

# An Introduction to Spin Polarization Torsional Spectroscopy in the Rotating Frame

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A simple torsional oscillator is employed to introduce Spin Polarization Torsional Spectroscopy (SPOTS) (1,2). This oscillator has only two levels populated in the temperature range of interest. Their splitting, in frequency units, is  $\omega_T$  (Figure 1). In the examples discussed later, these levels are thought of as a degenerate ground state multiplet, which is split because of spacial tunneling of the oscillator (3,4,5). However, the origin of the ground state splitting is unimportant for our purpose, and the discussion applies to any atomic system with a few levels in a solid lattice. The higher oscillator eigenstates are far above the two levels we introduce.

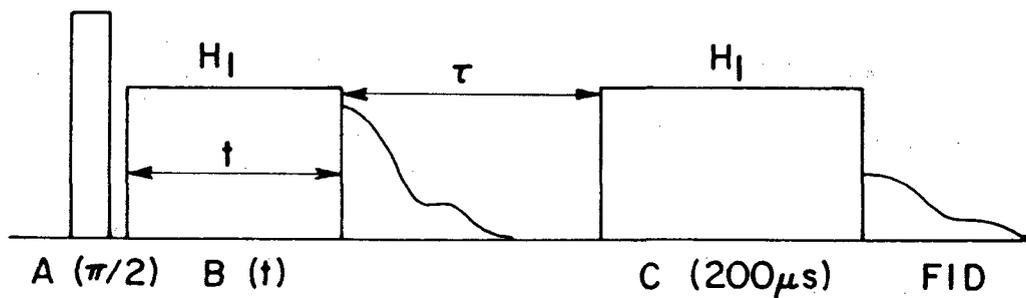
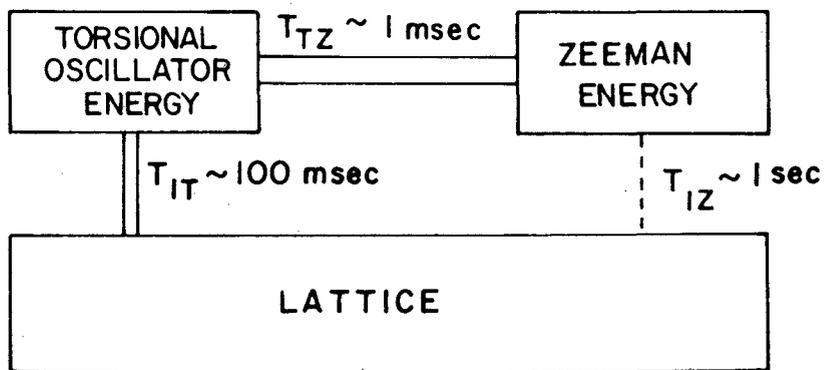
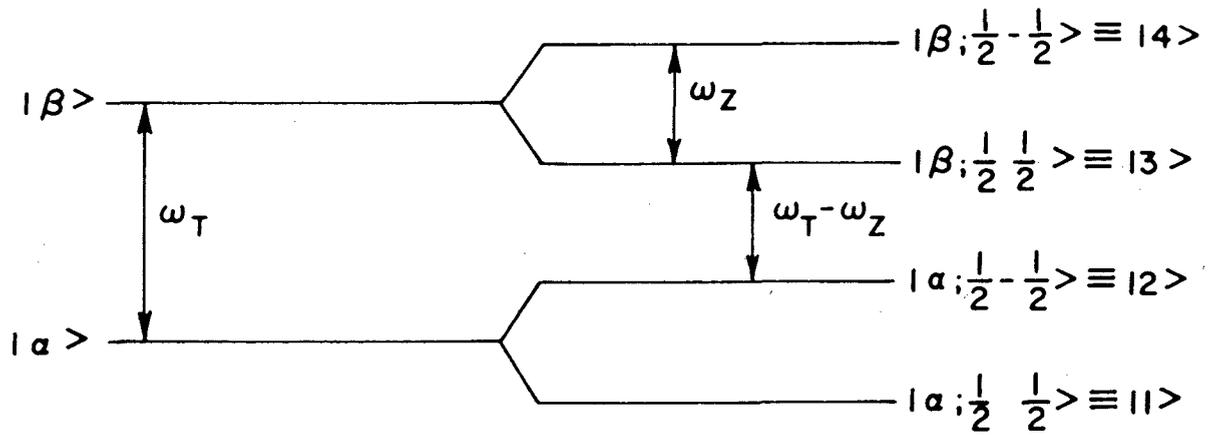
The oscillator contains one or more atoms bearing a nuclear magnetic dipole moment. Consider that only one such atom, with spin 1/2, is part of the oscillator. If a static magnetic field is applied, an oscillator may be in any of the four possible states shown in Figure 1.

In order to introduce the concept of temperature, we consider an ensemble of such oscillators which are weakly coupled among themselves and to a heat bath (lattice). With appropriate time-dependent interactions, the following transitions can be caused

may occur: torsional,  $|1\rangle \leftrightarrow |3\rangle$  and  $|2\rangle \leftrightarrow |4\rangle$ ; Zeeman,  $|1\rangle \leftrightarrow |2\rangle$  and  $|3\rangle \leftrightarrow |4\rangle$ ; and Zeeman-torsional,  $|1\rangle \leftrightarrow |4\rangle$  and  $|2\rangle \leftrightarrow |3\rangle$ . In equilibrium, the ratio of the populations is characterized by the lattice temperature. Upon excitation, the populations are disturbed but return to equilibrium with characteristic relaxation times (Figure 1).

SPOT spectroscopy is limited to those torsional oscillators in which the interaction between torsional and Zeeman energy reservoirs, which causes the transitions  $|2\rangle \leftrightarrow |3\rangle$  and  $|1\rangle \leftrightarrow |4\rangle$ , is much stronger than torsion-lattice or spin-lattice interactions. For example, a torsional oscillator  $\text{NH}_4$  in tetrahedral  $\text{NH}_4\text{I}$  has the following relaxation times in the rotating frame at 40 K:  $T_{TZ} \lesssim 1$  ms,  $T_{TT} \sim 100$  ms, and  $T_{12} \sim 1$  s. In such situations, the concept of a spin-torsional temperature may be applicable. In addition to these, there are also relaxation times which represent the friction within the spin system ( $T^2$ ) and an analogous relaxation time for the torsional system. The spin-spin relaxation time thus attenuates any oscillation of Zeeman populations.

If appropriate radio frequency (RF) pulse sequences are employed, it is possible to:



**Figure 1. TOP:** A model four-state system (see text). **Middle:** Thermostatic picture of relaxation with torsional and Zeeman states strongly coupled. **Bottom:** A particular

SPOT pulse sequence used for measuring the torsional relaxation time. The equal phases of pulses B and C are shifted  $90^\circ$  with respect to the pulse A.

1. observe the establishment of the spin-torsional semiequilibrium
2. measure the torsional specific heat  $C_T$
3. transfer the order from the Zeeman to the torsional system and in the reverse direction
4. measure the torsion-lattice relaxation time
5. measure the effective spin-lattice relaxation time in the rotating frame as well as the true spin-lattice relaxation time.

The above experiments are now introduced briefly, and the results with either  $\text{NH}_4\text{I}$  or  $\text{CH}_3\text{CD}_2\text{I}$  are given as examples.

(1) To study the establishment of a Zeeman-torsional semiequilibrium requires disturbance of the initial equilibrium. The most effective nonequilibrium situation is achieved by establishing a large nuclear spin magnetization in the rotating frame. This is accomplished with the so-called spin-locking pulse sequence (6). In this sequence, the first pulse  $A$  ( $\pi/2$ ) rotates the magnetization through  $90^\circ$  into the  $x$  direction in the rotating frame. The second pulse  $B(\omega, t)$  is phase shifted by  $90^\circ$  so that in the rotating frame the field is set parallel to the magnetization. Pulses  $A$  and  $B$  follow each other without delay. With this spin-locking technique, the nuclear spin temperature in the rotating frame is reduced by a factor  $H_1/H_0$ . In a typical experiment, the lattice temperature is kept at 10 K to ensure that  $T_{1T}$  is long enough to satisfy  $T_T \gg T_{1T}$ . If the static field is  $10^4$  G and the resonant RF field has an amplitude of 10 G, the nuclear spin population is characterized in the rotating frame by a spin temperature of  $10^{-2}$  K. This is achieved in  $\sim 10^{-6}$  s.

If the Zeeman-torsional interaction is strong, the transitions  $|3\rangle \leftrightarrow |2\rangle$  and  $|1\rangle \leftrightarrow |4\rangle$  occur quickly, and the initial very low temperature of the Zeeman energy reservoir rises sharply. The temperature of the torsional energy reservoir decreases correspondingly. In this process, a part of the nuclear dipolar order is transferred to the torsional system. If no energy is lost to the lattice, the final temperature will depend on the specific heats of the two energies as follows (7)

$$\beta_f(C_z + C_T) = \beta_i C_z + \beta_L C_T \quad (1)$$

in which the specific heat is defined as  $C_i = \partial E_i / \partial \beta$ , where  $\beta$  is the inverse temperature  $1/kT$ . The initial inverse temperature  $\beta_i$  is equal to the Zeeman inverse temperature established by spin-locking:  $\beta_i = \beta_L H_0 / H_1$  and the initial torsional inverse temperature

is equal to the lattice inverse temperature  $\beta_L$ . Since  $C_T \sim C_z$  near resonance ( $\omega_T \sim \omega_i$ ), the term  $\beta_i C_T$  is negligible in comparison to  $\beta_L C_z H_0 / H_1$  and is left out. Eq. 1 becomes

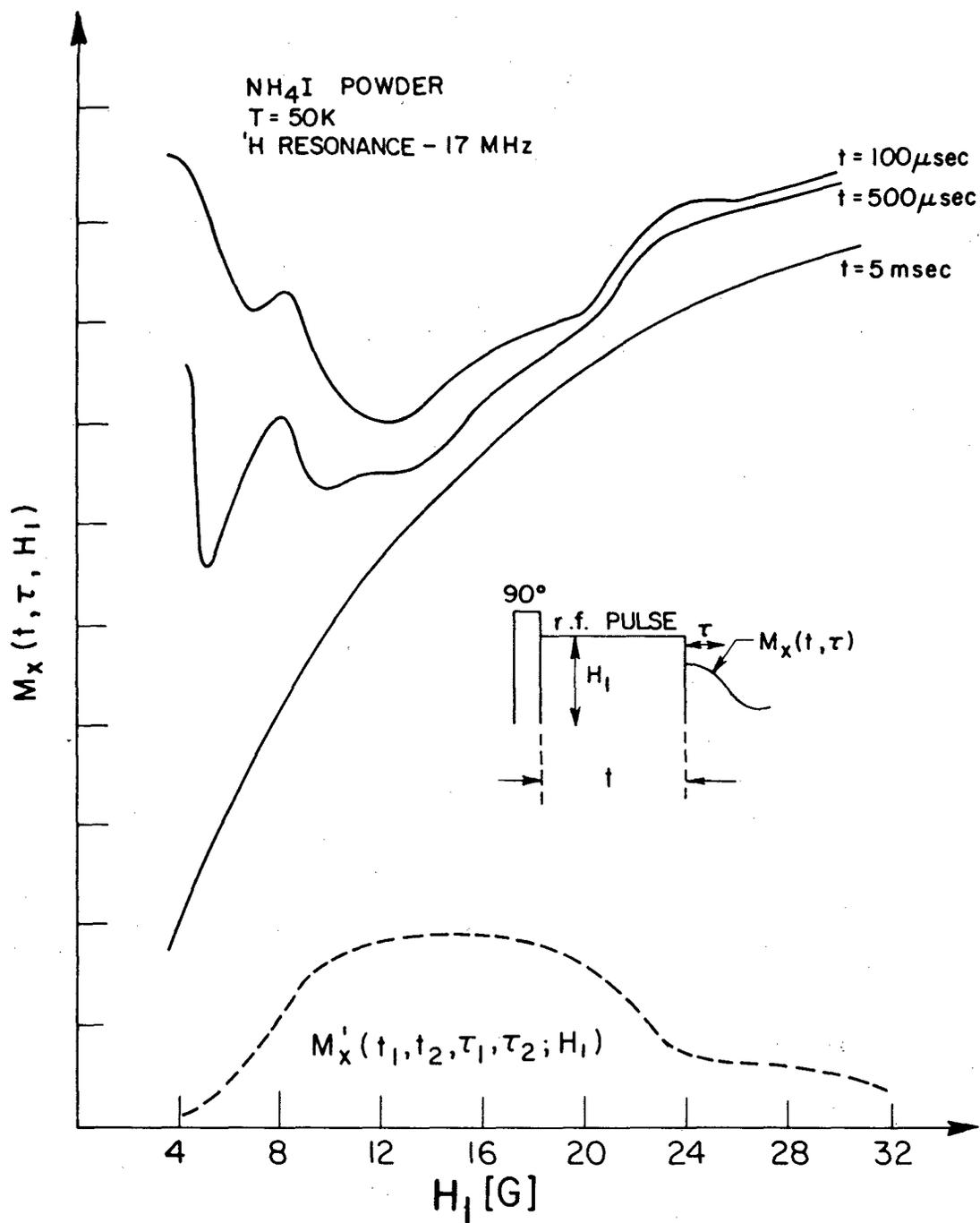
$$\beta_f = \beta_i C_z / (C_z + C_T) \quad (2)$$

If we reverse the argument, this relation can be used to test the existence of a semiequilibrium. It can be assumed that the interaction which causes fast Zeeman-torsional transitions in the RF frame of nuclear magnetic dipoles is strong near resonance and that it becomes weaker when the resonant condition is not fulfilled. As the Zeeman specific heat in the rotating frame is altered by changing the RF amplitude  $H_1$  ( $C_z \propto H_1^2$ ), the matching of the two energy reservoirs changes. On resonance, the semiequilibrium may be established in  $\sim 100 \mu\text{s}$ , but when the Zeeman levels do not match the torsional levels closely, it may take much longer.

This dependence is illustrated in Figure 2. The magnetization  $M_z$  of protons in  $\text{NH}_4\text{I}$  is shown as a function of the RF amplitude  $H_1$  (2). The durations  $t$  of the RF pulse  $B(t)$  are 0.1, 0.5, and 5 ms. The readings were taken  $9 \mu\text{s}$  after the RF pulse was switched off. If the RF field is on for  $100 \mu\text{s}$  when the torsional-Zeeman transitions occur, semiequilibrium is reached in the  $H_1$  interval 14 to 22 G approximately. If mixing occurs for  $500 \mu\text{s}$ , the equivalent  $H_1$  interval is slightly wider. After 5 ms, the semiequilibrium is reached at all fields from 4 to 32 G. However, it should be noted that in those 5 ms approximately 5% of the polarization was lost to the lattice (Figure 2).

In order to measure the relaxation time  $T_{1T}$ , the magnetization has to be measured as a function of  $B(t)$  duration at a set value of the RF amplitude  $H_1$ . This experiment has not been done. A rough estimate is  $T_{1T} \sim 100 \mu\text{s}$  in the 14 to 22-G range and longer outside this interval (Figure 2).

(2) In the RF frame which was set up by a spin-locking pulse, Eq. 2 is valid. It holds for all values of the Zeeman specific heat  $C_z$ , provided that true semiequilibrium has been reached. The specific heat  $C_T$  is obtained from the measurement of  $M_z$  at  $t = 5$  ms at various  $H_1$  fields in the range 4 to 32 G (Figure 2). According to Eq. (2),  $\beta_f = \beta_i/2$ , or  $M_z = M_0/2$ , when  $C_z = C_T$ . This is reached at  $H_1 = 12.5 \pm 1.0$  G (Figure 2). It follows that the torsional specific heat in  $\text{NH}_4\text{I}$  at 50 K is equal to the specific heat of the Zeeman reservoir at  $H_1 = 12.5$  G. Thus, the apparent torsional field  $H_T$  is 12.5 G. It should be noted that the apparent field



**Figure 2.** Proton magnetization  $M_x$  in powdered  $\text{NH}_4\text{I}$  at 40 K as a function of the RF field  $H_i$  plotted for three values of the allowed mixing time  $t$ : 100, 500, and 5000  $\mu\text{s}$ . The

reading was taken at  $\tau = 14\ \mu\text{s}$ . The shape of the lowest curve suggests that a spin-torsional semiequilibrium may have been reached.

$H_T$  is not equal to the tunneling (torsional splitting) frequency  $\omega_T$  divided by  $\gamma$ .

(3) During the RF pulse of the spin-locking sequence, the Zeeman-torsional transitions transfer some polarization from the Zeeman to the torsional energy reservoir. In  $\sim 200 \mu\text{s}$ , the two energy reservoirs are characterized by a common temperature. If the RF pulse is reintroduced after a delay  $\tau$  (Figure 1, bottom), the transfer of polarization occurs during the RF pulse  $C$  ( $200 \mu\text{s}$ ) in the opposite direction, i.e., from the torsional to the Zeeman energy. This occurs because during the delay  $\tau$  the Zeeman levels in the rotating frame do not exist. They are reestablished (with a very high Zeeman temperature) with the RF pulse  $C$ . This second pulse is on for  $200 \mu\text{s}$  to allow enough time for the two energy reservoirs to achieve a new semiequilibrium. The final inverse temperature which was characteristic of Zeeman and torsional states at the end of pulse  $B$  becomes the initial inverse temperature in pulse  $C$ . From Eq. 2, the final inverse temperature becomes

$$\beta_f = [\beta_i C_z / (C_z + C_T)] [C_T / (C_z + C_T)] \quad (3)$$

During pulse  $C$ , the torsional reservoir is "cold" and the Zeeman reservoir "hot". Therefore, the roles of  $C_T$  and  $C_z$  are reversed in Eq. 3 compared with Eq. 2.

The Zeeman magnetization  $M_z(t, \tau_1, t_2, \tau_2)$ , which was established during pulse  $C$ , was observed as a function of the field  $H_i$  (Figure 2, bottom line). The duration of pulse  $C$  was sufficient to permit a proper semiequilibrium to be reached only for  $10 \lesssim H_i \lesssim 24\text{G}$ . The experimental magnetization has the right magnitude, since the final inverse temperature  $\beta_f$  is  $\beta_i/4$  at  $C_z = C_T$ . This sets the maximum signal at  $0.25 M_0$ . The observed signal is  $\sim 0.2 M_0$ .

It should be noted the  $\beta_f$  in Eq. 3 has a maximum at  $C_z = C_T$ . Such a maximum was found experimentally in an analogous dipolar-Zeeman order transfer experiment (8).

(4) The same pulse sequence  $A B \tau C$  with a variable delay  $\tau$  was used to measure the torsional relaxation time  $T_{1T}$ . The order which is transferred from Zeeman to torsional states during  $B$  is lost because of the torsional-phonon interaction if the delay is long enough. Since during the delay  $\tau$  an states are switched off, the torsional states relax to the lattice undisturbed by spins. It is interesting to note that the relaxation process which is due to the torsional-phonon interaction appears to preserve the

symmetry of the spin state since it involves no spin operators.

It was observed that the order is lost exponentially (8) during the delay  $\tau$ . Any remaining order of the torsional energy reservoir is shared with Zeeman states during pulse  $C$ . The magnetization observed is an exponential function of the delay  $\tau$

$$M(\tau) \propto \exp(-\tau / T_{1T})$$

This relaxation time was measured in powdered  $\text{NH}_4\text{I}$  as a function of temperature from 4 to 60 K. It depends linearly on temperature in the interval of 4 to 40 K, and becomes progressively more temperature dependent as  $T$  is increased from 40 to 60 K. Some information about the oscillator states which are significantly populated in the temperature range of observation is contained in the temperature dependence of  $T_{1T}$  (9).

(5) If the torsional oscillator ground state multiplet is strongly coupled to the Zeeman states, the relaxation in the rotating frame is analogous to the relaxation when dipolar and Zeeman energies are strongly coupled. If the observed common spin-lattice relaxation time in the rotating frame is  $T_{1Q}$ , the following spin thermometric equation holds

$$T_{1Q}^{-1} (C_z + C_T) = T_{1z}^{-1} C_z + T_{1T}^{-1} C_T \quad (4)$$

Eq. 4 was tested in  $\text{NH}_4\text{I}$  at one value of  $H_i$  at 49 K. A  $T_{1T}$  of 100 ms and the specific heat were determined independently. When these values of  $T_{1T}$  and  $C_T$  were inserted in Eq. 4, the relaxation time  $T_{1Q}$  was calculated to be  $308 \pm 45$  ms. The measured  $T_{1Q}$  was  $315 \pm 20$  ms. This implies that the true Zeeman relaxation rate  $T_{1z}^{-1}$  was negligible (9). In addition,  $T_{1Q}$  was measured as a function of  $H_i$  in the region of strong Zeeman-torsional coupling and was found to obey Eq. 4 with  $T_{1z}^{-1} = 0$ . A more convenient form of Eq. 4 is

$$T_{1Q}^{-1} (H_i^2 + H_T^2) = T_{1z}^{-1} H_i^2 + T_{1T}^{-1} H_T^2 \quad (5)$$

With a computer fit of Eq. 5 to the experiment, the parameters  $T_{1T}$  and  $H_T$  were derived. Their values agreed with independent measurements of  $T_1$  and  $H_T$ .

The above thermostatic measurement in the rotating frame of nuclear magnetic dipoles provides only unresolved ( $C_T$ ) or indirect ( $T_{1T}$ ) information about the torsional ground state multiplet. In an attempt to improve the resolution, the establishment

of semiequilibrium was studied as well in the time interval before semiequilibrium was reached. It was observed that the magnetization oscillates. This is analogous to the situation when the Zeeman and dipolar reservoirs strongly coupled. The oscillations are damped by the spin-spin interaction and disappear when semiequilibrium is reached ( $\sim 100 \mu\text{s}$ ). Since the oscillations contain torsional frequencies and thus direct information about the tunneling split ground state, a pulse sequence was designed to study the time evolution of magnetization in the rotating frame (10,11).

The SPOTS sequence is a set of spin-locking pulses,  $A (\pi/2) B (t)$ , separated by approximately  $5T_1$ . Each spin-locking pulse sequence has its pulse  $B$  progressively longer than the previous spin-locking sequence. One- $\mu\text{s}$  time increments were used from 1 to 100  $\mu\text{s}$ . With such a set of 100 spin-locking pulses, the magnetization  $M_x(t)$  is monitored as it evolves in an oscillatory way from its initial nonequilibrium value  $M_0$  to its equilibrium value  $M_0 H_x / (H_x + H_y)$ . The time evolution of  $M_x(t)$  is then Fourier-transformed to give the SPOT spectrum.

The new method may be described as Fourier-transformed spectroscopy in the rotating frame. The central idea is to observe the time evolution of the nuclear magnetism of the sample under the conditions in which the nuclear Larmor frequency in an applied magnetic field is roughly equal to the torsional tunneling frequency of the atomic group containing the magnetic nuclei. Under these circumstances, the evolution is greatly affected by the magnitude of the tunneling frequency, which can therefore be measured. The Larmor frequency in the rotating frame implies that only small tunneling splittings may be studied.

Since the evolution of nuclear magnetization is observed in the rotating frame, the Hamiltonian has to be transformed. If the dipolar interaction is transformed in the rotating frame, only two terms are left which are capable of inducing Zeeman-torsional transitions:  $\mathcal{H}_D^{(2)}$  and  $\mathcal{H}_D^{(-2)}$ . They connect states which differ in  $m$  by  $\pm 2$ . This is in essence the selection rule for SPOT spectroscopy. A brief discussion of the procedure is as follows (12).

The Hamiltonian for the spin-torsional system in a static magnetic field  $\mathcal{H}_0 z$  and a rotating magnetic field  $\mathcal{H}_1 = 2\mathcal{H}_1 [\text{xcos } \omega t + \text{ysin } \omega t]$  is

$$\mathcal{H}(t) = \mathcal{H}_z + \mathcal{H}_R + \mathcal{H}_D + \mathcal{H}_x \quad (9)$$

The nuclear Zeeman term  $\mathcal{H}_z$  is the sum of the individual Zeeman terms

$$\mathcal{H}_z = \sum_i -h\omega_0 I_{zi}$$

The explicit form of the rotational Hamiltonian  $\mathcal{H}_R$  is not required. Only matrix elements of the torsional Hamiltonian will be introduced and treated as parameters of  $\mathcal{H}_R$ . The dipolar interaction  $\mathcal{H}_D$  contains products of spin and spatial operators and is written as a sum of terms  $\mathcal{H}_D(q)$

$$\mathcal{H}_D = \sum_{q=-2}^2 \mathcal{H}_D(q) = \sum_q \sum_{i < j} K_{ij} (-1)^q U_{ij}^{(q)} V_{ij}^{(q)}$$

The dipolar coupling constant is  $K_{ij} = \gamma^2 \hbar^2 / r_{ij}^3$ , where  $r_{ij}$  is the magnitude of the vector spins  $i$  and  $j$ . Since in  $\text{CH}_3$  and  $\text{NH}_4$  all the spin-spin distances are the same, we set  $K_{ij} = K_D = \gamma^2 \hbar^2 / r_0^3$ . The quantities  $U_{ij}^{(q)}$  and  $V_{ij}^{(q)}$  are the  $q$ th components of spherical tensor operators of rank 2, the former a spatial operator, and the latter a spin operator. The  $U_{ij}^{(q)}$  are expressed in terms of spherical harmonics as

$$U_{ij}^{(q)} = (6\pi/5)^{1/2} Y_2^{(q)}(\theta_{ij}, \phi_{ij})$$

where angles  $\theta_{ij}$  and  $\phi_{ij}$  are the spherical polar angular components of the vector  $r_{ij}$ .

The spin operators are written in terms of single spin raising and lowering operators,  $I_i^+$  and  $I_i^-$ , and  $I_i^0 = I_{zi}$

$$V_{ij}^{(0)} = -(\frac{8}{3})^{1/2} [I_i^0 I_j^0 - (I_i^+ I_j^- + I_i^- I_j^+)/4]$$

$$V_{ij}^{(+1)} = \pm (I_i^0 I_j^+ + I_i^+ I_j^0)$$

$$V_{ij}^{(+2)} = -I_i^+ I_j^+$$

The operator  $\mathcal{H}_D^{(q)}$  thus connect states whose spin quantum numbers  $M$  differ by  $\pm |q|$ , where  $|q| = 0, 1, 2$ .

The interaction of the spins with  $H_1$  is

$$O_x = 2\hbar\gamma\mathcal{H}_1 [I_x \cos \omega t + I_y \sin \omega t]$$

In the rotating frame the density matrix depends on time because of  $\mathcal{H}(t) - \mathcal{H}_z$ . The corresponding time evolution operator is

$$U(t) = \exp(i\omega I_x t)$$

Upon transformation  $U\mathcal{H}_x U^\dagger$ , at exact resonance, the Hamiltonian becomes

$$\mathcal{H}_p = -\hbar\gamma H_1 I_x + \mathcal{H}_R + \mathcal{H}_D(t)$$

Since the torsional Hamiltonian contains no spin operators, it is unaffected by this transformation which is a rotation in spin space only.

The time dependence of  $\mathcal{H}_x$  has vanished and  $\mathcal{H}_D(t)$  has taken on the time dependence

$$\mathcal{H}_D(t) = \sum_q \mathcal{H}_D^{(q)}(t) = \sum_q e^{iq\omega_0 t} \mathcal{H}_D^{(q)}$$

With the exception of the secular term  $\mathcal{H}_D^{(0)}$  which commutes with  $I_z$ , the rotating frame dipolar operator is time dependent. Since the frequencies  $\omega_0$  and  $2\omega_0$  are so much greater than the characteristic frequencies of the rest of the system (assuming that the tunneling splittings are comparable to the Zeeman splittings in the rotating frame), we drop the time dependent terms and retain only  $\mathcal{H}_D^{(0)}$ .

We must perform a rotation of the axes in spin space. This transforms the operator  $I_x$  into  $I_z$ , through the transformation  $U_y = \exp(-i\pi I_y/2)$ . The transformed Hamiltonian is

$$\begin{aligned} \tilde{\mathcal{H}}_D = & \hbar\gamma H_1 I_z + \mathcal{H}_R - \frac{1}{2} \mathcal{H}_D^{(0)} + \\ & \sqrt{\frac{3}{8}} [\mathcal{H}_D^{(2)} + \mathcal{H}_D^{(-2)}] \end{aligned}$$

It is customary to write  $\frac{1}{2} \mathcal{H}_D^{(0)}$  as  $\mathcal{H}'_D + \mathcal{H}''_D$ , where  $\mathcal{H}'_D$  is diagonal, while  $\mathcal{H}''_D$  connects only states of different symmetry and is therefore off diagonal.

The Hamiltonian has thus been written as the sum of two commuting operators,  $\mathcal{H}_Z$  and  $\mathcal{H}_{RD} \equiv \mathcal{H}_R + \mathcal{H}'_D$ , plus an operator  $D$  which commutes with neither  $\mathcal{H}_Z$  nor  $\mathcal{H}_{RD}$ . It is convenient to choose a representation in which  $\mathcal{H}_Z$  and  $\mathcal{H}_{RD}$  are diagonal. In this representation, the relevant quantum numbers are the magnetic quantum number  $M$  and a number  $R$  which identifies a secular torsional-dipolar stationary state

$$\mathcal{H}_0 |RM\rangle = \hbar\omega_{RM} |RM\rangle$$

with

$$\mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_{RD}$$

$$\mathcal{H}_Z |RM\rangle = \hbar\omega_M |RM\rangle$$

and

$$\mathcal{H}_{RD} |RM\rangle = \hbar\omega_R |RM\rangle$$

For symmetry in the notation, the Zeeman frequency  $-M\omega$  has been written  $\omega_M$ , and  $(\omega_R + \omega_M)$  written  $\omega_{RM}$ .

If the torsional splittings are much larger than the dipolar splittings, it is reasonable to assume that the energy levels of the combined system will be essentially those of the torsional system, with small shifts which are due to the dipolar interaction  $\mathcal{H}'_D$ . The dipolar shifts depend on the angles between the magnetic field and the spin-spin vectors. In a polycrystalline material, the powder-averaged dipolar shift gives rise to a broadening of the torsional levels.

When the torsional splittings are comparable to the dipolar splittings,  $\mathcal{H}''_D$  causes a strong mixing of states of different symmetry (the eigenstates of  $\mathcal{H}_R$ ) within the manifold of the torsional-dipolar system. For this reason, the splittings which result cannot easily be related to the eigenvalues of  $\mathcal{H}_R$  alone.

The eigenvalues  $\hbar\omega_R$  were calculated earlier for the methyl group when the lineshape for tunneling methyl groups was evaluated (13).

It is assumed that at the beginning of pulse  $B$  the initial conditions are such that the Zeeman and torsional-dipolar systems are each in a different internal equilibrium so that they may be assigned the inverse temperatures  $\alpha_0$  and  $\beta_0$  respectively. In the high temperature approximation, the initial density matrix is

$$\rho_0 = Q^{-1} (1 - \alpha_0 \mathcal{H}_Z - \beta_0 \mathcal{H}_{RD})$$

where  $Q$  is the partition function  $\text{Tr}\{1\}$ . The trace of  $\mathcal{H}_Z$  vanishes because of the symmetry of its eigenvalues about the zero of Zeeman energy. The zero of torsional energy is not defined, and so it is convenient to choose it such that  $\text{Tr}\{\mathcal{H}_{RD}\} = 0$  within the manifold of the ground torsional state. The contributions of the higher excited torsional states to  $Q$  are neglected. For this reason, this calculation applies to low temperature solids.

The time evolution of the density matrix which is due to the non-diagonal perturbation  $D$  was calculated with a perturbation series approach, taking  $\mathcal{H}_0$  as the unperturbed Hamiltonian. For the perturbation approach to be valid,  $D$  must be small compared with  $\mathcal{H}_0$ . The perturbation series for the expectation value of an observable  $A$  contains terms of various orders in  $\langle A \rangle / \langle D \rangle$  and only the lowest order non-zero term was calculated. This result describes the time evolution of the Zeeman energy quite well.

Similarly, if the tunneling splittings are large compared with the non-secular dipolar interaction, the lowest order term will describe the time evolution of the torsional-dipolar system. For smaller splittings in the order of the dipolar splittings, higher order terms may be required for  $\langle \mathcal{H}_{RD}(t) \rangle$ . The calculation was done in an interaction picture described by

$$A(t) = S(t) A S^\dagger(t), \quad i\hbar \partial_{Q_i} / \partial t = [D(t), Q_i],$$

and

$$S(t) = \exp(i/\hbar \mathcal{H}_0 t).$$

The initial density matrix in this interaction picture coincides with the equilibrium density matrix  $\rho_0$ .

The solution for  $\rho_i(t)$  is found in series form by iteration. The equation of motion is integrated to second order, taking  $\rho_i = \rho_0$  as the zeroth approximation

$$\rho_i(t) = \rho_0 - (i/\hbar) \int_0^t d\tau [D(\tau), \rho_0] - (1/\hbar^2) \int_0^t d\tau \int_0^{\tau} d\tau' [D(\tau), [D(\tau'), \rho_0]]$$

With  $\rho_i(t)$ , the time-dependent expectation value of an observable  $A$  is calculated as

$$\langle A \rangle = \text{Tr}\{\rho_i(t) A_i(t)\}$$

The expectation value of the Zeeman energy  $\langle \mathcal{H}_z \rangle$  is calculated first. The expectation value of the z-component of magnetization may be derived directly from  $\langle \mathcal{H}_z \rangle$  as follows

$$\langle M_z \rangle = \langle \mathcal{H}_z \rangle / \omega$$

Since  $\mathcal{H}_z$  commutes with  $\mathcal{H}_0$ , it is unaffected by the transformation to the interaction picture. The expectation value is

$$\langle \mathcal{H}_z(t) \rangle = \{A_0 + A_1 + A_2 + \dots\}$$

where the  $A_i$  represent the contributions of the various terms in the series for  $\rho_i(t)$

$$A_0 = \text{Tr}\{\mathcal{H}_z \rho_0\}$$

$$A_1(t) = -(i/\hbar) \int_0^t d\tau \text{Tr}\{\mathcal{H}_z [D(\tau), \rho_0]\}$$

$$A_2(t) = -(1/\hbar^2) \int_0^t d\tau \int_0^{\tau} d\tau' \text{Tr}\{\mathcal{H}_z [D(\tau), [D(\tau'), \rho_0]]\}$$

The traces are evaluated in the basis  $\{|MR\rangle\}$  of  $\mathcal{H}_0$ . The details of the calculations are given in reference 13. The first term gives the zero order static contribution corresponding to the initial conditions

$$A_0 = -\alpha_0 Q^{-1} \text{Tr}\{\mathcal{H}_z^2\}$$

and the first order term vanishes identically. The second order term,  $A_2$ , is time dependent

$$A_2(t) = Q^{-1} \sum_{R'M'} \sum_{R''M''} [\alpha_0(\omega_M - \omega_{M'})^2 + \beta_0(\omega_M - \omega_{M'}) (\omega_R - \omega_{R'})] / (\omega_{RM} - \omega_{R'M'})^2 \times |\langle RM | D | R' M' \rangle|^2 \{1 - \cos[(\omega_{RM} - \omega_{R'M'})t]\}$$

To second order, the expectation value of the Zeeman energy is

$$\langle \mathcal{H}_z(t) \rangle = A_0 + A_2(t)$$

In complete analogy to second order, the expectation value of the secular torsional-dipolar energy is

$$\langle \mathcal{H}_{RD} \rangle = B_0 + B_2(t)$$

The form of the time dependence is identical to that of the Zeeman energy. The contribution of the non-secular interaction must be taken into account as well

$$\langle D \rangle = C_0 + C_1(t) + C_2(t) + \dots$$

Comparison of terms  $A_2(t)$ ,  $B_2(t)$ , and  $C_1(t)$  shows that, to second order in  $D$ , the total energy of the Zeeman, secular torsional-dipolar, and non-secular torsional-dipolar systems is a constant

$$A_2(t) + B_2(t) + C_1(t) = 0$$

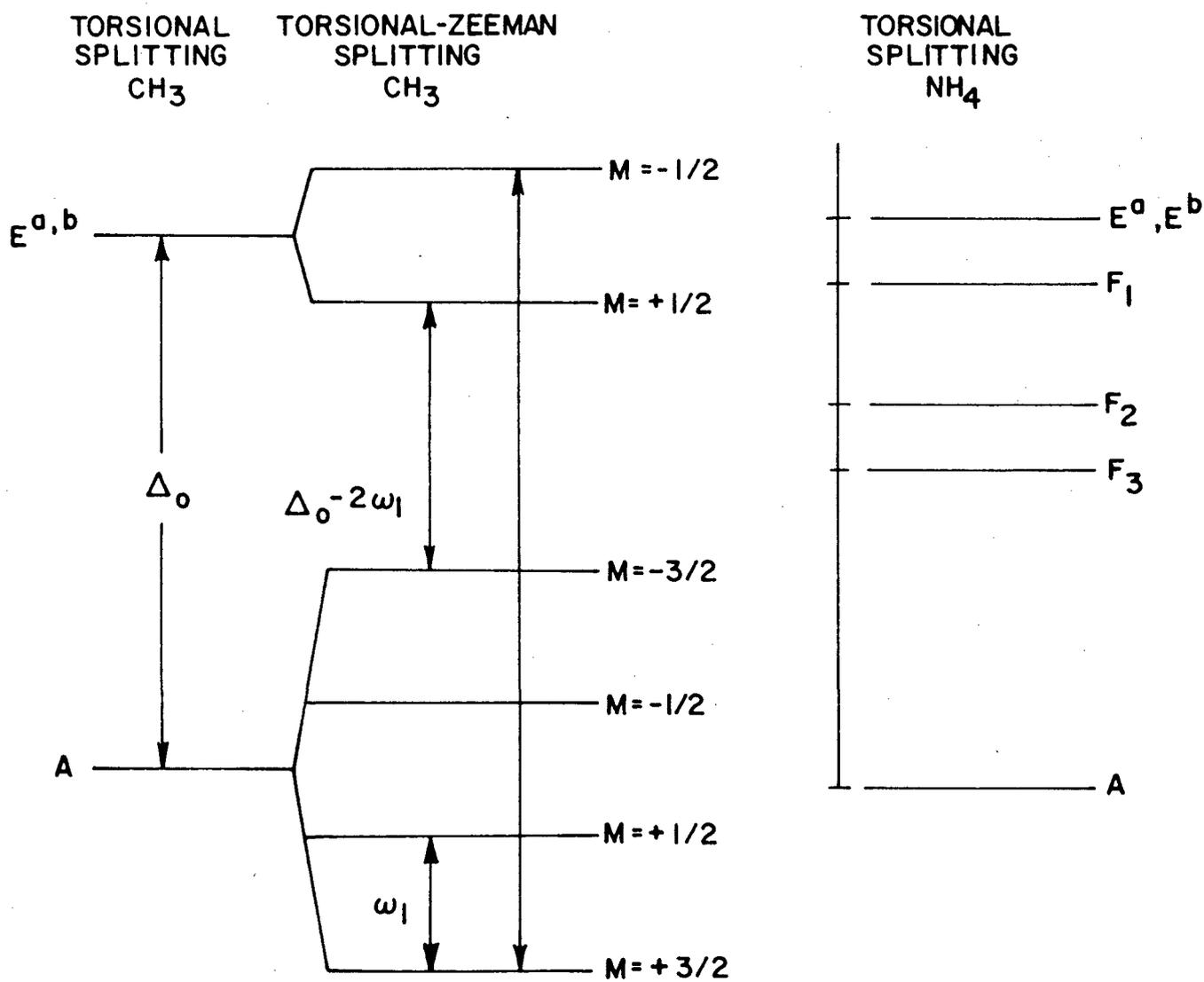
However, the energy of each system varies with time in an oscillatory way, indicating that energy is shuttled among the three systems. The frequencies of this oscillatory energy exchange are

$$(\omega_{RM} - \omega_{R'M'}) = (\omega_M - \omega_{M'}) + (\omega_R - \omega_{R'})$$

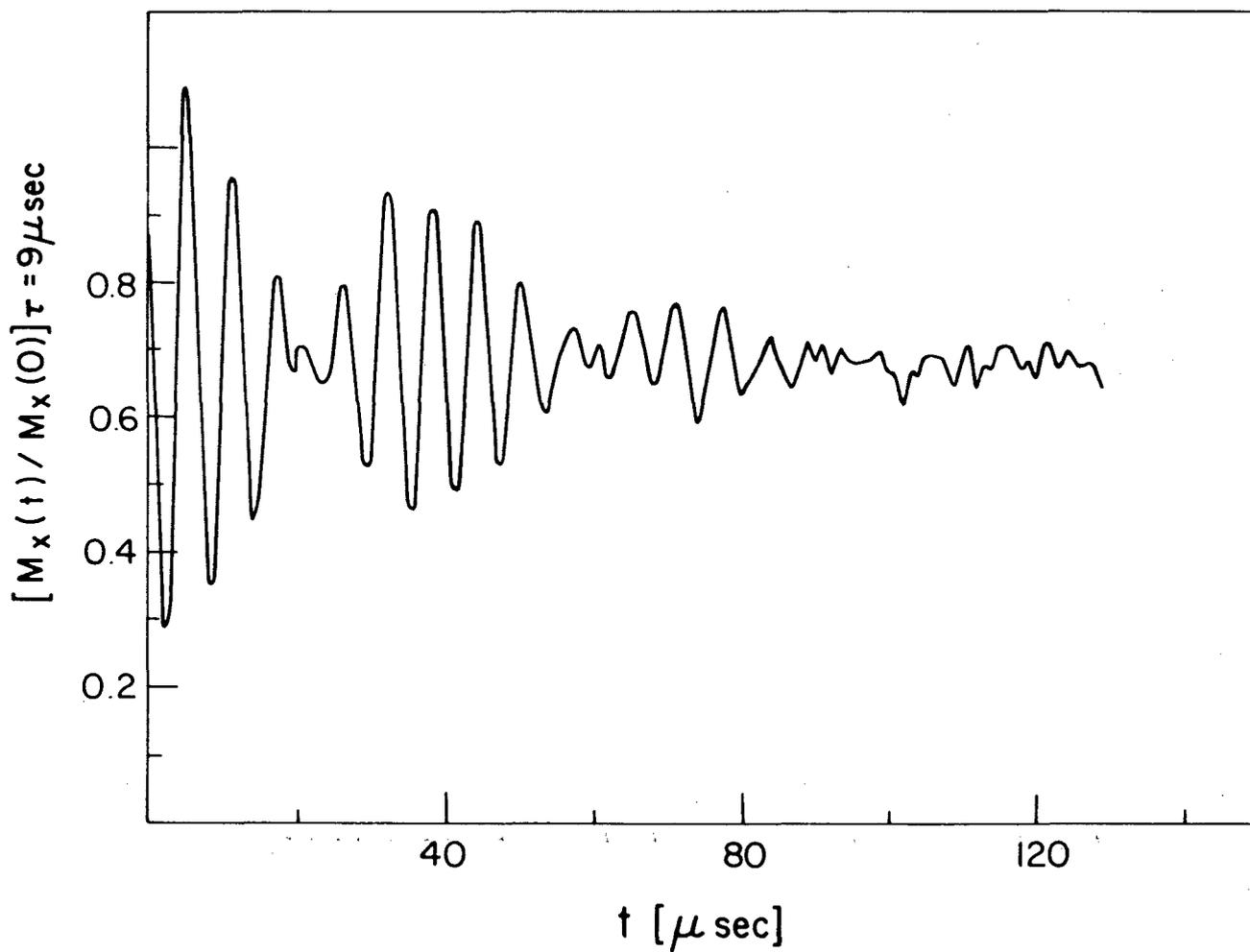
The selection rules for allowed combinations of  $R$ ,  $M$ ,  $R'$ , and  $M'$  are determined by the matrix elements of  $D$ . In the laboratory frame of reference, the magnetic quantum number may change by  $\pm 1, 2$ . The corresponding selection rule in the rotating frame of reference is  $\Delta M = \pm 2$ , since the interaction term couples only these states. Transitions in which  $M$  is not changed are also allowed.

SPOT spectra were measured in  $\text{CH}_3\text{CD}_2\text{I}$  and in  $\text{NH}_4\text{I}$ . The former material has a simple two-level ground state (Figure 3). The magnetization evolution and its Fourier transform are shown in Figures 4 and 5, respectively. The SPOT spectrum is a doublet with a  $2\omega_1 + \omega_T$  and a  $2\omega_1 - \omega_T$  line. The separation of the two lines is  $2\omega_T$  and the center of the doublet is at  $2\omega_1$  (Figure 5). Since there are only two torsional states, the magnetization evolution clearly shows beating of the  $2\omega_1 + \omega_T$  and  $2\omega_1 - \omega_T$  frequencies (Figures 3 and 4).

A more involved problem is the SPOTS line shape. In a perturbation calculation, a good agreement with the measured spectrum of  $\text{CH}_3$  (Figure 5) was found. It was proven that, in solids where the tunneling splitting is small on the scale of the dipolar coupling, the middle part of the spectrum is a saddle, as in Figure 5. As the tunneling splitting of the ground state increases, the Zeeman-only transitions bring



**Figure 3.** Torsional ground state splittings of oscillators CH<sub>3</sub> and NH<sub>4</sub>. The NH<sub>4</sub> oscillator may have a simpler spectrum if symmetry of the crystal field is higher.



**Figure 4.** Magnetization  $M$ , as a function of the mixing time  $t$  (duration of the RF field pulse  $B$ ). The function is drawn as if the experiment were continuous. Since after each observation an equilibrium with the lattice has to be restored (this takes  $\sim 5 T_1$ ), only 200 readings were taken, with the RF pulse duration increased in  $1\text{-}\mu\text{s}$  steps. The material is  $\text{CH}_3\text{CD}_2\text{I}$  at  $66\text{ K}$ , and  $H_1 = 19\text{ G}$ . The magnetization was read at  $\tau = 25\mu\text{s}$ .

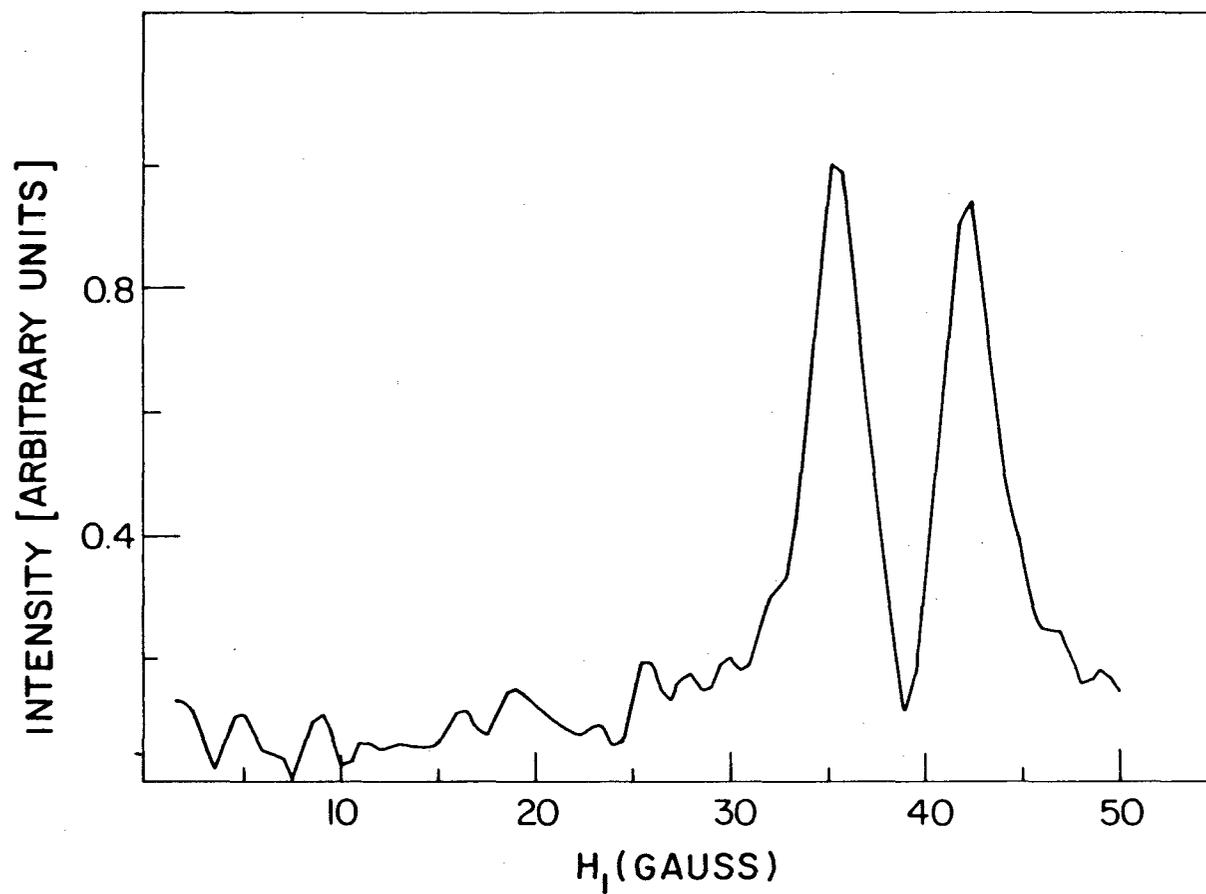
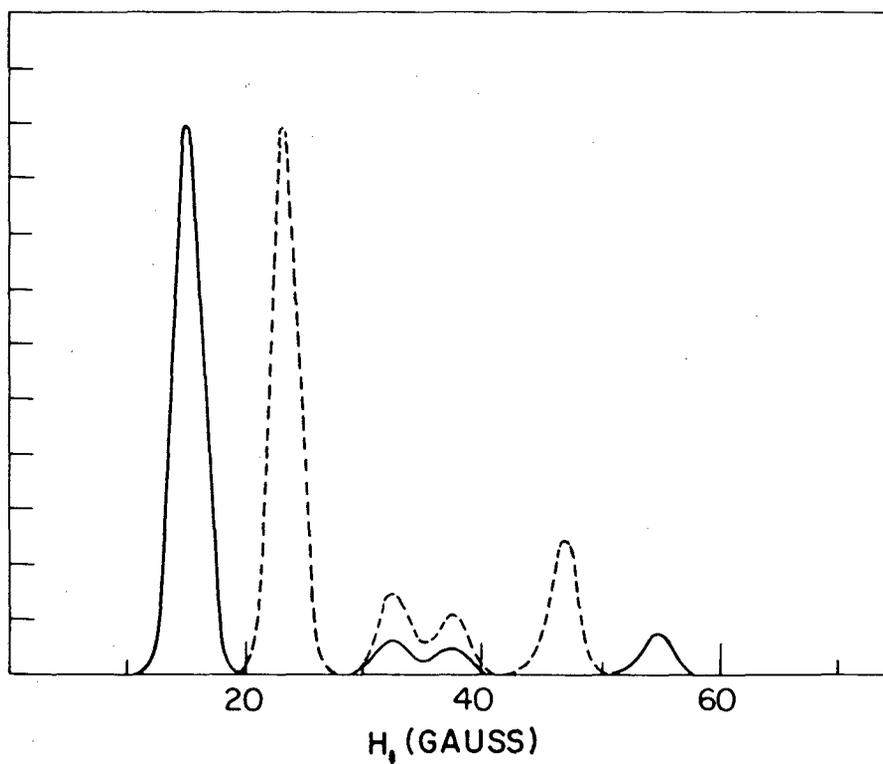
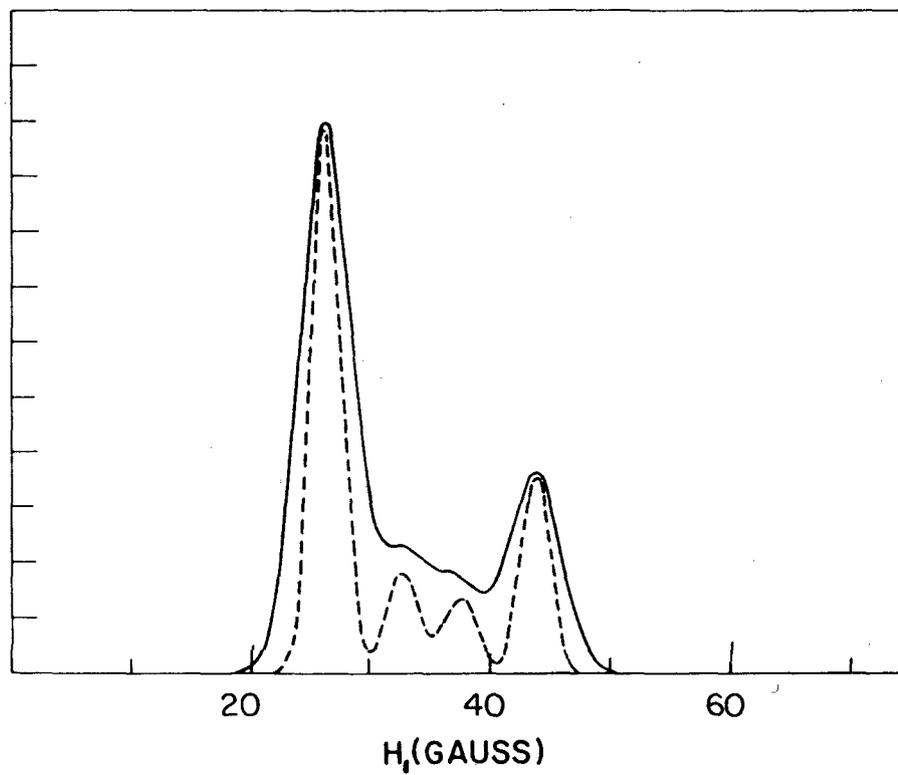


Figure 5. Fourier transform of the time dependence at Figure 4. The calculated spectrum agrees well with this experimental one.



**Figure 6.** Two calculated SPOT spectra of a  $\text{CH}_3$  oscillator essentially equal to the one shown in Figures 4 and 5 except for the magnitude of the A-to-E splitting. The larger splitting (continuous line) is 19 G, the smaller 11 G. The RF field is 17.5 G and the assumed Gaussian broadening parameter is 1 G.



**Figure 7.** If the A-to-E splitting is reduced to 8 G, the doublet in the center is almost lost, depending on broadening. If the broadening parameter is 1 G, the doublet is still well resolved. If the parameter is 2 G, the inner doublet is almost lost (continuous line).

about a central peak. This peak becomes progressively more distinct as the ground state splitting increases (Figures 6 and 7).

Such is the situation in the SPOT spectrum of the torsional oscillator  $\text{NH}_4$  in  $\text{NH}_4\text{I}$ . This spectrum is complicated (Figure 3) and has a strong central line.

To improve the resolution in SPOT spectra, research is being pursued in the off-field rotating frame. Best of all would be SPOTS at high fields, but we have not yet seen these.

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