rotational polarization systems respectively, i.e.,

$$O_1 = \frac{I_Z}{\sqrt{\text{Tr}(I_Z)^2}} = \frac{I_Z}{\sqrt{54}}$$

$$O_2 = \sqrt{\frac{176}{27}} \left(\frac{1}{11} |A\rangle\langle A| - \frac{1}{16} |E\rangle\langle E| \right)$$

$$O_3 = \frac{1}{3\sqrt{2}} T_A^{(0)}$$

$$O_4 = \frac{1}{4} (|E^a\rangle\langle E^a| - |E^b\rangle\langle E^b|)$$

where $|A\rangle\langle A|$, $|E^a\rangle\langle E^a|$ and etc. are projection operators.

The equation governing the relaxation of the system toward equilibrium with the lattice can be expressed by [11,13]

$$\dot{\alpha} = -S \cdot (\alpha - \alpha^{eq})$$

where α is a column-vector with components α_k . The symmetric relaxation

matrix S has the components [11,13,16]

$$S_{k\ell} = \frac{1}{2} \sum_{\mu=E^a, E^b} G_{\mu}^{(m)}(0) \sum_{m=2}^{\infty} \int_{-\infty}^{\infty} d\tau e^{-|\tau|/t_c} \text{Tr}([O_k, e^{-iH\tau} T_{\mu}^{(m)} e^{iH\tau}] [T_{\mu}^{+(m)}, O_{\ell}])$$

$$= \sum_{\mu} \sum_m G_{\mu}^{(m)}(0) \cdot \frac{2\tau_c}{1+(m\omega_o + \omega_t)^2 \tau_c^2} \text{Tr}(P[O_k, T_{\mu}^{(m)}] [T_{\mu}^{+(m)}, O_{\ell}])$$

where ω_t is the observable tunneling frequency [11] and the projection operator $p = |A\rangle\langle A|$.

The non-zero relaxation rates $S_{k\ell}$ were evaluated, yielding:

$$S_{11} = \sum_{m=1,2} \sum_{\mu=E^a, E^b} \left[\frac{G_{\mu}^{(m)}(0)}{1+(m\omega_o + \omega_t)^2 \tau_c^2} + \frac{G_{\bar{\mu}}^{(m)}(0)}{1+(-m\omega_o + \omega_t)^2 \tau_c^2} \right] 3m^2 \tau_c$$

$$S_{12} = \sum_{m=1,2} \sum_{\mu=E^a, E^b} \left[\frac{G_{\mu}^{(m)}(0)}{1+(m\omega_o + \omega_t)^2 \tau_c^2} - \frac{G_{\bar{\mu}}^{(m)}(0)}{1+(-m\omega_o + \omega_t)^2 \tau_c^2} \right] 162 \sqrt{\frac{27}{176}} m \tau_c$$

$$S_{22} = \sum_{m=0, \underline{+1}, \underline{+2}} \sum_{\mu=E^a, E^b} \frac{G_{\mu}^{(m)}(0)}{1+(m\omega_o + \omega_t)^2 \tau_c^2} \cdot \left(\frac{81}{2}\right)^2 \tau_c$$

$$S_{33} = \sum_{\mu=E^a, E^b} \left[\frac{G_{\mu}^{(1)}(0)}{1+(\omega_o + \omega_t)^2 \tau_c^2} + \frac{G_{\bar{\mu}}^{(1)}(0)}{1+(-\omega_o + \omega_t)^2 \tau_c^2} \right] 81 \tau_c$$

$$S_{44} = \sum_{m=0, \underline{+1}, \underline{+2}} \sum_{\mu=E^a, E^b} \left[\frac{G_{\mu}^{(m)}(0)}{1+(m\omega_o + \omega_t)^2 \tau_c^2} \right] 162 \tau_c$$

The quadrupole system and the rotational polarization system are characterized by a single relaxation rate S_{33} and S_{44} , respectively. However, the Zeeman system and the tunneling system are coupled through

S_{12} , which is non zero for $\omega_t \neq 0$. The spin lattice relaxation is non-exponential, in fact a sum of two exponentials. At high temperatures, when $\omega_t = 0$, the Zeeman system and the tunneling system become decoupled since $S_{12} = 0$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The spin-lattice relaxation of toluene with the methyl group deuterated and diluted in a normal protonated toluene matrix (~10% by mole) was measured at liquid nitrogen and liquid helium temperatures in a field of 42.5 kG. The corresponding resonance frequency of the deuteron NMR is 23.4 Mhz. A three-pulse sequence $180_X - \tau - 90_X - \tau' - 90_Y$ is used to measure spin-lattice relaxation. The first π pulse is to reverse the magnetization. The second and third $\pi/2$ pulses are to generate a quadrupole echo for improving S/N ratio and easier detection.

The spin-lattice relaxation time was measured on the recovery of the sharp singularity in the powder spectrum. The recovery of intensity at liquid nitrogen and liquid helium temperatures are plotted on a semi-logarithmic scale as shown in Figure 3. The relaxation is found to be exponential with a T_1 of 1.1 ± 0.1 sec. at liquid nitrogen temperature. At liquid helium temperature the spin-lattice relaxation is characterized by two exponents with relaxation rates λ_1 and λ_2 , $\lambda_1^{-1} = 0.9 \pm 0.1$ sec. and $\lambda_2^{-1} = 26 \pm 3$ sec. λ_1 and λ_2 are related to S_{kl} by

$$\lambda_1 + \lambda_2 = S_{11} + S_{22}$$

$$\lambda_1 \lambda_2 = S_{11} S_{22} - S_{12}^2$$

S_{11} , the initial slope of curve in Fig. 3(b), is measured with $S_{11}^{-1} = 12 \pm 1$ sec. S_{12} and S_{22} are calculated to be $S_{12} = -0.23 \pm 0.02$ sec.⁻¹ and $S_{22} = 0.9 \pm 0.1$ sec.⁻¹.

The non-exponentiality of spin-lattice relaxation provides evidence of the coupling between the Zeeman and tunneling systems. The inter-system coupling S_{12} is non-zero at low temperature when the tunneling is in communication with the Zeeman system, i.e., $\omega_t \sim \omega_0$ or $\sim 2\omega_0$ such that both systems may exchange energy through phonons.

Finally, we briefly compare the relaxation processes between the system of methyl protons and the system of methyl deuterons. In the first case, the protons are coupled to the lattice by dipolar interaction. This is a two-body interaction between protons. The existence of cross-correlations among the intramolecular dipolar interactions results in coupled, i.e., non-exponential spin-lattice relaxations. However, in the CD_3 case, the deuterons are coupled to the lattice by quadrupole interactions which are single particle interactions. One expects that each deuteron should be relaxed by its own interaction with the lattice and the relaxation is exponential. It is then not surprising to find the relaxation of three identical deuterons is exponential as in the case of high temperatures. However, at low temperature we apparently cannot consider each deuteron independently from the others. We are forced by the Bose-Einstein statistics to consider three deuterons as a collective system and classify the eigenstates in an appropriate manner. We then find coupled relaxation due to the statistics and the fact that when $\omega_t \neq 0$ the A states are lower in energy than the E states.

The above illustrates that the relaxation coupling is not due to cross-correlation effects, [1] but to what we like to call a statistical interference. Some of the couplings in the CH_3 case [11,13] which vanish when ω_t becomes zero are of the same nature.

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- Fig. 1 The geometry of methyl group. θ is the angle between the C_3 axis and C-D bond, and β is the angle between C_3 axis and magnetic field.
- Fig. 2 Energy level scheme with classification according to A, E^a and E^b states. ω_t is the tunneling splitting between A and E states.
- Fig. 3 The recovery of the intensity of the spectrum is plotted on a semi-logarithmic scale. (a) shows the spin-lattice relaxation at liquid nitrogen temperature is exponential with $T_1 = 1.1 \pm 0.1$ sec. (b) shows the spin-lattice relaxation at liquid helium temperature is sum of two exponentials.

TABLE 1

The symmetry-adapted correlation functions $G_{\mu}^{(m)}(o)$

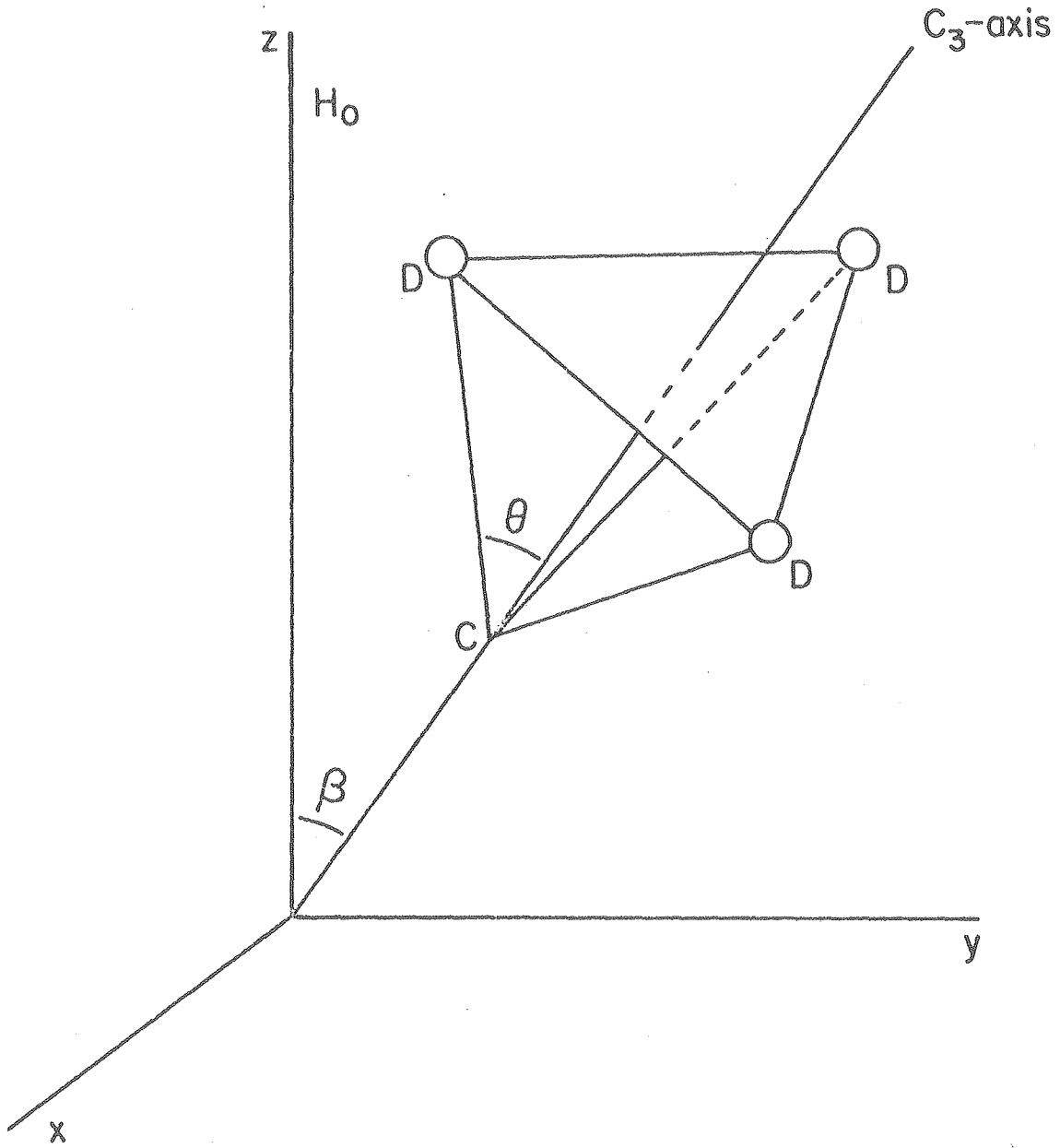
$$G_{E^a}^{(0)}(o) = G_{E^b}^{(0)}(o) = \frac{\omega_0^2}{64} \sin^4 \theta \sin^4 \beta (1 + 16 \cos^2 \theta \cos^2 \beta)$$

$$G_{E^a}^{(1)}(o) = G_{E^b}^{(-1)}(o) = \frac{\omega_0^2}{96} \left[\sin^4 \theta \sin^2 \beta (1 + \cos \beta)^2 + \sin^2 2\theta (\cos 2\beta - \cos \beta)^2 \right]$$

$$G_{E^a}^{(-1)}(o) = G_{E^b}^{(1)}(o) = \frac{\omega_0^2}{96} \left[\sin^4 \theta \sin^2 \beta (1 - \cos \beta)^2 + \sin^2 2\theta (\cos 2\beta + \cos \beta)^2 \right]$$

$$G_{E^a}^{(2)}(o) = G_{E^b}^{(-2)}(o) = \frac{\omega_0^2}{96} \left[\frac{1}{4} \sin^4 \theta (1 + \cos \beta)^4 + \sin^2 2\theta \sin^2 \beta (-1 + \cos \beta)^2 \right]$$

$$G_{E^a}^{(-2)}(o) = G_{E^b}^{(2)}(o) = \frac{\omega_0^2}{96} \left[\frac{1}{4} \sin^4 \theta (1 - \cos \beta)^4 + \sin^2 2\theta \sin^2 \beta (1 + \cos \beta)^2 \right]$$



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Figure 1

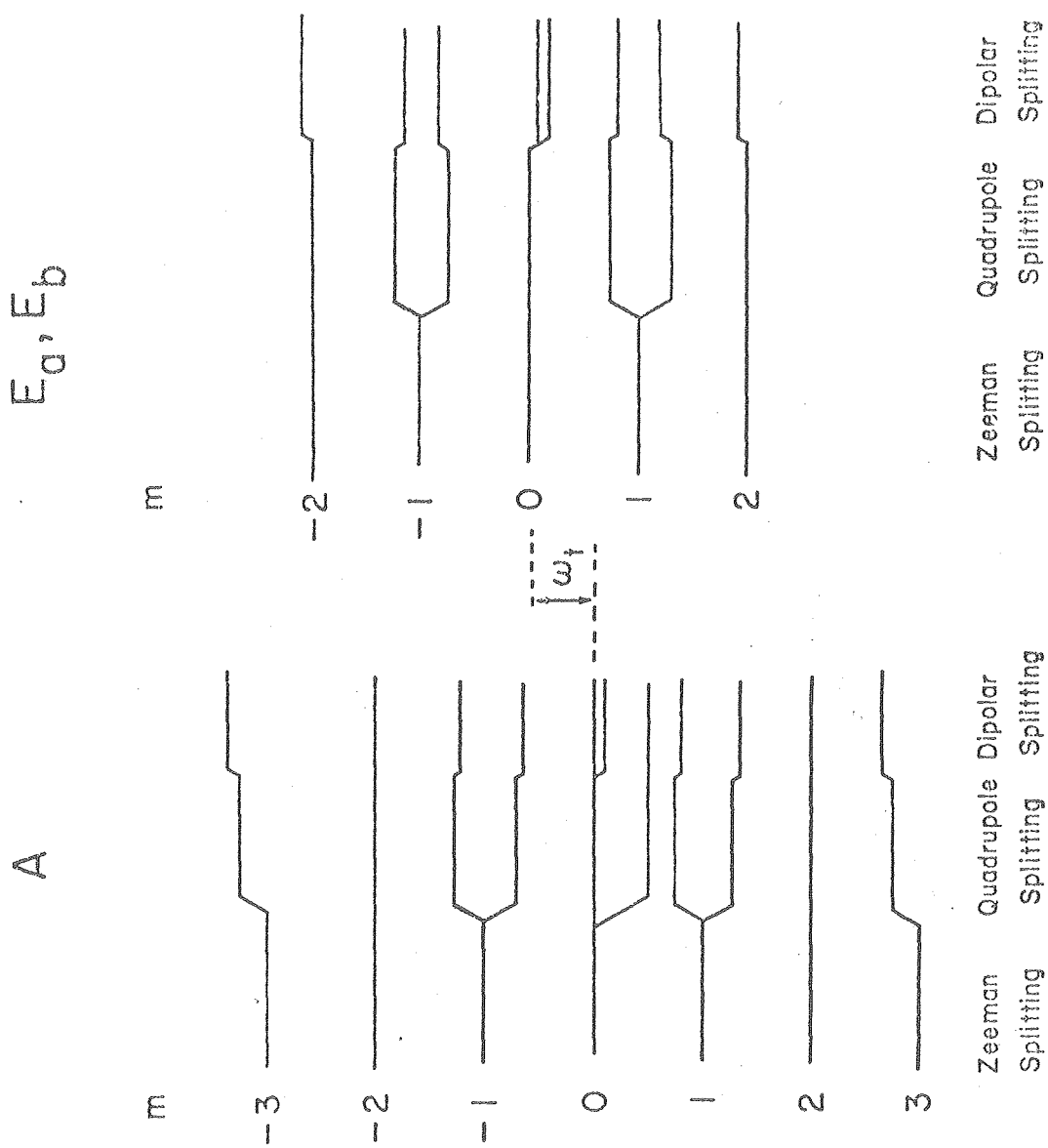
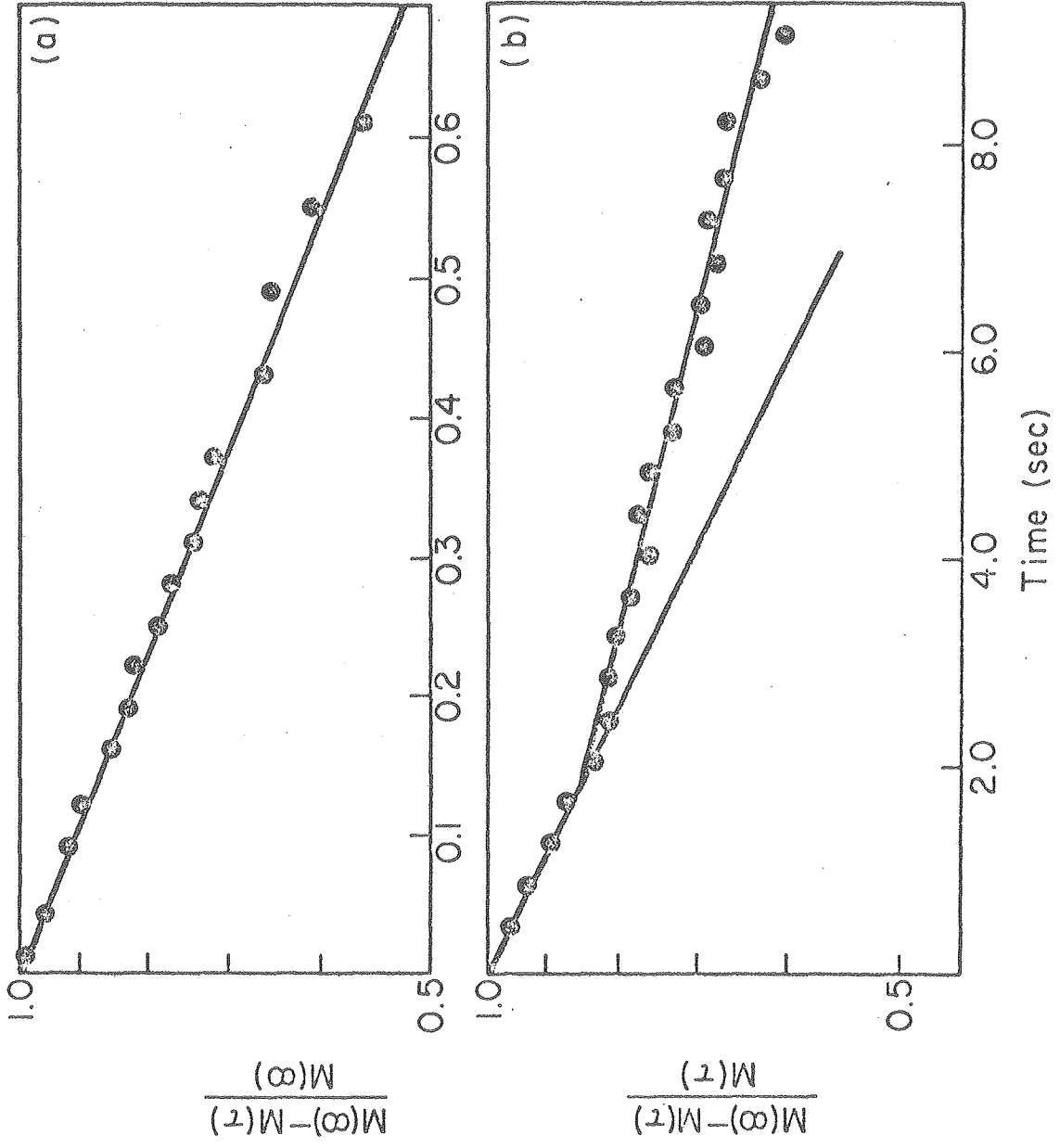


Figure 2



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