

Method for calculating polarization and alignment from the NMR spectrum of polarized deuterons

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Some practical formulas for calculating the polarization and the actual shape function of quadrupole-broadened NMR transitions have been found. The formulas use the spectrum of polarized deuterons with unresolved structure in the case of an axisymmetric tensor of the electric field gradient. A method has been developed for determining the polarization and the alignment on the sole basis of the amplitudes of three extrema in the NMR spectrum in the case of a Boltzmann distribution of spins. A good agreement is found with results of numerical calculations by means of algorithms which are far more complex. This agreement is found in the cases of both single and double quadrupole bonds in the molecules of the amorphous materials which are used most commonly as polarized targets. (This work was carried out in the Ultrahigh Energy Laboratory of the Joint Institute for Nuclear Research.)

In this letter we propose a method for calculating the polarization and actual lineshape of quadrupole-broadened NMR transitions of a polarized deuteron spin system. This method was developed in the course of an effort by the CERN SMC collaboration to optimize the material of the world's largest frozen polarized deuteron target. The calculations are based on the axial symmetry of the tensor of the electric field gradient in molecules, the theoretical lineshape of quadrupole transitions for amorphous materials, and the experimental NMR spectrum. The results of this study can be used to investigate the electronic structure of molecules.

The NMR spectrum of deuterons ($I = 1$) has two peaks (Fig. 1), which correspond to two mutually overlapping, quadrupole-broadened transitions: $m = +1 \leftrightarrow m = 0$ and $m = 0 \leftrightarrow m = -1$, where $m = \langle I_z \rangle$.

If there is a Boltzmann distribution in the spin system, the ratio of the intensities of these transitions, $I_+/I_- = R$, completely determines the sublevel populations p_{+0-} and therefore the principal parameters of the polarized target, specifically, its polarization p_z and its alignment p_{zz} :

$$R = \frac{p_+ - p_0}{p_0 - p_-} = \frac{p_+}{p_0} = \frac{p_0}{p_-} = \exp \left[\frac{h\nu}{kT_s} \right], \quad p_+ + p_- + p_0 = 1, \quad (1)$$

$$p_z = p_+ - p_- = \frac{R^2 - 1}{R^2 + R + 1}, \quad p_{zz} = 1 - 3p_0 = \frac{R^2 - 2R + 1}{R^2 + R + 1}.$$

Here h and k are the Plack constant and the Boltzmann constant, ν_D is the Larmor

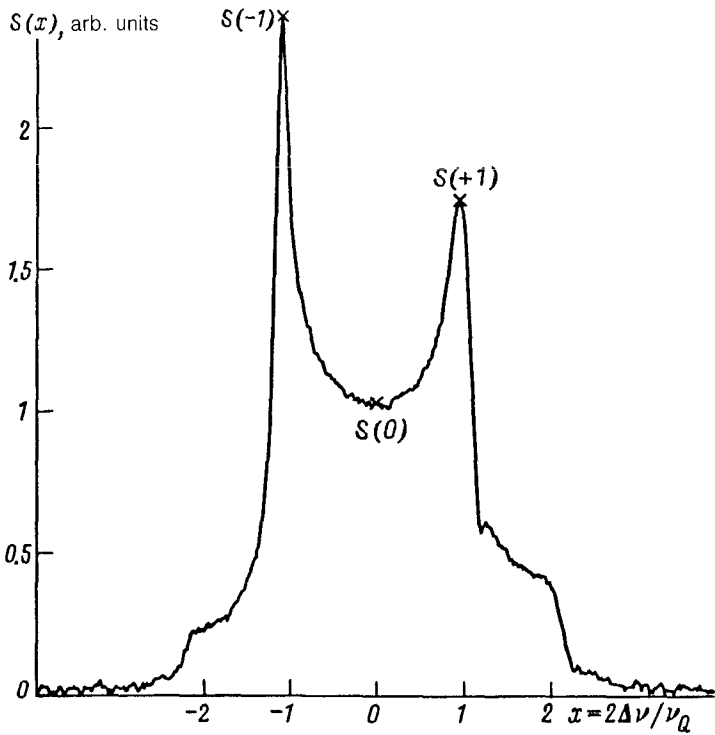


FIG. 1. Nuclear-magnetic-resonance spectrum of 1-butanol D10 with a polarization of 31.1%. Here x represents the values of the extrema of the spectrum, from which R is calculated in expression (9).

frequency of deuterons, and T_s is the temperature of the deuteron spin system.

We denote the frequency distributions of the intensities of the transitions $m = +1 \leftrightarrow m = 0$ and $m = 0 \leftrightarrow m = -1$ as $J^+(x)$ and $J^-(x)$, respectively, where $x = 2\Delta\nu/\nu_0$ is the normalized frequency shift with respect to the deuteron Larmor frequency,¹ and

$$\nu = \nu_D + \frac{1}{2}\nu_Q x. \quad (2)$$

Here $\nu_Q = 3eQV_{zz}/(2h)$, eQ is the deuteron quadrupole moment, and V_{zz} is the electric field gradient along the principal axis of the gradient tensor. The problem is to determine the functions J^+ and J^- and the ratio of their total intensities (R) from the experimental NMR spectrum of the deuterons, $S(x) = J^+(x) + J^-(x)$, in the case in which the functions $J^\pm(x)$ overlap in frequency. We introduce some auxiliary functions, a symmetric function $C(x)$ and an antisymmetric one $A(x)$, defined by

$$C(x) = \frac{1}{2}[S(x) + S(-x)], \quad A(x) = \frac{1}{2}[S(x) - S(-x)]. \quad (3)$$

It follows from the axial symmetry of the field-gradient tensor that the NMR spec-

trum is symmetric with respect to an axis drawn through ν_D , which determines the relationship between the functions $J^+(x)$ and $J^-(x)$:

$$J^+(x)/J^-(-x) = R. \quad (4)$$

Using (3) and (4), we can easily derive general expressions for the functions $J^\pm(x)$. These expressions are valid for not only a quadrupole broadening but also a dipole-dipole broadening of the NMR spectrum:

$$J^+(x) = \frac{R}{R^2 - 1} [(R + 1)A(x) + (R - 1)C(x)], \quad (5)$$

$$J^-(x) = \frac{1}{R^2 - 1} [(R - 1)C(x) - (R + 1)A(x)],$$

The only unknown quantity in (5) is the parameter R . To determine it, we need some further information on the functions $J^\pm(x)$. This information was found in Ref. 2 through the use of the fairly general and theoretically grounded assumption that the functions $J^+(x = -1)$ and $J^-(x = +1)$ are "smooth" curves at the maxima of the functions $J^-(x = -1)$ and $J^+(x = +1)$, respectively. A third-degree polynomial is selected as a model curve, and the parameter R is calculated from the minimum of the mean square deviation of $J^\pm(x)$ from this model curve. Some more-detailed theoretical arguments regarding the functions J^\pm , which incorporate a dipole-dipole broadening of the spectrum of quadrupole transitions, are made in Refs. 1 and 3. Here R is found by fitting the theoretical NMR lineshape to the experimental curve. Although this method is useful for determining the asymmetry parameter of the field-gradient tensor, additional parameters (characterizing the dipole-dipole broadening of the spectrum) are used in calculating the polarization and the alignment. Equation (4) with $x = \pm 2$, i.e., with the values of the NMR spectra in the wings, were used to determine R in Ref. 4. That approach leads to only an approximate estimate of R , since the molecules of the materials which are the most promising for use as polarized targets contain double quadrupole bonds, which distort the shape of the wings of the NMR signal.

In the method proposed below, R is calculated [see expression (9)] from the values of three extrema of the deuteron NMR spectrum. The statistical errors are then reduced through a refinement based on a minimum of the mean square deviation from the model curve.

Here are the theoretical functions⁵ $J_i^\pm(x)$ describing the lineshape of quadrupole transitions in amorphous materials:

$$J_i^+(x) = B(-x + 1)^{-1/2}, \quad -2 < x < 1, \quad (6)$$

$$J_i^-(x) = \frac{B}{R}(x + 1)^{-1/2}, \quad -1 < x < 2,$$

where B is a normalization constant. We assume that the contribution of dipole-dipole

interactions to the values of these functions is negligible far from the pole of these functions. The value of B can then be determined easily from the experimental spectrum at $x = 0$. Since we have $A(0) = 0$, we have $C(0) = S(0) = J^+(0) + J^-(0)$ and therefore $B = S(0)R/(R + 1)$. It is also obvious that the values of the experimental functions $J^+(-1)$ and $J^- (+1)$ are

$$J^+(+1) = S(+1) - J_t^-(+1), \quad J^-(-1) = S(-1) - J_t^+(-1). \quad (7)$$

Using (6) and (7), we find the following equation for R :

$$R \left[S(-1) - \frac{R}{(R+1)} \frac{S(0)}{2^{1/2}d} \right] = \left[S(+1) - \frac{S(0)}{(R+1)2^{1/2}d} \right], \quad (8)$$

where the correction factor d reflects the presence of single or double quadrupole bonds in the molecule. In the simplest case, of single bonds, we have $d \equiv 1$. Equation (8) is satisfied identically with

$$R = \frac{S(+1) - S(0)/(2^{1/2}d)}{S(-1) - S(0)/(2^{1/2}d)}. \quad (9)$$

Equations (1) and (9) show that all that is needed in order to calculate p_z and p_{zz} are the amplitudes of three extrema of the NMR signal. The actual lineshape of each quadrupole transition in the case of dipole-dipole broadening can be calculated from (5) with R from (9). Expression (9) gives a surprisingly accurate description of the polarization of deuterons according to the spectra given in Refs. 1-3 and as calculated in the original studies by algorithms which are incomparably more complex. This comment applies to spectra with not only single but also double quadrupole bonds. It furthermore applies to spectra with small asymmetry parameters of the field-gradient tensor. The error in the determination of the polarization through the use of graphical information from these papers is less than $\pm 3\%$. A better agreement, with an error of less than $\pm 2\%$, is found through the use of numerical data on the spectra of 1-2-propanediol-D6, D8 and deuterated ethandiol. On the other hand, the spectrum for the latter substance (Fig. 1 from Ref. 6) differs substantially with the results calculated by our method. That spectrum apparently does not correspond to thermal equilibrium in the deuteron spin system.

Let us calculate the correction d in expression (9) for double quadrupole bonds. We assume that most of the deuterons, with a relative number C_1 , have $\nu_Q = \nu_Q(1)$, while the other deuterons correspondingly have C_2 and $\nu_Q(2)$, where $C_2 \leq C_1$ and $C_1 + C_2 = 1$. The presence of double bonds leads to changes in model curves (6), which are now written as the sum of two single transitions with weights C_1 and C_2 . The normalization coefficient B , expressed in terms of $S(0)$, remains the same in the case of double bonds as in the case of single bonds, since the central frequency ν_D does not change for either component of the spectrum. The values of the functions $J_t^-(+1)$ and $J_t^+(-1)$ in (7) change by, respectively,

$$J_{td}^-(+1) = J_t^-(+1)d^{-1}, \quad J_{td}^+(-1) = J_t^+(-1)d^{-1}, \quad (10)$$

where

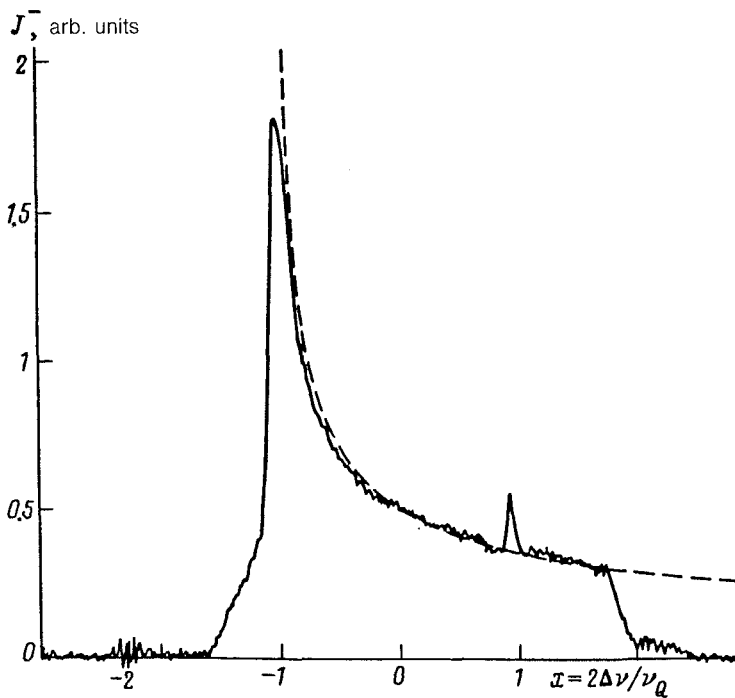


FIG. 2. The transition lineshape $J_1^-(x)$ in 1-2-propanediol D8 calculated from (5). The dashed line shows a model function $J_1^-(x)$ from (6) with $d = 1$.

$$d = [C_1 + 2^{1/2}C_2(1 + \nu_Q(1)/\nu_Q(2))^{-1/2}]^{-1}. \quad (11)$$

Using the data of Ref. 3 (see Figs. 2 and 4 of that paper) for 1-2-propanediol D8, we find $C_1 = 6/8$ —(CD bond), $C_2 = 2/8$ —(OD bond), and $\nu_Q(1)/\nu_Q(2) = 166.3/197.9 = 0.84$. We have $d = 0.989$. The correction to the polarization is only 0.2%, and it goes in the direction of improving the agreement with the results of Ref. 3. Note that the excellent agreement between the results calculated from expression (9) and the results of Ref. 3 is found even at a small value of the asymmetry parameter of the field gradient tensor.

It is not difficult to see that the correction factor d in (9) can be determined far more simply and accurately without using (11), by an iterative method. Varying d in (9) near 1, while leaving the other amplitudes of the extrema fixed, we can optimize this parameter by minimizing the mean-square deviation of $J^\pm(x)$ from model curves (6). Consequently, in determining R we do not need to know the constants C_1 , C_2 , $\nu_Q(1)$, and $\nu_Q(2)$. The method for calculating R acquires an importance in its own right. Calculations show that the polarizations usually found in this manner differ by less than 1% from the values with $d = 1$. Figure 2 shows the model function $J_1^-(x)$ and the actual shape function $J_1^-(x)$ of the NMR transitions for the cases of quadru-

pole and dipole–dipole broadening for 1–2-propanediol D8 according to calculations from (6) and (5), respectively ($d = 1$).

We note in conclusion that the method developed here is of practical usefulness for physics experiments using polarized deuteron targets.

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