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Influence of Sample Rotation on the NMR Spin-Lattice Relaxation of CH_3 Groups in Solids

R. A. Wind and S. Emid
Laboratorium voor Technische Fysika, Technische Hogeschool Delft, Delft, The Netherlands

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When nuclear spin-lattice relaxation in solids is due to rapid random rotation of methyl groups, the Zeeman relaxation can be nonexponential. This is because the magnetization is dynamically coupled to the so-called rotational polarization. It is shown that rotating the sample perpendicular to the magnetic field with angular velocity large compared with the relaxation rate decouples these parameters, resulting in an almost exponential Zeeman relaxation close to that predicted by the spin-temperature theory.

When the random reorientation of CH_3 groups is the dominant relaxation mechanism in a solid, the NMR spin-lattice relaxation is often nonexponential, not only in single crystals[1] or diluted samples,[2-4] but also in polycrystalline nondiluted materials.[5-7] This has been explained by Emid and Wind[8] by modifying the Hilt and Hubbard theory[9] where the relaxation of isolated methyl groups is considered, taking into account the cross correlations in the motion of the methyl protons. This modification consists of the inclusion of the spin-diffusion process. It is found that under motional-narrowing conditions the spin diffusion cannot restore a Boltzmann distribution between all adjacent energy levels of the CH_3 groups, but only between energy levels within one of the A, E^a, and E^b symmetry species characterizing the CH_3 group (this has been called symmetry-restricted spin diffusion). This has been further evaluated by Emid and co-workers[10-12] and it is found that firstly, the dipolar energy is dynamically coupled to the population difference between the A and E species, and secondly, the Zeeman magnetization is dynamically coupled to the population difference between the E^a and E^b species, which has been called rotational polarization. As a result the observed nonexponentiality could be explained satisfactorily. It is the purpose of this paper to demonstrate that a specific rotation of the sample decouples the Zeeman magnetization and the rotational polarization, and that this can cause a considerable change in the observed spin-lattice relaxation, not only for single crystals, but also for a powder.

To this end we first consider a nonrotating single crystal consisting of methyl groups with an angle β_j between their symmetry axes and the static magnetic field. With restriction to the case of extreme narrowing, $\omega_0\tau_c \ll 1$ (ω_0 is the Larmor frequency, τ_c is the correlation time for the random rotation of the groups), the Zeeman relaxation due to the intramethyl dipolar interaction is given by the following rate equations[12]:

$$\begin{pmatrix} \dot{\Psi}_1 \\ \dot{\Psi}_4 \end{pmatrix} = C \begin{pmatrix} -2(1+3\cos^2\beta_j) & 6\cos\beta_j \\ 4\cos\beta_j & -3 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_4 \end{pmatrix}, \qquad (1)$$

where $\Psi_1 = M_z - M_0$, $\Psi_4 = P_{E^a} - P_{E^b}$, M_z is the Zeeman magnetization and M_0 its equilibrium value, and P_{E^a} and P_{E^b} are the total populations of the E^a and E^b species, respectively. $C = \frac{9}{16}\tau_c\gamma^4\hbar^2/r_0^6$; r_0 is the proton-proton distance. The result is a

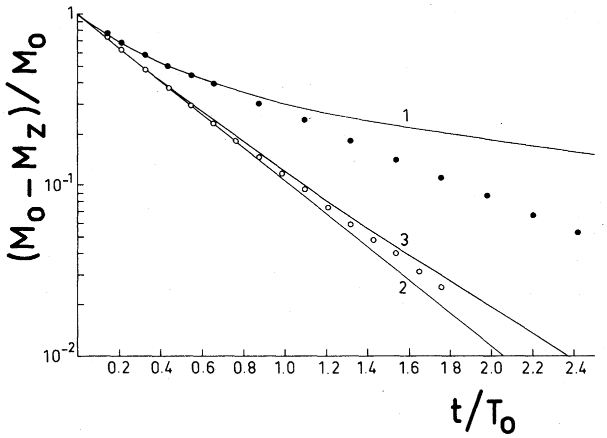

FIG. 1. Recovery of the magnetization after a 90° pulse, or after saturation. Curve 1: limit I for a nonrotating sample; curve 2: limit II for a rotating a nonrotating sample; curve 3: limit I for a rotating sample. $T_0^{-1} = (\gamma^4\hbar^2/r_0^6)\tau_c$. Dots: recovery from saturation of 2, 6-dimethylphenol at room temperature for a nonrotating sample, with $T_0 = 45.6$ sec; open circles: idem for a rotating sample. The absolute error in the magnetization is ± 0.01.

two-exponential relaxation behavior of $M_z(t)$.

In a polycrystalline sample the resulting Zeeman relaxation depends on the actual situation, such as the region in which spin diffusion is effective and the presence of protons other than methyl protons (ring protons, etc.). However, as the various results appeared to be rather similar, we shall confine ourselves to considering the case of noninteracting, randomly oriented crystallites of the type described above. Now the isotropic average of $\Psi_1(\beta_j, t)$ is observed as a function of time, $\Psi_1(\beta_j, t)$ being the solution of Eq. (1) (this will be called limit I). Curve 1 in Fig. 1 gives the magnetization as a function of time after a 90° pulse or after saturation. In this figure the relaxation behavior following from the usual spin-temperature theory[13] is also given (curve 2). The result of this theory, which has often been used to explain the experiments, is a purely exponential Zeeman relaxation with a time constant $(4C)^{-1}$. We observe that this relaxation behavior is quite different from that according to limit I, though it must be emphasized that the more the intermethyl relaxation, which has been neglected so far, is taken into account, the more the two curves approach. Therefore curve 2 will be adopted as a second limit, limit II. So in practice the observed Zeeman relaxation will lie in the region bounded by the curves 1 and 2.

We now consider the case that the single crystal described above is rotated with angular velocity ω_s around an axis of rotation making an angle β_s with the static magnetic field. Then $\cos\beta_j$, which now is a function of time, can be expressed as[14]

$$\cos\beta_j(t) = \cos\beta_s \cos\beta_j' + \sin\beta_s \sin\beta_j' \cos(\omega_s t + \varphi_j), \tag{2}$$

where β_j' is the angle between the CH_3 symmetry axes and the axis of rotation, and φ_j is the azimuth angle at time $t = 0$. We suppose that ω_s is small compared with the spin-diffusion rate, but large compared with the spin-lattice relaxation rate. Then the spin diffusion remains unaffected, and in the rate equations (1) the time-averaged value of $\cos\beta_j$ and $\cos^2\beta_j$ can be used. The result is

$$\begin{pmatrix} \dot{\Psi}_1 \\ \dot{\Psi}_4 \end{pmatrix} = C \begin{pmatrix} -2(1 + 3\cos^2\beta_s \cos^2\beta_j' + \frac{3}{2}\sin^2\beta_s \sin^2\beta_j') & 6\cos\beta_s \cos\beta_j' \\ 4\cos\beta_s \cos\beta_j' & -3 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_4 \end{pmatrix}. \tag{3}$$

Hence we find as an important result that for $\beta_s = 90°$ the parameters Ψ_1 and Ψ_4 are decoupled, so that $\Psi_1(t)$ now becomes exponential with a time constant $T' = [C(5 - 3\cos^2\beta_j')]^{-1}$.

For a polycrystalline sample the result depends again on the actual situation. The limit II is not affected by sample rotation, as was to be expected. For the limit I the observed magnetization is given by the isotropic average of $\exp(-t/T')$. The result is given by curve 3 in Fig. 1. So for a rotating sample the observed Zeeman relaxation will be in the region between the curves 2 and 3.

For the discussion it must firstly be emphasized that in practice often the crystal structure of the material under investigation is unknown or rather complicated. This means that for a nonrotating sample, where the Zeeman relaxation is somewhere in the region between the curves 1 and 2 of Fig. 1, it will be very difficult to determine accurately quantities such as activation energy or correlation time. It has been suggested[7] to use the initial-rate approximation, but this will hardly be applicable in practice, because the signal-to-noise ratio is usually rather poor and because the intermethyl relaxation will obscure the nonexponential character of the relaxation. Indeed we think that for this reason in the past often the nonexponentiality may not have been recognized, and that the results of the spin-temperature theory have been applied erroneously to the observed decay. This means that a too large value of T_{1z} has been used. As the nonexponentiality depends on the value of $\omega_0\tau_c$, and so of the temperature, this may explain the often systematic difference in values of the activation energy obtained by NMR with use of the spin-temperature theory and by other spectroscopic techniques, and may also cause a difference in the slope of $\ln(T_{1z})$ versus T^{-1} for $\omega_0\tau_c \ll 1$ and $\omega_0\tau_c \gg 1$, as has been reported in the literature. For a rotating sample it follows clearly from Fig. 1 that the Zeeman relaxation, now being in the region between the curves 2 and 3, is always almost exponential and hardly depends on the experimental situation (and this is the more true if the intermethyl relaxation is taken into account). This means that in any case the time constant obtained in this way can rather accurately (at least within 2%) be approximated by $(4C)^{-1}$.

As an illustration we investigated the recovery from saturation of a polycrystalline sample of 2, 6-dimethylphenol at room temperature, with $\omega_0 \simeq 2\times10^8$ sec^{-1} and $\tau_c \simeq 10^{-12}$ sec.[15] Figure 1 shows the average of thirty measurements (corrected for the finite value of the induced-transition probability used for the observation of the signal) of a nonrotating sample (dots) and of a sample rotating around an axis perpendicular to the magnetic field with a frequency 4 Hz (open circles). We observe that, though in the case of nonrotation the relaxation is almost exponential, the change in relaxation is considerable: From the nonrotating sample the value of T_{1z} would be 38 sec (we have ascertained that this was independent of the position of the sample with respect to the magnetic field), whereas with rotation this value becomes 21 sec.

Concluding we propose that rotating the sample around an axis perpendicular to the magnetic field and with an angular velocity large compared to the spin-lattice relaxation rate (but small compared to the spin-diffusion rate) should be introduced as a standard tool for the investigation of reorientating CH_3 groups, because in any case the Zeeman relaxation observed with the rotating sample can be described with very good accuracy by the result following from the usual spin-temperature theory. We finally note that sample rotation can also be used to get information about the crystal structure of the material, and that similar experiments can be performed to investigate the coupling between dipolar and tunneling energy, as observed at low temperatures.[16]

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