

# The Impact of the Symmetry Properties of Classical Reorienting and Tunnelling Methyl Groups on the Spin-lattice Relaxation in Solids

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## I. INTRODUCTION

During the last two decades the random reorientations of methyl groups in solids have been the subject of many NMR studies. The purpose of such investigations can be the motional mechanism itself and/or the determination of the magnitude and shape of the hindering barrier governing the reorientations. This contributes to a better knowledge of the conformation of the molecule to which the methyl group is attached. To this end in a large majority of cases the Zeeman spin-lattice relaxation has been measured as a function of temperature. In the high temperature region, where the groups can be regarded as classical rotors, the experiments are usually interpreted with the results of the Bloembergen, Purcell and Pound theory, elaborated for the case of

methyl groups (1,2). At low temperatures the quantum character of the rotors becomes important, which induces new phenomena in the temperature dependence of the relaxation time (3-12).

In practice, discrepancies have been observed between the theoretical and experimental results, such as too small a value for the relaxation constant (13-22), a difference in slope of the curve  $\ln T_1^{-1}$  versus  $T^{-1}$  on the high and low temperature side of the maximum in the temperature region where tunnelling can be neglected (3,17,19,23,24) and, last but not least, non-exponential relaxation, both for non-tunnelling (15,24-31) and tunnelling (32-34) groups. Especially the last discrepancy was in complete disagreement with the existing relaxation theories, where essentially an exponential relaxation is predicted. In some publications the

results were explained with the Hilt and Hubbard theory (35), where the spin-lattice relaxation is calculated for non-tunnelling, mutually isolated methyl groups. Indeed this theory results in a non-exponential relaxation, but the model used is rather unrealistic, because in most samples the methyl groups are close to each other and to other protons (if present) in the material. Under these circumstances it is well known that spin diffusion plays an important role. This process tends to establish a situation of internal equilibrium for the Zeeman and dipolar system on a time scale fast compared with the spin-lattice relaxation time (ref. (36) chap. 5, ref. (37) chap. 1). Incorporation of the spin diffusion leads to the exponential spin-lattice relaxation obtained in the other theories (1,2,5).

The problem of the above discrepancies has been solved by taking into account the symmetry properties of the methyl groups in the various parts of the hamiltonian necessary for the description of the spin-lattice relaxation. It was then found (38) that also in the presence of spin diffusion, a non-exponential relaxation is obtained.

In this paper a review of this theory is given, emphasizing the manner in which the symmetry should be included. This will be done both for classical reorienting and tunnelling methyl groups. The results will be illustrated with experimental examples.

## II. THEORY

### A. Introduction

A methyl group consists of three protons located at the corners of an equilateral triangle with side  $r$ , see Figure 1. A carbon atom is located somewhat below the center of the triangle. This atom is bonded to another one, often another carbon atom, of the molecule. In Figure 1  $\beta$  denotes the angle between the symmetry axis of the methyl group and the external magnetic field  $H_0$ .  $V(\psi)$  is the potential barrier due to the steric hindrance of the methyl groups. As an example  $V(\psi)$  is taken to have three-fold symmetry,

which means that the steric hindrance is invariant for a rotation of  $120^\circ$  of the methyl group.

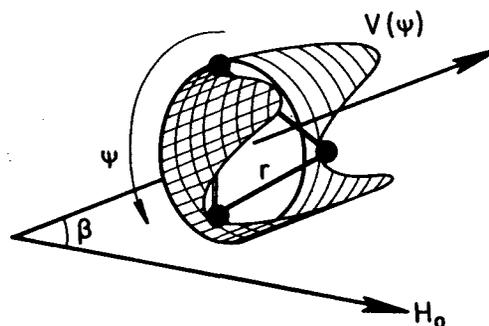


Figure 1. The methyl group in the presence of a three-fold hindering potential  $V(\psi)$  and an external magnetic field  $H_0$ .

In the presence of an external magnetic field with a strength  $H_0$  the relevant hamiltonian is given by

$$\hat{H} = \hat{H}_Z + \hat{H}_R + \hat{H}_P + \hat{H}_{RP} + \hat{H}_D, \quad (1)$$

where  $\hat{H}_Z$ ,  $\hat{H}_R$  and  $\hat{H}_P$  represent the zeroth-order operators of the Zeeman system, the rotor system and the phonon system, respectively.  $\hat{H}_{RP}$  and  $\hat{H}_D$  are perturbations describing the interactions between the rotor and phonon system and the dipolar interactions between the various protons, respectively.

The spin-lattice relaxation, observed with NMR, is caused by that part  $\hat{H}_D(t)$  of  $\hat{H}_D$  which is rendered time-dependent by random motions of the whole molecule or part of the molecule. Often in solids containing methyl groups the random reorientations of these groups are the dominant motional mechanism, as we shall assume in this paper.  $\hat{H}_D(t)$  causes transition probabilities between the various spin eigenstates following from Eq. (1). These transition probabilities tend to restore, after some perturbation, the population differences between these

eigenstates towards the values corresponding to thermal equilibrium.

For a complete description of the spin-lattice relaxation, the different transition probabilities and the constants of the motion need to be determined. The latter quantities can be defined as the set of  $i$  populations  $N_i$  or a set of  $i$  combinations of populations  $\sum_k c_{ki} N_{ki}$ , which remain constant in time on a time scale short compared with the spin-lattice relaxation, and become time-dependent because of  $\hat{H}_D(t)$ . Consequently, if the hamiltonian consisted only of  $\hat{H}_Z + \hat{H}_R + \hat{H}_D(t)$ , the constants of the motion would be the individual populations of the eigenstates corresponding to  $\hat{H}_Z + \hat{H}_R$ ; actually the number of constants of the motion is one less because of the constraint that the total population of all eigenstates is not influenced by  $\hat{H}_D(t)$ . However, it will be shown below that due to the terms  $\hat{H}_{RP}$ ,  $\hat{H}_P$  and the time-independent part of  $\hat{H}_D$ , extra transition probabilities exist between specific eigenstates with rates large compared with the relaxation rates, which reduce the number of constants of the motion.

In the next sections the unperturbed hamiltonian  $\hat{H}_Z + \hat{H}_R$  will be considered first. Then the influence of  $\hat{H}_{RP} + \hat{H}_P$  and the time-independent part of  $\hat{H}_D$ , and the resulting constants of the motion will be considered. Finally the spin-lattice relaxation due to  $\hat{H}_D(t)$  will be investigated.

### B. The Unperturbed Hamiltonian $\hat{H}_Z + \hat{H}_R$

$\hat{H}_Z$  describes the interaction of the magnetic moments of the protons with  $H_0$  and is, therefore, determined by the spin coordinates of the protons.  $\hat{H}_R$  describes the rotations of the methyl group around its axis of symmetry in the presence of a hindering potential  $V(\psi)$ , and depends on the space coordinates of the three protons.  $\psi$  is a variable angle defined in the plane through the three protons, see Figure 1.

The first task is determining the eigenfunctions which diagonalize  $\hat{H}_Z + \hat{H}_R$ . Now it is well known that the search is simplified considerably if

the symmetry of the hamiltonian is taken into account (39). For a methyl group, bonded to a molecule, the feasible symmetry is given by the point group  $C_3$ . This means that  $\hat{H}_Z$  is invariant for a cyclic permutation of the spin coordinates and that  $\hat{H}_R$  is invariant for a cyclic permutation of the space coordinates of the protons. Hence, if an operator  $\hat{C}_3$ , which might be  $\hat{C}_3^S$  or  $\hat{C}_3^R$ , is defined as the cyclic permutation operator exchanging the spin (or respectively space) coordinates of the protons 1, 2, and 3 for those of 3, 1, and 2,  $\hat{H}_Z$  commutes with  $\hat{C}_3^S$  and  $\hat{H}_R$  commutes with  $\hat{C}_3^R$ . Then the search for eigenfunctions of  $\hat{H}_Z$  or  $\hat{H}_R$  can be made separately within the classes of functions  $\Psi(\lambda)$  having different eigenvalues  $\lambda$  of  $\hat{C}_3$ , following from  $\hat{C}_3 \Psi(\lambda) = \lambda \Psi(\lambda)$ . In our case  $\lambda = 1, \epsilon, \text{ or } \epsilon^*$ , with  $\epsilon = \exp(2\pi i/3)$ , which follows easily from the relation  $\hat{C}_3 \hat{C}_3 \hat{C}_3 \Psi(\lambda) = \lambda^3 \Psi(\lambda) = \Psi(\lambda)$ . Hence the eigenfunctions  $\Psi_S(\lambda)$  of  $\hat{H}_Z$  and  $\Psi_R(\lambda_R)$  of  $\hat{H}_R$  can be classified according to the A ( $\lambda_R, \lambda_S = 1$ ),  $E^a$  ( $\lambda_R, \lambda_S = \epsilon$ ) or  $E^b$  ( $\lambda_R, \lambda_S = \epsilon^*$ ) irreducible representations of the point group  $C_3$ . For explicit expressions of  $\Psi_S(\lambda_S)$  and  $\Psi_R(\lambda_R)$  see ref. (5).

Another advantage of the incorporation of the symmetry is that it also provides rules for the matrix elements due to perturbation operators. In our case an operator  $\hat{O}$ , which may depend on the spin and/or space coordinates, can be classified according to the A,  $E^a$ , or  $E^b$  symmetry, depending whether in the relation  $\hat{C}_3 \hat{O}(\lambda) \hat{C}_3^{-1} = \lambda \hat{O}(\lambda)$ ,  $\lambda$  equals 1,  $\epsilon$ , or  $\epsilon^*$ . It can be shown that an operator with symmetry  $\lambda_j$  has possible non-zero matrix elements  $\langle \Psi(\lambda_i) | \hat{O}(\lambda_j) | \Psi(\lambda_k) \rangle$  only if the condition

$$\lambda_i^* \lambda_j \lambda_k = 1, \quad (2)$$

is satisfied. This relation will prove to be very useful when the influence of  $\hat{H}_{RP}$  and  $\hat{H}_D$  is investigated.

We now return to the unperturbed hamiltonian  $\hat{H}_Z + \hat{H}_R$ . The eigenfunctions  $\Psi_R(\lambda_R, R)$  of  $\hat{H}_R$  correspond to eigenvalues  $E_R(\lambda_R, R)$ , where  $R$  ( $R = 0, 1, \dots$ ) denotes the  $R$ -th rotor level. For a given value of  $R$  a difference in energy  $\Delta_R$  is obtained for  $\lambda_R = 1$  (A

symmetry) and  $\lambda_R = \epsilon, \epsilon^*$  ( $E^a$  and  $E^b$  symmetry). The magnitude of  $\Delta_R$  depends on the shape and height of the hindering barrier and is a measure of the probability that a methyl group tunnels through the barrier.  $\Delta_R$  is called the tunnelling splitting of the R-th rotor state. The eigenfunctions of  $\hat{H}_Z$  are characterized by  $\Psi_S(\lambda_S, m)$ , where  $m$  denotes the total magnetic quantum number of the three protons, with eigenvalues  $E_S(m)$ . For the total energy level scheme of  $\hat{H}_Z + \hat{H}_R$  corresponding to the product eigenfunctions  $\Psi_R \Psi_S$  the Pauli principle has to be taken into account, stating that an exchange of two protons changes  $\Psi_R \Psi_S$  into  $-\Psi_R \Psi_S$ . Hence a rotation of the methyl group over  $120^\circ$ , characterized by the operation  $\hat{C}_3 R \hat{C}_3^{-1} \Psi_R \Psi_S$  which gives the same result as two successive exchanges, would leave the eigenfunction invariant. As  $\hat{C}_3 R \hat{C}_3^{-1} \Psi_R \Psi_S$  is also equal to  $\lambda_R \lambda_S \Psi_R \Psi_S$ , it follows that the symmetry parameters  $\lambda_R$  and  $\lambda_S$  of the rotor and spin system must obey the relation

$$\lambda_R \lambda_S = 1. \quad (3)$$

The energy level scheme of  $\hat{H}_Z + \hat{H}_R$  is depicted in Figure 2. Here the energy gap  $E_{10}$  corresponds to the energy difference of the ground and first rotor level in case of an infinitely high barrier for which  $\Delta_0 = \Delta_1 = 0$ . The next step is the incorporation of  $\hat{H}_{RP} + \hat{H}_P$  of Eq. (1).

### C. The Terms $\hat{H}_{RP} + \hat{H}_P$

As has been stated above,  $\hat{H}_{RP}$  is regarded as a perturbation of  $\hat{H}_R$ . It causes fluctuations of the hindering potential, both in amplitude and phase, which are rendered time dependent in a random way because of thermal excitations due to the phonon system. As a result non-magnetic transitions  $W_{RR'}$  between the various rotor levels  $R$  and  $R'$  occur. Because  $\hat{H}_{RP}$  operates only on the rotor system and because of Eq. (3) these transitions exist only between levels with a same spin eigenfunction  $\Psi_S(\lambda_S, m)$  and between rotor states belonging to a same symmetry species  $A, E^a,$  or  $E^b$  and corresponding to a same value of  $m$ . The effect of these transitions is twofold:

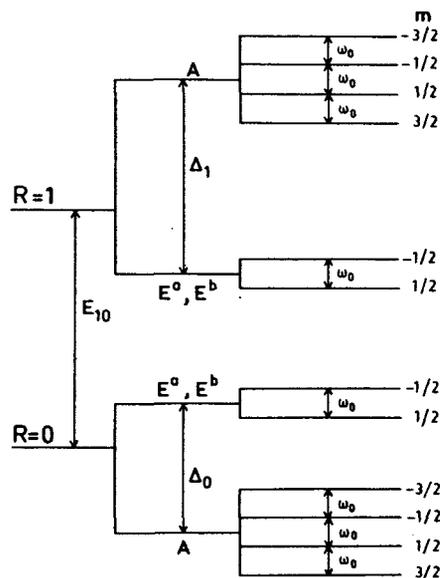


Figure 2. The energy level scheme of the lowest two torsional levels corresponding to  $\hat{H}_Z + \hat{H}_R$ .

(i) After some perturbation a state of internal equilibrium is restored within each symmetry species  $A, E^a,$  and  $E^b$  in a time of the order  $W_{RR'}^{-1}$ . Though  $W_{RR'}$  differs for different values of  $R$  and  $R'$ , this time, being of the order of the correlation time  $\tau_c$ , see below, is much smaller than the relaxation time. Hence on the time scale of the relaxation the non-magnetic transitions maintain a Boltzmann distribution over the rotor levels within each symmetry species  $A, E^a,$  and  $E^b$ , corresponding to the same value of  $m$ . As a result the constants of the motion are no longer the individual populations corresponding to each value of  $R$  and  $m$ , the only populations which remain constant are the total populations of each symmetry species for a give magnetic quantum number  $m$ ,  $\sum_R \alpha(m)$ , where  $\alpha$  denotes  $A, E^a,$  or  $E^b$ . Using the assumption of ergodicity each methyl group belonging to the same symmetry species has the same average rotor energy. As a consequence the energy level scheme of Figure 2 is reduced to the effective eight-level scheme of Figure 3. Using

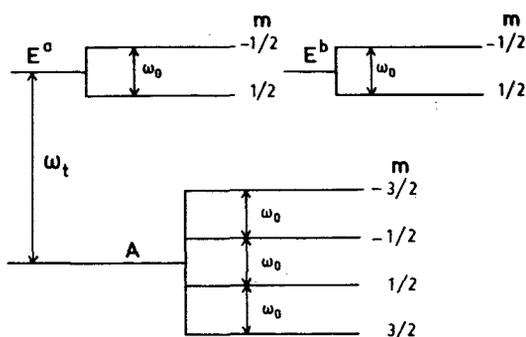


Figure 3. The effective energy level scheme corresponding to  $\hat{H}_Z + \hat{H}_R + \hat{H}_{RP} + \hat{H}_P$ .

again the constraint of conservation of the total population of all levels, it follows that the number of constants of the motion, which has to be regarded in spin-lattice relaxation, is reduced to seven. The energy difference between the A and E species is called the effective tunnelling splitting  $\omega_t$ . The values of  $\omega_t$  depends on the temperature. At very low temperatures (typically below 20 K), where the ground torsional levels are mainly occupied,  $\omega_t$  equals  $\Delta_0$ . At higher temperatures the populations of the higher torsional levels increase and  $\omega_t$  is found to decrease (10,40,41). Usually  $\omega_t$  becomes negligibly small above ca. 50 K (moreover, for higher temperatures the meaning of  $\omega_t$  becomes doubtful because then the broadening of the energy levels due to the non-magnetic transitions becomes comparable to or larger than  $\omega_t$ ). We note that at this moment different theories exist to explain the temperature dependence of  $\omega_t$  (42-46). However, they all show the features described above.

(ii) Due to the non-magnetic transitions the methyl group may jump randomly from one well of the hindering potential into another. Though obviously this is a very complicated process and a result of many different transitions, in practice this random jumping can often be characterized by a single correlation time  $\tau_c$ . Usually the temperature dependence of  $\tau_c$  is

described by the Arrhenius law

$$\tau_c = \tau_0 \exp(E_a/kT) \quad (4)$$

where the activation energy  $E_a$  and the correlation constant  $\tau_0$  may depend on the temperature. At low temperatures (typically below 70 K) the lower torsional levels are mainly occupied. Then the random tunnelling of the methyl groups through the barrier is the dominant motional mechanism. At temperatures below ca. 30 K only the non-magnetic transition between the ground and first torsional levels is important, so that  $E_a$  is approximately given by  $E_{1,0}$ , see Figure 2. At temperatures above 70 K the classical random hopping of the methyl group over the hindering barrier becomes the dominant motion and  $E_a$  then is of the order of the barrier height (47,48).

#### D. The Term $\hat{H}_D$

The last term of Eq. (1) to be taken into account is  $\hat{H}_D$ , representing the dipolar interaction between the various protons. For the sake of simplicity we restrict ourselves to the case that all protons in the sample belong to methyl groups which experience the same hindering potential. The directions of their symmetry axes need not be the same. The results can easily be extended for the case that other protons are present as well (49).

It is well-known (ref. (36) chap. 4, ref (37) chap. 3) that the dipolar hamiltonian consists of several terms which can be classified according to the change  $\Delta m$  in the total magnetic quantum number caused by the spin operators

$$\hat{H}_D = \sum_{\mu} \hat{H}_D^{\mu} \quad \mu = \Delta m = 0, \pm 1, \pm 2. \quad (5)$$

Each term can be written as

$$\hat{H}_D^{\mu} = \sum_i (\hat{H}_i^{\mu} + \sum_{j < i} \hat{H}_{ij}^{\mu}) \quad (6)$$

where  $\hat{H}_i^{\mu}$  represents the intra-methyl dipolar interaction within group  $i$ , and  $\hat{H}_{ij}^{\mu}$  the inter-methyl dipolar interactions between the groups  $i$  and  $j$ . All terms in  $\hat{H}_D$  consist of product functions of a spatial operator  $\hat{V}$ , depending on the angles  $\beta$  and  $\psi$ , depicted in

Figure 1, and a (bilinear) spin operator  $\hat{S}$ . Both operators can be classified with a symmetry parameter  $\lambda_D = 1, \epsilon, \epsilon^*$  with the rule that the parameters of  $\hat{V}$  and  $\hat{S}$  are each others conjugate (5,49-52). Therefore Eq. (5) can be written as

$$\hat{A}_D = \sum_{\mu} \hat{A}_D^{\mu} = \sum_{\mu} [\hat{A}_i^{\mu}(\lambda_{Di}) + \sum_{j < i} \hat{A}_{ij}^{\mu}(\lambda_{Di}, \lambda_{Dj})], \quad (7)$$

where  $\hat{A}_D$  contains both first-order and second-order perturbation terms. In a large magnetic field  $H_0$  in first order, only the terms with  $\mu = 0$  need to be taken into account. Moreover, if the random reorientations of the methyl groups are so fast that  $|H_D|\tau_c \ll 1$ , the first-order term is reduced to the time-averaged value of  $\hat{A}_D^{\mu=0}$ . In this respect it is important to note that, as the reorientations can be represented by rapid random rotations of the methyl groups over  $120^\circ$ ,  $240^\circ$ , or  $360^\circ$  around their symmetry axes, the terms with A-symmetry, which are invariant for these rotations, are not influenced by the motion. Hence we reach the important conclusion that the terms in Eq. (7) with  $\lambda_{Di} = \lambda_{Dj} = 1$  are time independent. The terms with  $\lambda_{Di}, \lambda_{Dj} = \epsilon, \epsilon^*$  are time dependent, with an average value of zero. We shall consider these terms separately.

### 1. The Time-independent part of $\hat{A}_D$

The first-order term  $\hat{A}_1$  of  $\hat{A}_D$  is given by

$$\begin{aligned} \hat{A}_1 &= \overline{\hat{A}_D^{\mu=0}} = \sum_i [\hat{A}_i^{\mu=0}(\lambda_{Di} = 1) \\ &\quad + \sum_{j < i} \hat{A}_{ij}^{\mu=0}(\lambda_{Di} = \lambda_{Dj} = 1)] \\ &\equiv \hat{A}_1^{\text{intra}} + \hat{A}_1^{\text{inter}} \quad (8) \end{aligned}$$

To illustrate the effect of  $\hat{A}_1$  we consider an ensemble of methyl groups with a same orientation angle  $\beta$  between their symmetry axes and  $H_0$ . It can be shown (53) that  $\hat{A}_1^{\text{intra}}$  results in a shift  $d$  of the Zeeman levels corresponding to the A symmetry species, with

$$d = \frac{3\gamma^2\hbar}{4r^3}(1 - 3/2 \sin^2\beta),$$

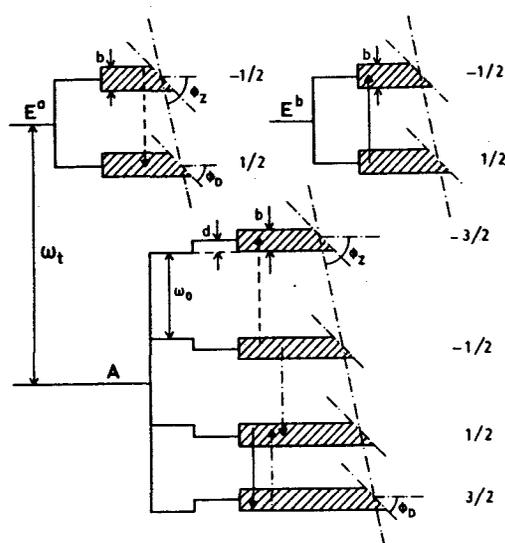


Figure 4. The effective energy level scheme corresponding to  $\hat{A}_Z + \hat{A}_R + \hat{A}_{Rp} + \hat{A}_p + \hat{A}_1$ . The different arrows are examples of pairs of simultaneous flip-flop transitions, which establish a single inverse Zeeman temperature  $\alpha_Z$  and a single inverse dipolar temperature  $\alpha_D$ .  $\alpha_Z$  is proportional to  $\text{tg}^{-1}\phi_Z$ , and  $\alpha_D$  is proportional to  $\text{tg}^{-1}\phi_D$ .

see Figure 4. The inter-methyl term  $\hat{A}_1^{\text{inter}}$  consists of two parts, one proportional to the product spin operators  $\hat{I}_Z^i \hat{I}_Z^j$ , whereas the other one, the so-called flip-flop term, is proportional to  $\hat{I}_{+i} \hat{I}_{-j} + \hat{I}_{-i} \hat{I}_{+j}$ . Here for example  $\hat{I}_Z^i$  is given by  $\hat{I}_Z^i = \hat{I}_Z^{i1} + \hat{I}_Z^{i2} + \hat{I}_Z^{i3}$ , where 1, 2, and 3 label the three protons of methyl group  $i$ . Similar formulae can be given for the other spin operators. Both terms give rise to shifts of the Zeeman levels of all symmetry species, and as this shift usually is different for the different groups, the result is a broadening  $b$ , see Figure 4. In most non-diluted solids this broadening is of the same order of magnitude as the intra-methyl splitting  $d$ . Now the broadening due to the flip-flop is a result of the so-called flip-flop transitions, which are simultaneous jumps, occurring at a rate of the order  $b^{-1}$ , between pairs of adjacent Zeeman levels, in opposite

directions. For an extensive treatment of this phenomenon see refs. (36) chap. 5 and (37) chap. 1. The result of this so-called spin diffusion process is that, on a time scale of the order  $b^{-1}$ , the population distributions are given by a Boltzmann distribution, both over the energy levels split by the Zeeman and the dipolar interactions. As in most solids  $b^{-1}$  is much shorter than the spin-lattice relaxation time, the spin diffusion further reduces the number of constants of the motion. Until some years ago it was commonly assumed that only two constants of the motion remained, one proportional to the Zeeman energy and the other proportional to the dipolar energy. Both are characterized with single reciprocal spin temperatures  $\alpha_Z$  and  $\alpha_D$ , respectively, which after some perturbation were found to relax independently of each other, hence with single exponentials [(37) chap. 3].

For the case of reorienting methyl groups the situation is more complicated. It has already been stated above that both the spatial- and spin-operator of  $\hat{H}_1$  are of A symmetry. This means that the flip-flop transitions occur only between pairs of Zeeman levels, where each pair corresponds to a same symmetry species. This process has been called Symmetry Restricted Spin Diffusion (38), and is illustrated in Figure 4. The important result is that the Zeeman and dipolar energies can still be characterized by  $\alpha_Z$  and  $\alpha_D$  respectively; the latter statement is only true if  $b \approx d$ , otherwise more reciprocal temperatures have to be defined (38,54). However, the total populations  $N_A$ ,  $N_{Ea}$ , and  $N_{Eb}$  are unaffected by the spin diffusion. As a result two more constants of the motion have to be defined.

It is useful to consider the following constants of the motion:

- (i) the population difference between the E and A states,  $(N_{Ea} + N_{Eb}) - N_A$ . This has been called the tunnelling system, because in thermal equilibrium it equals the population difference due to the tunnelling splitting;
- (ii) the population difference between

the  $E^a$  and  $E^b$  states,  $N_{Ea} - N_{Eb}$ . This has been called the rotational polarization system (55).

In order to be consistent with the characterization of the Zeeman and dipolar systems by  $\alpha_Z$  and  $\alpha_D$ , we characterize the tunnelling system by the so-called reciprocal tunnelling temperature  $\alpha_T$  proportional to  $(N_{Ea} + N_{Eb}) - N_A$ , and the rotational polarization system by  $\alpha_R$ , proportional to  $N_{Ea} - N_{Eb}$ .

Summarizing we have found that due to the first type of perturbations  $\hat{H}_{RP}$  and  $\hat{H}_1$  in Eq. (1), the number of constants of the motion has been reduced to four, namely  $\alpha_Z$ ,  $\alpha_D$ ,  $\alpha_R$ , and  $\alpha_T$ . Each quantity can only vary in time due to the spin-lattice relaxation, which we shall now investigate. Before doing so, however, it must be remarked that the situation is more complicated in samples where the orientation angle  $\beta$  of the methyl groups can take more than one value.

It can be shown (49) that the Zeeman and dipolar systems can still be characterized by single inverse temperatures  $\alpha_Z$  and  $\alpha_D$ . This is not the case with the rotational polarization and tunnelling systems. These systems have to be divided into subsystems corresponding to methyl groups with orientation angles between  $\beta$  and  $\beta + d\beta$ . Each subsystem can be characterized by inverse temperatures  $\alpha_R(\beta)$  and  $\alpha_T(\beta)$ . In thermal equilibrium all  $\alpha_R(\beta)$  are equal to one another, but during relaxation they can become different. The same holds for  $\alpha_T(\beta)$ . Consequently, besides  $\alpha_Z$  and  $\alpha_D$  all  $\alpha_R(\beta)$  and  $\alpha_T(\beta)$  have to be taken as constants of the motion.

## 2. The Time-dependent Part of $\hat{H}_D$

The time-dependent part  $\hat{H}_D(t)$  of  $\hat{H}_D$  gives rise to spin-lattice relaxation. It follows from the previous section that  $\hat{H}_D(t)$  is given by

$$\begin{aligned} \hat{H}_D(t) &= \sum_{\mu=-2}^2 [\hat{H}_i^\mu(\lambda_{Di} = \epsilon, \epsilon^*) \\ &\quad + \sum_{j < i} \hat{H}_{ij}^\mu(\lambda_{Di}, \lambda_{Dj} = \epsilon, \epsilon^*)] \\ &\equiv \hat{H}_2^{\text{intra}}(t) + \hat{H}_2^{\text{inter}}(t). \quad (9) \end{aligned}$$

It follows from Eqs. (2) and (9) that the spin operators of  $\hat{H}_D(t)$ , being of either  $E^a$  or  $E^b$  symmetry, only result in possible non-zero transition probabilities  $W_{ij}$  between spin energy levels  $i$  and  $j$  belonging to different symmetry species, and with a difference in magnetic quantum number of zero, one or two. Hence only  $A \leftrightarrow E^a$ ,  $A \leftrightarrow E^b$ , or  $E^a \leftrightarrow E^b$  transitions are possible. Moreover, calculations show that for the intra-methyl relaxation due to  $\hat{H}_2^{\text{intra}}(t)$  the  $E^a \leftrightarrow E^b$  transitions are zero, so that only  $A \leftrightarrow E^a$  and  $A \leftrightarrow E^b$  transitions remain (5,35,43,49,54,56), where also explicit expressions for the different transition probabilities are given. Here we shall confine ourselves by remarking that generally  $W_{ij}$  is given by

$$W_{ij} = a_{ij} J(\Delta\omega_{ij}, \tau_c) \quad (10)$$

where  $a_{ij}$  is a constant depending on the orientation angle  $\beta$  of the methyl groups, and  $\Delta\omega_{ij}$  the energy difference between the levels  $i$  and  $j$ .  $J(\omega, \tau_c)$  is the spectral density function corresponding to the random reorientations of the methyl groups. It is usually assumed that  $J(\omega, \tau_c)$  is of the Lorentzian type

$$J(\omega, \tau_c) = \tau_c / (1 + \omega^2 \tau_c^2). \quad (11)$$

It follows that:

- (i) the intra-methyl relaxation rates contain only the spectral density functions  $J[(\omega_t \pm n\omega_0), \tau_c]$ ,  $n = 0, 1, 2$ ;
- (ii) the inter-methyl relaxation rates contain the spectral density functions  $J[(\omega_t \pm n\omega_0), \tau_c]$  as well as  $J(n\omega_0, \tau_c)$ ,  $n = 0, 1, 2$  [the latter follows from the fact that non-zero inter-methyl relaxation transitions exist between the  $E^a$  and  $E^b$  species (5,49)].

The relaxation equations of the constants of the motion have to be calculated. It can be shown (43,49) that for equally oriented methyl groups these equations consist of a coupled set of four first-order differential equations, where, for example,  $\dot{\alpha}_Z$  is given

by

$$\dot{\alpha}_Z = S_{ZZ}\bar{\alpha}_Z + S_{ZR}\bar{\alpha}_R + S_{ZT}\bar{\alpha}_T + S_{ZD}\bar{\alpha}_D \quad (12a)$$

$$\bar{\alpha} = \alpha^{\text{eq}} - \alpha \quad (12b)$$

$\alpha^{\text{eq}}$  denotes the thermal equilibrium value of  $\alpha$ . Similar equations can be given for  $\alpha_R$ ,  $\alpha_T$ , and  $\alpha_D$  and the total set of equations can be summarized as

$$\dot{\vec{\alpha}} = \vec{S} \vec{\alpha} \quad (13)$$

where the vector  $\vec{\alpha}$  has components  $\alpha_Z$ ,  $\alpha_R$ ,  $\alpha_T$ , and  $\alpha_D$ . Explicit expressions for  $\vec{S}$  are given elsewhere (43,49), and also for the case of a distribution of the methyl orientation angles (in the latter case the number of differential equations has to be extended, because the number of constants of the motion is increased, see previous section).

To illustrate the effect of the various dynamical couplings we consider the case in which the sample consists of equally oriented methyl groups with an angle  $\beta = 0$  between their symmetry axes and  $H_0$ . For simplicity we assume that the inter-methyl interactions can be neglected, so that both the spin diffusion and the inter-methyl relaxation are zero. It can be shown (43) that in this case the only non-zero relaxation transitions  $W_1$  and  $W_2$  are between the  $A_{-3/2}$  and  $E_{+1/2}^b$  and the  $A_{+3/2}$  and  $E_{-1/2}^a$  levels respectively, with equal amplitudes but with different spectral densities if  $\omega_t \neq 0$ , see Figure 5a.

We consider the Zeeman relaxation, and we suppose that, starting from thermal equilibrium, the magnetization is destroyed by irradiating with a  $90^\circ$  rf pulse at exact resonance and with a duration short compared with the relaxation rates  $W_1$  and  $W_2$ . Then immediately after the pulse, which we shall call  $t = 0$ , the populations  $N_1$  to  $N_8$  of the eight levels are as depicted in Figure 5a. The Zeeman system, proportional to  $(1/2) [(N_2 - N_1) + (N_4 - N_3) + (N_7 - N_6)] + (3/2) (N_8 - N_5)$ , is zero, whereas the dipolar system, proportional to  $N_5 + N_8 - (N_6 + N_7)$ , the

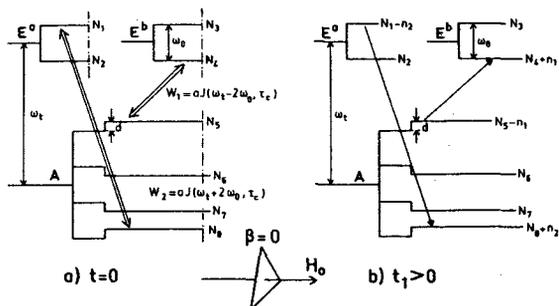


Figure 5. Intra-methyl relaxation for isolated methyl groups with  $\beta = 0$ . a)  $t = 0$ , immediately after a  $90^\circ$  rf pulse; b)  $t_1 > 0$ .

tunnelling system, proportional to  $(N_1 + N_2 + N_3 + N_4) - (N_5 + N_6 + N_7 + N_8)$ , and the rotational polarization system, proportional to  $(N_1 + N_2) - (N_3 + N_4)$  remain in thermal equilibrium. The relaxation transitions will restore the population differences between the levels 1 and 8 and between 4 and 5 towards their thermal equilibrium values. It can easily be seen that immediately after the  $90^\circ$  pulse at  $t = 0$  the population difference  $N_8 - N_1$  is smaller than the value corresponding to thermal equilibrium, whereas  $N_5 - N_4$  is larger than at thermal equilibrium. This means that if we observe the system at some instant  $t_1 > 0$ , the populations  $N_5$  and  $N_1$  have decreased by some amount  $n_1$  and  $n_2$ , whereas  $N_4$  has increased by  $n_1$  and  $n_8$  by  $n_2$ , see Figure 5b. It follows that now both the dipolar, the tunnelling and the rotational polarization systems are no longer in thermal equilibrium, provided that  $n_1 \neq n_2$ , thus proving the existence of non-zero coupling terms  $S_{ZD}$ ,  $S_{ZT}$ , and  $S_{ZR}$  in Eq. (12). The reader can easily convince himself that the same result is found if the (symmetry restricted) spin diffusion and the inter-methyl relaxation are incorporated. It also follows from Figure 5b that if  $n_1 = n_2$  the total  $(E^a + E^b)$  population, the total A population as well as  $(N_5 + N_8)$  remain equal to the values for  $t = 0$ , so that then both the tunnelling system and the dipolar system remain in thermal equilibrium. However, the population difference between the  $E^a$  and  $E^b$  species

becomes different from that at  $t = 0$ , so that  $S_{ZR}$  still remains non-zero. Hence we can deduce the following rules for the different dynamic couplings.

- If  $\omega_t = 0$ ,  $(\omega_t \pm n\omega_0)^2 \tau_c^2 \ll 1$ , or  $\omega_t \gg n\omega_0$ ,  $n = 0, 1, 2$ , it follows from Eq. (11) that  $W_1 = W_2$ . Then  $n_1 = n_2$  and the only dynamic couplings are between the Zeeman and rotational polarization system on the one hand and between the dipolar and tunnelling system on the other hand (the latter coupling can easily be seen from Figure 5 by choosing another initial condition where for example the tunnelling system is out of thermal equilibrium).
- If  $\omega_t \neq 0$ , if at least one of the terms  $(\omega_t \pm n\omega_0)^2 \tau_c^2$  becomes comparable or larger than unity, and if  $\omega_t$  is not much larger than  $n\omega_0$ ,  $W_1 \neq W_2$  and dynamic couplings exist between all four constants of the motion.

These rules appear to hold also for arbitrary orientations of the methyl groups and for polycrystalline samples.

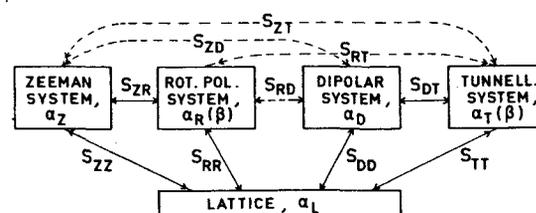


Figure 6. The constants of the motion and their dynamic couplings for reorienting or tunnelling methyl groups. Solid lines: non-zero couplings for  $\omega_t = 0$ ,  $\omega_t \gg n\omega_0$  or  $(\omega_t \pm n\omega_0)^2 \tau_c^2 \ll 1$ ,  $n = 0, 1, 2$ . Solid lines + dashed lines: non-zero couplings for  $\omega_t \neq 0$ ,  $\omega_t$  comparable to  $n\omega_0$  and at least one of the terms  $(\omega_t \pm n\omega_0)^2 \tau_c^2$  comparable or larger than one;  $n = 0, 1, 2$ .

Figure 6 gives a summary of the different couplings, where the solid lines give the situation for condition (a) and the solid and dotted lines for

condition (b). As both  $\omega_t$  and  $\tau_c$  are temperature dependent, it follows that the validity of the conditions (a) and (b) depends on the temperature as well. This will be investigated in the next section.

### III. EXPERIMENTS

In this section examples will be given of the effect of the various dynamic couplings on the observed spin-lattice relaxation. The emphasis will lay on the relaxation of the Zeeman system, because this is mostly investigated in practice. Most experiments have been performed with the help of a Bruker CXP 4-100 pulse spectrometer and a home-built cryostat (57). With this cryostat, operating in the frequency range 9 - 73 MHz, the temperature could be varied from 10 - 300 K. Moreover, in the whole temperature region the sample could be rotated around an axis perpendicular to  $H_0$  with a frequency maximum of 100 Hz. The utility of the latter possibility will become clear later on.

As stated in section II.D.2, the number of non-zero dynamic couplings depends on the value of the effective tunnelling splitting  $\omega_t$ . Therefore it is useful to discriminate between the case that  $\omega_t$  is zero and non-zero.

#### A. The Limit of Non-tunnelling

$$\omega_t = 0$$

In this limit the only non-zero dynamic couplings are between  $\alpha_z$  and  $\alpha_R(\beta)$  and between  $\alpha_D$  and  $\alpha_T(\beta)$ . Within the temperature range where  $\omega_t = 0$  the value of  $\omega_0\tau_c$  can be both smaller and larger than one. It is useful to investigate these limits separately as well.

##### 1. $\omega_t = 0, \omega_0\tau_c \ll 1$

In this limit even for a polycrystalline sample the relaxation of  $\alpha_z$  is described by a weighted sum of two exponentials (58). If for  $t = 0; \alpha_z = 0$ , the relaxation is given by

$$\begin{aligned} (\alpha_z^{eq} - \alpha_z) / \alpha_z^{eq} &= C \exp(-\lambda_1 t) \\ &+ (1 - C) \exp(-\lambda_2 t) \end{aligned} \quad (14)$$

The constant  $C$  and the relaxation rates  $\lambda_1$  and  $\lambda_2$  depend on the various elements of the relaxation matrix. Moreover, the value of  $C$  is determined by the initial values of  $\alpha_z$  and  $\alpha_R$  at  $t = 0$ . As a consequence the observed relaxation depends on the way the spin system has been prepared. This is illus-

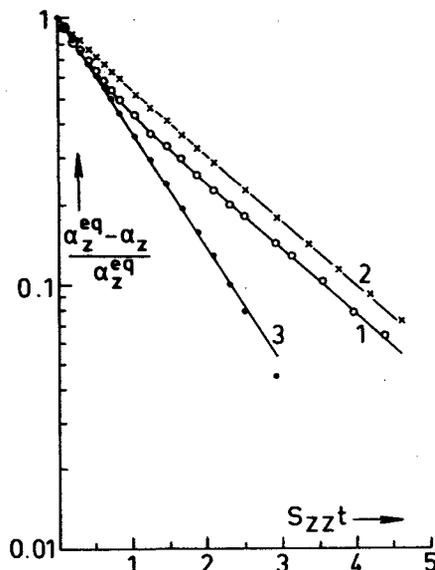


Figure 7. Zeeman relaxation of partially deuterated l-alanine,  $ND_3^+CHCH_3COO^-$ .  $\omega_0/2\pi = 60.8$  MHz,  $T = 296$  K,  $\omega_0\tau_c = 0.48$ . Curve 1: without sample rotation, after a single  $90^\circ$  rf pulse, duration  $4 \mu s$ ; curve 2: without sample rotation, after saturation during 500 ms; curve 3: with sample rotation,  $\omega_r/2\pi = 40$  Hz, after a single  $90^\circ$  pulse or saturation.  $S_{zz}^{-1} = 48$  ms.

trated in Figure 7, curves 1 and 2. Curve 1 displays the Zeeman relaxation of a polycrystalline sample of partially deuterated l-alanine,  $ND_3^+CHCH_3COO^-$ , after a single  $90^\circ$  rf pulse with a duration much shorter than the inverse relaxation rates (49,57). Hence immediately after the pulse, which we define as  $t = 0$ ,  $\alpha_z = 0$  and  $\alpha_R = \alpha_R^{eq} = 0$ . The result is a rather obvious non-exponential relaxation, which can be described very accurately by a sum of two exponentials. The curve

2 of Figure 7 shows the relaxation obtained by saturating the system during a time long compared with the inverse relaxation rates. In this case at  $t = 0$ , defined as the time immediately after saturation,  $\alpha_Z = 0$  but  $\alpha_R$  is non-zero. This is due to the fact that during saturation the various relaxation transitions are able to establish a non-equilibrium population difference between the  $E^a$  and  $E^b$  species (in the example of Figure 5 the total  $E^a$  population would decrease, and the total  $E^b$  population would increase during saturation). It can be shown (58) that the coefficient corresponding to the smallest time constant in Eq. (14) decreases, in accordance with the experimental results.

Another relaxation behavior is observed if the sample is rotated around an axis perpendicular to  $H_0$  and with an angular frequency  $\omega_r$  much larger than the relaxation rates (59). In this case the relaxation becomes exponential and independent of the preparation of the system, see curve 3 in Figure 7. The explanation of this phenomenon is that due to the sample rotation, the Zeeman and rotational polarization system become decoupled, so that  $\alpha_R$  remains at thermal equilibrium both during the preparation time as well as during the relaxation time. As a result  $\alpha_Z$  relaxes with a single exponential with the rate  $S_{ZZ}$ . We note that the decoupling of  $\alpha_Z$  and  $\alpha_R$  by sample rotation also occurs for tunnelling methyl groups, where  $\omega_t \neq 0$ . A full explanation is given in ref. (60), here we shall confine ourselves by considering the example of Figure 5. For  $\beta = 0^\circ$  the relaxation rates  $W_1$  and  $W_2$  operate between the levels 4 and 5 and between 1 and 8. Instead of sample rotation we consider an experiment where the sample is flipped through an angle of  $180^\circ$  around an axis perpendicular to  $H_0$  with a fast repetition rate. This means that  $\beta$  jumps quickly between  $0^\circ$  and  $180^\circ$ . However, for  $\beta = 180^\circ$ , the non-zero relaxation rates are between the levels 2 and 5 with a strength  $W_1$ , and between the levels 3 and 8 with a strength  $W_2$ . Hence for  $\beta = 0^\circ$  the total  $E^a$  population decreases whereas it increases for  $\beta = 180^\circ$ . As a consequence during the flipping on the

average the total  $E^a$  population, and also the total  $E^b$  population remain constant, so that  $\alpha_R$  remains at thermal equilibrium.

For a polycrystalline sample  $S_{ZZ}$  is given by (58)

$$\begin{aligned} S_{ZZ} &= S_{ZZ}^{\text{intra}} + S_{ZZ}^{\text{inter}} \\ &= (9/20) Kpd [J(\omega_0, \tau_c) \\ &\quad + 4J(2\omega_0, \tau_c)] \\ &\quad + S_{ZZ}^{\text{inter}} \end{aligned} \quad (15)$$

$K = \gamma^4 \hbar^2 / r^6$ ,  $d$  is the so-called efficiency factor (5,49) which usually is close to one and  $p$  takes into account that the total number of protons  $N_H$  need not be equal to the number of protons  $N_{Me}$  belonging to the methyl groups. This causes a reduction in  $S_{ZZ}$  by the factor  $p$  given by

$$p = N_{Me} / N_H \quad (16)$$

We note that for  $p = d = 1$ ,  $S_{ZZ}^{\text{intra}}$  represents the well-known BPP formula for  $T_{1Z}^{-1}$ , elaborated for reorienting methyl groups (1,2). It has been shown (58) that from the different experiment-dependent relaxation measurements all elements of the relaxation matrix governing the relaxation of  $\alpha_Z$  and  $\alpha_R$  as well as the magnitude of  $S_{ZZ}^{\text{inter}}$  can be determined. Moreover, other experiments can be performed by which the state of non-equilibrium of  $\alpha_R$  during the relaxation can be demonstrated (61).

2.  $\omega_t = 0$ ,  $\omega_0 \tau_c$  arbitrary

In general the auto-relaxation rate  $S_{RR}$  of  $\alpha_R$  contains a term proportional to  $J(\omega = 0, \tau_c)$ . (This is due to  $A_{\frac{1}{2}}^{+1} \leftrightarrow E^a_{\frac{1}{2}}, E^b_{\frac{1}{2}}$  relaxation transitions.) It follows simply from Eqs. (11) and (17) that in the limit  $\omega_0 \tau_c \gg 1$ :  $S_{RR} \gg S_{ZZ}$ . Then  $\alpha_R$  is driven towards thermal equilibrium in a time short compared with the other relaxation times, and as a result the observed relaxation of  $\alpha_Z$  becomes almost a single exponential again with  $S_{ZZ}$  as a relaxation rate (62). This is illustrated in Figure 8a, where the Zeeman relaxation of  $ND_3^+CHCH_3COO^-$  after a single  $90^\circ$  pulse

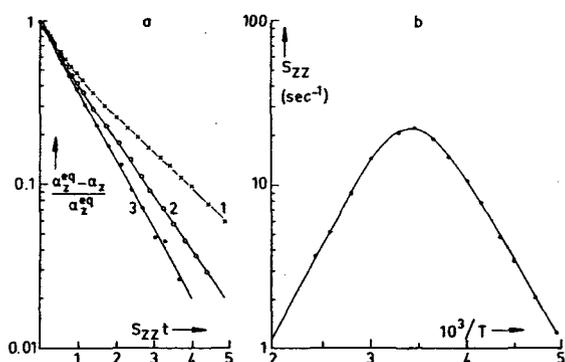


Figure 8. a) Zeeman relaxation of  $\text{ND}_3\text{CHCH}_3\text{COO}^-$  for a non-rotating sample after a single  $90^\circ$  pulse.  $\omega_0/2\pi = 60.8$  MHz. Curve 1:  $T = 327$  K,  $\omega_0\tau_c = 0.2$ ,  $S_{ZZ}^{-1} = 70$  ms; Curve 2:  $T = 258$  K,  $\omega_0\tau_c = 1.6$ ,  $S_{ZZ}^{-1} = 68$  ms; Curve 3:  $T = 202$  K,  $\omega_0\tau_c = 23$ ,  $S_{ZZ}^{-1} = 830$  ms. b)  $S_{ZZ}$  of  $\text{ND}_3\text{CHCH}_3\text{COO}^-$ , determined with a rotating sample, as a function of temperature. Dots: experimental; solid curve: theoretical, using the data given in the text.

is given for three temperatures. In all cases the values of  $S_{ZZ}$  has been determined from the relaxation observed with a rotating sample (not shown here). Indeed for the lowest temperature the non-exponentiality has disappeared. As a consequence, if the relaxation rate  $S_{ZZ}$ , measured with a rotating sample, is compared with the apparent relaxation rate, observed in case of a non-rotating sample after long saturation, these rates will differ for  $\omega_0\tau_c \ll 1$  and become equal for  $\omega_0\tau_c \gg 1$ .

We conclude that for  $\omega_0\tau_c \ll 1$ , experiment-dependent relaxation measurements are useful, for instance, for the determination of  $S_{ZZ}^{\text{inter}}$ , whereas especially the temperature dependence of  $S_{ZZ}$ , given by the Eqs. (4) and (17), can be used for determining the relaxation constant  $K$ , the activation energy  $E_a$  and the correlation constant  $\tau_0$ . The most accurate way to perform this is to use a rotating sample, because then problems like analyzing the non-exponentiality are avoided.

Figure 8b shows the temperature

dependence of  $S_{ZZ}$  for  $\text{ND}_3\text{CHCH}_3\text{COO}^-$  as obtained in this manner. As is well-known,  $\ln S_{ZZ}$  is proportional to  $T^{-1}$  for  $\omega_0\tau_c \ll 1$  and  $\omega_0\tau_c \gg 1$ , from which the activation energy  $E_a$  can be determined. The maximum occurs at  $\omega_0\tau_c = 0.616$  from which the correlation constant  $\tau_0$  can be calculated. Finally, the relaxation constant  $K$  can be obtained from the magnitude of the maximum.

For  $\text{ND}_3\text{CHCH}_3\text{COO}^-$  the results are (44,53): (i) the strength of  $S_{ZZ}^{\text{inter}}$  is ca. 3% of that of  $S_{ZZ}^{\text{intra}}$ ; (ii)  $E_a = (20.9 \pm 1.0)$  kJ/mol; (iii)  $\tau_0 = (2.7 \pm 1) \times 10^{-13}$  s; and (iv)  $K = (1.29 \pm 0.06) \times 10^{10}$  s $^{-2}$ , corresponding to a value for the intra-methyl proton-proton distance  $r$  of 1.79 Å. The latter result is in accordance with neutron scattering measurements (63).

We note that the dynamic coupling between  $\alpha_D$  and  $\alpha_T$ , which, for example, results in a non-exponential, experiment-dependent relaxation of the dipolar system, has also been established experimentally (49,64). It is also shown in these references that the non-exponentiality is most pronounced when  $\omega_0\tau_c \gg 1$ .

#### B. The Limit of Tunnelling,

$$\omega_t \neq 0$$

In this section the effect of tunnelling on the spin-lattice relaxation is investigated. The results are illustrated with measurements, performed on a polycrystalline sample of tetramethylgermanium,  $\text{Ge}(\text{CH}_3)_4$ , in the temperature region  $170 \text{ K} > T > 33 \text{ K}$  (56,57). As stated in section II.C, for decreasing temperatures  $\omega_t$  becomes non-zero and increases towards its final value  $\Delta_0$ , the ground torsional splitting. The values of  $\omega_t(T)$  and  $\Delta_0$  strongly depend on the shape and magnitude of the hindering potential. For  $\text{Ge}(\text{CH}_3)_4$  the hindering barrier was found to be a three-fold cosine shaped potential with a height of 5.8 kJ/mol (56,65) and Figure 9 shows the corresponding curve of  $\omega_t$  as a function of  $T$ , calculated by a formula given in (43). In Figure 9 the temperature dependence of the correlation time  $\tau_c$  of the methyl groups is given (56). It has been argued in section II.D.2 that the dynamic couplings between  $\alpha_Z$ ,  $\alpha_R(\beta)$  and  $\alpha_D$ ,  $\alpha_T(\beta)$  become

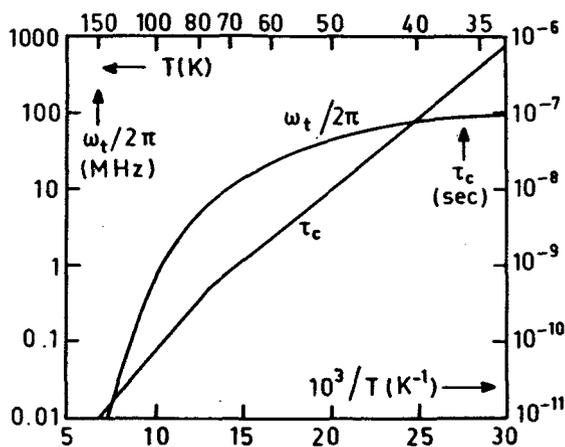


Figure 9.  $\omega_t/2\pi$  and  $\tau_c$  as a function of temperature for  $\text{Ge}(\text{CH}_3)_4$ .

non-zero when  $J[(\omega_t + n\omega_0), \tau_c]$  differs from  $J[(\omega_t - n\omega_0), \tau_c]$ ,  $n = 1, 2$ , which occurs when  $\omega_t \neq 0$ ,  $\omega_t \tau_c \geq 1$  and  $\omega_t$  is comparable to  $\omega_0$ . Consequently we expect the non-exponentiality in the relaxation of  $\alpha_z$  to increase for decreasing temperature. Moreover, the coupling terms between  $\alpha_z$  and  $\alpha_T(\beta)$ ,  $\alpha_D$  appear to be independent of sample rotation. This can be understood from Figure 5. The population difference corresponding to the tunnelling and dipolar system, induced during the relaxation, is the same for  $\beta = 0^\circ$  and  $180^\circ$ . Hence a rapid flipping of the methyl groups between  $0^\circ$  and  $180^\circ$  will not average out the deviation from non-equilibrium, as was the case for the rotational polarization system. Therefore we expect that sample rotation only partly removes the non-exponentiality. In practice sample rotation influences the effect of  $\alpha_D$  on  $\alpha_z$  as well. This rotation induces an extra time dependence in  $\alpha_D$  such that  $\alpha_D$  decays towards its thermal equilibrium value in a time which, depending on the spinning speed, can be short compared with the spin-lattice relaxation time (66). If this is the case the influence of  $\alpha_D$  on the Zeeman relaxation can be neglected, for the same reason as that the influence of  $\alpha_R$  could be neglected for  $\omega_0 \tau_c \gg 1$ , see section III.A.

In Figure 10 the Zeeman relaxation

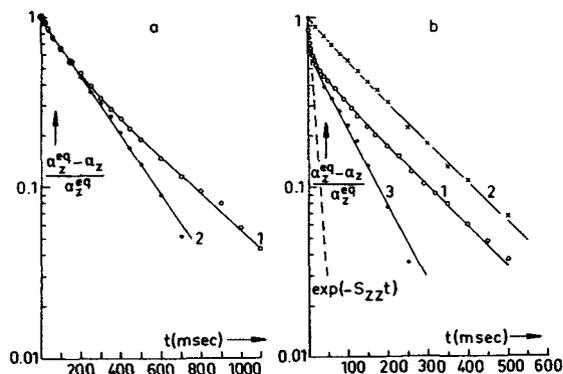


Figure 10. Zeeman relaxation of  $\text{Ge}(\text{CH}_3)_4$ ,  $\omega_0/2\pi = 38$  MHz. a)  $T = 99$  K,  $\omega_t \ll \omega_0$ ,  $\omega_0 \tau_c = 0.02$ . Curve 1: without sample rotation, after a single  $90^\circ$  rf pulse; curve 2: with sample rotation,  $\omega_r/2\pi = 30$  Hz, after a single  $90^\circ$  pulse;  $S_{ZZ}^{-1} = 250$  ms. b)  $T = 44$  K,  $\omega_t/2\pi = 66$  MHz,  $\omega_0 \tau_c = 3.6$ . Curve 1: without sample rotation, after a single  $90^\circ$  pulse; curve 2: without sample rotation, after saturation during 300 ms; curve 3: with sample rotation,  $\omega_r/2\pi = 100$  Hz, after a single  $90^\circ$  rf pulse;  $S_{ZZ}^{-1} = 12$  ms.

of  $\text{Ge}(\text{CH}_3)_4$  is shown, observed after single  $90^\circ$  rf pulses, for two temperatures. In Figure 10a  $T = 99$  K, which is high enough to neglect tunnelling effects. Moreover,  $\omega_0 \tau_c \ll 1$  so that we encounter the same conditions as in section III.A.1;  $\alpha_z$  is coupled only to  $\alpha_R(\beta)$  and sample rotation results in an exponential Zeeman relaxation. In Figure 10b, where  $T = 44$  K,  $\omega_t/2\pi$  is of the order of magnitude as  $\omega_0/2\pi = 38.2$  MHz, whereas  $\omega_t \tau_c \approx 6.2$ . Hence the coupling terms between all constants of the motion are non-zero and the relaxation remains non-exponential during sample rotation, mainly due to the coupling between  $\alpha_z$  and  $\alpha_T$  (67). In Figure 10b the relaxation after long saturation has also been given. Similarly to the case of non-tunnelling we observe that the fastest relaxation rates have disappeared almost completely.

The temperature dependence of the Zeeman relaxation for tunnelling methyl

groups is much more complicated than for non-tunnelling groups because of (i) the many dynamic couplings, (ii) the many different spectral density functions, and (iii) the temperature dependence of both  $\tau_c$  and  $\omega_t$ .

As a result  $\alpha_z(t)$  is governed by a weighted sum of many exponentials with corresponding rates which are complicated functions of the elements of the relaxation matrix  $\bar{S}$ , so that analysis of the observed relaxation is very complex. However, there is one exception; when after preparation of the spin system only the Zeeman system has been brought out of thermal equilibrium (e.g., by a short rf pulse), then the short time behavior of  $\alpha_z$  is governed by its auto-relaxation rate  $S_{ZZ}$ . This follows readily from Eq. (12a): after a  $90^\circ$  pulse  $\bar{\alpha}_R$ ,  $\bar{\alpha}_D$ , and  $\bar{\alpha}_T$  are still zero, so that on a time scale short compared with the relaxation times  $\dot{\alpha}_z \approx S_{ZZ}\bar{\alpha}_z$ . Consequently,  $S_{ZZ}$  equals the initial rate constant of the Zeeman relaxation. In Figure 10 is shown the way in which  $S_{ZZ}$  is obtained. In Figure 10a, the initial rate of curve 1 equals the rate following from curve 2, because the latter one is governed solely by  $S_{ZZ}$ . Therefore we focus our attention on the temperature dependence of  $S_{ZZ}$ . For a polycrystalline sample  $S_{ZZ}$  is given by (56)

$$\begin{aligned}
 S_{ZZ} &= S_{ZZ}^{\text{intra}} + S_{ZZ}^{\text{inter}} \\
 &= (9/40) \text{Kpd} [J\{(\omega_t + \omega_0), \tau_c\} \\
 &\quad + J\{(\omega_t - \omega_0), \tau_c\} \\
 &\quad + 4J\{(\omega_t + 2\omega_0), \tau_c\} \\
 &\quad + 4J\{(\omega_t - 2\omega_0), \tau_c\}] \\
 &\quad + S_{ZZ}^{\text{inter}} [J\{(\omega_t \pm n\omega_0), \tau_c\}, \\
 &\quad J(n\omega_0, \tau_c)] \\
 n &= 1, 2 \qquad (17)
 \end{aligned}$$

Depending on the experimental circumstances and the material under investigation,  $S_{ZZ}$  as a function of temperature can show different features:

- (i) If  $\omega_0\tau_c < 1$  for these temperatures where  $\omega_t$  becomes non-zero, the

"classical" maximum in  $S_{ZZ}$  due to  $\omega_0\tau_c \approx 1$  has not yet been reached. However, when  $\omega_t \gg \omega_0$  a maximum can be expected for  $\omega_t\tau_c \approx 1$ .

- (ii) When  $\omega_t \gg \omega_0$  and  $\omega_t\tau_c \gg 1$  the inter-methyl relaxation, which at high temperature usually is of the order of 30% of the intra-methyl relaxation (68), can become dominant for the relaxation, because, unlike  $S_{ZZ}^{\text{intra}}$ , it contains the spectral density functions  $J(n\omega_0, \tau_c)$ ,  $n = 1, 2$ , see Eq. (17). This can give rise to a classical maximum again occurring at those temperatures where  $\omega_0\tau_c \approx 1$  (69,70).
- (iii) When at some temperature  $\omega_t \approx \omega_0$  or  $\omega_t \approx 2\omega_0$  and  $\omega_t\tau_c \gg 1$ , so-called tunnelling-assisted maxima in  $S_{ZZ}$  occur due to the terms  $J[(\omega_t - \omega_0), \tau_c]$  and  $J[(\omega_t - 2\omega_0), \tau_c]$  in Eq. (17).

To illustrate these features we con-

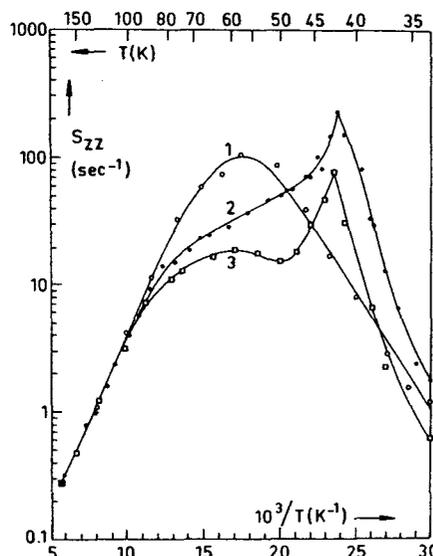


Figure 11.  $S_{ZZ}^{-1}$  of  $\text{Ge}(\text{CH}_3)_4$  as a function of temperature. Curve 1:  $\omega_0/2\pi = 9$  MHz; curve 2:  $\omega_0/2\pi = 38$  MHz; curve 3:  $\omega_0/2\pi = 73$  MHz.

sider Figure 11, where  $S_{ZZ}$  of  $\text{Ge}(\text{CH}_3)_4$

has been given as a function of temperature for three rf frequencies. It follows:

1.  $\omega_0/2\pi = 9 \text{ MHz}$

For  $T > 80 \text{ K}$ ,  $\omega_t$  can be neglected, and  $S_{ZZ}$  is given by Eq. (15) again, with  $\omega_0\tau_c \ll 1$ . The maximum at  $T = 57 \text{ K}$  is determined mainly by the condition  $\omega_t\tau_c \approx 1$ , as here  $\omega_t \approx 4.2\omega_0$ . Though it has been found (56) that for  $T < 40 \text{ K}$  the intermethyl relaxation is dominant, no separate maximum corresponding to  $\omega_0\tau_c \approx 1$  is observed. This is because this maximum is expected at ca.  $48 \text{ K}$ , where the intra-methyl relaxation still dominates. Tunnelling assisted maxima, which would occur for  $\omega_t/2\pi = 9 \text{ MHz}$  and  $18 \text{ MHz}$ , are not observed, because  $\omega_t\tau_c \ll 1$  at the corresponding temperatures, see Figure 9.

2.  $\omega_0/2\pi = 38 \text{ MHz}$

The relaxation shows a pronounced maximum at  $42 \text{ K}$ . Inspection of Figure 9 shows that at this temperature  $\omega_t/2\pi \approx 76 \text{ MHz}$ , so that this is a tunnelling-assisted maximum corresponding to  $\omega_t = 2\omega_0$ . The maximum corresponding to  $\omega_t = \omega_0$  would occur at  $55 \text{ K}$ , but this is not observed because there the condition  $\omega_t\tau_c \gg 1$  is not fulfilled.

3.  $\omega_0/2\pi = 73 \text{ MHz}$

The relaxation is maximal at  $43 \text{ K}$ , where  $\omega_t \approx \omega_0$ . Hence this is also a tunnelling-assisted maximum. The magnitude of this maximum is ca. 3 times smaller than that observed for  $38 \text{ MHz}$ , which would be expected because for  $\omega_t = \omega_0$  the term  $J[(\omega_t - \omega_0), \tau_c]$  in Eq. (17) is dominant, and for  $\omega_t = 2\omega_0$  the term  $4J[(\omega_t - 2\omega_0), \tau_c]$ . Since according to Figure 9 the maximal value of  $\omega_t$  is ca.  $90 \text{ MHz}$ , no tunnelling-assisted maximum can occur for  $\omega_t = 2\omega_0$  and  $\omega_0/2\pi = 73 \text{ MHz}$ .

At low temperatures the dipolar system can also be coupled to all other constants of the motion, resulting in a

non-exponential dipolar relaxation. This has been observed in  $\text{Ge}(\text{CH}_3)_4$ . However, as the dipolar relaxation has not been analyzed in great detail, the results will not be shown here.

A much more striking experiment, which clearly confirms the dynamic coupling between the dipolar and tunnelling system, has been performed by Haupt (71,72). He considered the dipolar signal of  $\gamma$ -picoline at low temperatures and found that after a sudden temperature jump the dipolar signal increased to a value much larger than the Zeeman signal and then decreased to its thermal equilibrium value  $\approx 0$  again, see Figure 12. The explanation

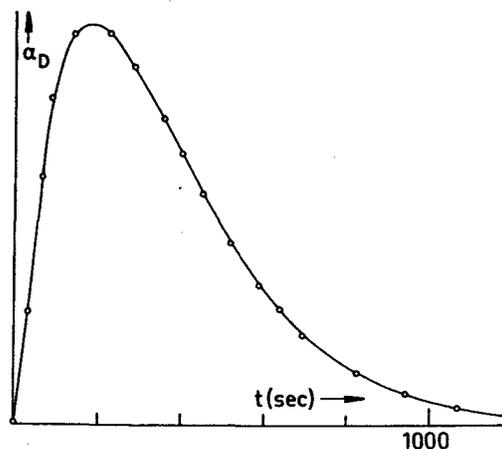


Figure 12. Dipolar polarization of  $\gamma$ -picoline after a temperature jump from  $11 \text{ K}$  to  $26 \text{ K}$ . After Haupt (72).

of this phenomenon is that in  $\gamma$ -picoline, which has a very low potential barrier, the tunnelling splitting is of the order of GHz, much larger than the rf frequency. Hence the tunnelling system is coupled only to the dipolar system. If starting from thermal equilibrium, a temperature jump is applied, then  $\omega_t$  changes, but the population difference between the ( $E^a + E^b$ ) and the A symmetry species still corresponds to the value of  $\omega_t$  before the jump. Thus after the temperature change the tunnelling system is in a state of

non-equilibrium, and will relax towards the new thermal equilibrium value with rates determined by the elements of  $\tilde{S}$ . Due to the dynamic coupling between  $\alpha_T$  and  $\alpha_D$  the dipolar polarization effect described above is induced.

#### IV. CONCLUSIONS

It has been shown that in solids the symmetry properties of the methyl groups lead to extra constants of the motion, the so-called rotational polarization and tunnelling system. At low temperatures, where the tunnelling splitting becomes non-zero, on the time scale of spin-lattice relaxation these systems are coupled dynamically to the Zeeman and dipolar systems. At high temperatures, where the tunnelling splitting can be neglected, non-zero couplings exist only between the Zeeman and rotational polarization and between the dipolar and tunnelling systems. The result is a Zeeman and dipolar relaxation which generally consist of weighted sums of many exponentials with rates determined by the various auto- and cross-relaxation rates. As a consequence the temperature dependence of the Zeeman relaxation is a complicated function of  $\tau_C(T)$  and  $\omega_t(T)$ , which makes difficult the determination of these quantities from the measurements. However, there is one exception: the auto-relaxation rate of the Zeeman or dipolar system can be obtained rather easily, provided that the proper relaxation experiment has been chosen. From this quantity the values of  $\tau_C(T)$  and  $\omega_t(T)$ , and so the height and shape of the hindering potential, can be determined rather accurately.

In the past the existence of the extra constants of the motion has not been recognized. This is due to the fact that it was assumed implicitly that the spin diffusion was not submitted to symmetry restrictions, leading to fast flip-flop transitions also between levels corresponding to different symmetry species. The result of this so-called complete spin diffusion (CSD) was that the rotational polarization and tunnelling systems are driven towards thermal equilibrium on a time scale fast compared with the spin-lattice relaxation, and the only remaining

constants of the motion are the Zeeman and dipolar systems each relaxing with a single exponential. Therefore in a lot of cases the apparent relaxation rate of e.g. the Zeeman relaxation has been interpreted with the CSD theory. Now it has been shown in this paper that in reality  $S_{ZZ}$  is equal to the initial rate value of the Zeeman relaxation, provided that only  $\alpha_Z$  has been brought out of thermal equilibrium, or that  $S_{ZZ}$  is equal to the relaxation rate observed for a rotating sample (the latter is only true when  $\omega_t = 0$ ). As  $S_{ZZ}$  can differ considerably from the apparent time constant, this can lead to erroneous results. For instance, if for the case of partially deuterated l-alanine the apparent time constant, observed after long saturation, has been interpreted with the CSD theory, the following results would have been obtained (62,73): (i)  $\omega_0\tau_C \ll 1$ :  $E_a = 20.9$  kJ/mol; (ii)  $\omega_0\tau_C \gg 1$ :  $E_a = 16.7$  kJ/mol; (iii)  $\tau_0 = 1.9 \times 10^{-13}$  s and (iv)  $K = 0.87 \times 10^{10}$  s<sup>-2</sup>, corresponding to a value of  $r$  of 1.92 Å. These results differ considerably from those obtained with a rotating sample, see section III.A. Also, a misinterpretation of the measurements can also lead to a disregarding of the tunnelling-assisted maxima (56).

Finally it should be emphasized that the existence of constants of the motion as a result of symmetry properties is not restricted to methyl groups, but occur in any reorienting or tunnelling molecular group. Indeed, these constants of the motion have been found, both theoretically and experimentally, in flipping spin pairs (74) and have been predicted in reorienting groups with a 6-fold symmetry, like benzene rings (75,76). In the latter case, however, the relaxation couplings are small and the result is a relaxation close to that following from the CSD theory.

Note. We would like to mention that since submission of this paper an interesting and still ongoing discussion exists between Clough (77,78) and us (79). The discussion centers around the question of whether there are two distinguishable E species, as is the common view and also adopted by us, or

only one E species as is Clough's view.

In the first paper (77) Clough argued that the existence of two long-lived E symmetry species would be in conflict with the classical reorientation model. In a reply to this Emid (79) showed that the existence of two long-lived E symmetry species at high (as well as low) temperatures was in perfect harmony with the classical reorientation.

In the latest paper (78) Clough and McDonald argued that there could not be two distinguishable E species also at low temperatures, because the proper symmetry group is  $C_{3v}$  instead of  $C_3$ , and because the wave functions should be fully antisymmetric for single pair exchange. In a paper to be published elsewhere we shall show that the use of  $C_{3v}$  instead of  $C_3$  symmetry still allows two distinguishable E species (two partner states) to exist even when the full antisymmetric requirement is taken into account, see also Stevens (80). Finally, we note that our model has been fruitfully applied by others, see e.g. (81) and references therein.

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