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07 JUL. 1986

TRI-PP-86-27
May 1986

THE FROZEN SPIN ORIENTATION OF DEUTERIUM NUCLEI IRRADIATED AT RADIO-FREQUENCIES

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Abstract

A dynamically polarized deuterium target was constructed to determine the second-order analyzing power T_{20} in π -d elastic scattering. The required deuterium alignment can be enhanced by high-intensity rf irradiation of oriented deuterium nuclei. A method was developed to obtain the target-averaged alignment from NMR spectra. Of the irradiation schemes that were tested experimentally, the rf burning of the pedestal area at the edge of the NMR spectrum provided the largest alignment increase (more than a factor 1.5). For this spin reorientation lifetimes longer than 50 hours were measured.

(submitted to Nuclear Instruments and Methods A)

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1. Introduction

In the recent past, the tensor polarization T_{20} of the recoil deuterons in π -d elastic scattering has been measured at SIN [1], LAMPF [2] and TRIUMF [3]. There exist considerable discrepancies in the data for pion energies around 140 MeV. Therefore, interest emerged in measuring this observable with an aligned deuterium target to avoid the complications of determining polarizations by a double-scattering experiment [12].

A certain degree of spin alignment is always present in a deuterium target if polarization is produced by microwave irradiation. Cooling of the sample to a temperature below 0.1 K increases the relaxation time of the polarization to several hundreds of hours and, in effect, freezes the spin orientation. Then, the deuterium orientation can be manipulated by radio-frequency irradiation. Along this line, very interesting nuclear magnetic resonance (NMR) spectra were produced quite some time ago at CERN [4] in a magnetic field of 2.5 T. High intensity irradiation at 16 MHz (rf burning) produced holes in the deuterium NMR spectrum which disappeared after a lifetime of minutes. Slightly off-resonance irradiation of the proton system at 106 MHz (rf pumping) resulted in high values for the alignment in some parts of the deuterium spin system with decay times of a few hours. No sample-averaged value for the alignment was determined. Recently an increase from 15% to 20% for the alignment in ND_3 was reported by the group in Bonn [5], but it was not discussed how the value of 20% was measured.

For an explanation of the observations it must be realized that NMR spectra show the differences of the magnetic substate populations as a function of frequency. Due to the interaction of the quadrupole moment

of a deuteron with the molecular electric field gradient at the position of the nucleus a change of the resonance frequency occurs. The size of the frequency shift is proportional to the quadrupole energy. This energy depends on the angle between the electric field gradient and the external magnetic field. Therefore, the choice of a particular frequency for rf irradiation selects that part of the ensemble of deuterium nuclei that, due to the quadrupole energy, has a resonance frequency equal to the chosen rf frequency. Here, we develop a framework to calculate the magnetic substate populations of oriented deuterium nuclei as a function of the quadrupole energy. The summation over all occurring quadrupole energies yields sample-averaged values. This formalism is tested with three rf irradiations for which the changes in level populations are calculated. These are compared with the results that are obtained from the NMR spectra.

For the experiments at TRIUMF, the set-up that was used to polarize protons [9], has been upgraded with a dilution refrigerator, new microwave equipment and a new NMR system, that is described elsewhere [11]. The previously reported results [4] were checked in our set-up. Furthermore, decay times were measured in a magnetic field of 1.25 T and rf burning was applied after rf pumping, to study the relaxation mechanisms.

2. Radiative transitions

The level energies E_m ($m = 1, 0, -1$) of a deuterium nucleus in a magnetic field and an electric field gradient with rotational symmetry are given by [5,6]:

$$E_m = -mh\nu_D + h\nu_Q(3 \cos^2\theta - 1)(3m^2 - 2), \quad (1)$$

where $h\nu_D$ is the deuterium Zeeman energy, $h\nu_Q$ is the quadrupole energy, h is Planck's constant and θ is the angle between the magnetic field and the electric field gradient. The transition from the magnetic substate with $m=0$ to the state with $m=-1$, which is denoted below as the $(0 \rightarrow -1)$ transition, will occur in the NMR spectrum at a frequency ν_- determined by:

$$E_{-1} - E_0 = h\nu_- = h\nu_D + 3h\nu_Q(3 \cos^2\theta - 1), \quad (2a)$$

and the $(1 \rightarrow 0)$ transition at ν_+ according to:

$$E_0 - E_1 = h\nu_+ = h\nu_D - 3h\nu_Q(3 \cos^2\theta - 1). \quad (2b)$$

The level scheme is shown for $\theta=0$ and $\theta=\pi/2$ in fig. 1(a), where the quadrupole interaction strength is defined as $\delta=h\nu_Q$. The intensities of the transitions reflect the differences in magnetic substate populations a_{-1} and a_0 and a_0 and a_{+1} , respectively. It should be noted that these two intensities with the normalization provide three relations that determine the magnetic substate populations. If a temperature T can be defined for the deuterium spin system and the quantization axis is coincident with the magnetic field direction, the normalized level populations a_m are given by the Maxwell-Boltzmann distribution:

$$a_m = \exp(-E_m/kT) / \sum_m \exp(-E_m/kT) \quad (3)$$

To obtain the occupation numbers the quadrupole interaction is neglected in E_m .

Our NMR spectra are measured with a Q-meter system [11]. The output voltage is proportional to the absorption or emission of photons $h\nu$ during deuterium transitions between energy levels with occupation numbers a_m and a_{m+1} . To determine this voltage for the frequency range $\nu = \nu_D - 6\nu_Q$ to $\nu = \nu_D + 6\nu_Q$, the rf intensity (at 16 MHz) is kept so low

that the disturbance of the substrate populations is negligible. Saturation of a transition to burn a spectrum implies that the rf intensity (at 16 MHz) is high enough to equalize the substrate populations for a specified frequency range and consequently a range of the angle θ . It may affect only one transition (for $\nu_D - 6\nu_Q < \nu < \nu_D - 3\nu_Q$ and $\nu_D + 3\nu_Q < \nu < \nu_D + 6\nu_Q$) or both transition (for $\nu_D - 3\nu_Q < \nu < \nu_D + 3\nu_Q$). The rf pumping in the deuteron quadrupole reservoir [fig. 1(b)] through the proton spin system can be explained in terms that are very similar to the ones describing the microwave pumping of the proton Zeeman reservoir through the electron spin system. To increase the proton polarization, the photon energy of the microwave radiation $h\nu_R$ in the electron spin system is chosen slightly off resonance:

$$h\nu_R = \Delta E - \Delta p \quad \text{or} \quad h\nu_R = \Delta E + \Delta p ,$$

for positive and negative polarization respectively [fig. 2(a)]. A photon induces a flip-flop transition followed by an electron relaxation which is very fast compared to the proton relaxation time. Theoretical work [7] is still in progress to explain the dynamics of this process.

To increase the quadrupole orientation of the deuterons, the photon energy of the rf radiation (106 MHz) in the proton spin system is chosen slightly off resonance:

$$h\nu_R = \Delta p - \Delta d \quad \text{or} \quad h\nu_R = \Delta p + \Delta d ,$$

for positive and negative peak alignment ($\theta = \pi/2$) respectively [fig. 2(b)]. The dynamics of this process is at present not understood.

Without rf radiation, the relaxation time of the protons is very long. Furthermore, the Zeeman energy has been neglected for the deuterium

spins. Nevertheless, the experimental observations can be explained very well with this simplified scheme.

3. NMR line shape of deuterium

To deduce the magnetic substrate populations after any rf manipulation from the NMR spectrum, it is necessary to determine the intensity of the $(1 + 0)$ and $(0 + -1)$ transition relative to each other over the whole deuterium spectrum, which means as a function of the frequency ν or of the angle θ . The line broadening will be neglected to simplify the calculations. For a polycrystalline sample the directions of the electric field gradient are distributed randomly. Then, the number of field gradients with their principal axis in $[\theta, \theta + d\theta]$, is proportional [10] to the solid angle:

$$n(\theta)d\theta = \int_0^{2\pi} \sin\theta d\phi d\theta = 2\pi \sin\theta d\theta . \quad (4)$$

The normalization constant is:

$$\int_0^\pi n(\theta)d\theta = 4\pi . \quad (5)$$

The normalized frequency shift ν_0 is defined by:

$$\nu_0 = \frac{\nu - \nu_D}{3\nu_Q} , \quad (6)$$

and substitution of (2a) for the $(0 + -1)$ transition gives:

$$\nu_0 = 3 \cos^2\theta - 1 , \quad (7)$$

with $-1 < 3 \cos^2\theta - 1 < 2$.

In terms of this frequency, the distribution of the electric field gradients for a homogeneous spin system is given by:

$$n(v_0)dv_0 = n(\theta) \frac{d\theta}{dv_0} dv_0 = 2\pi \sin\theta \frac{d\theta}{dv_0} dv_0, \quad (8)$$

and together with eq. (7), this leads to:

$$n_-(v_0)dv_0 = \frac{\pi}{-\sqrt{3}(v_0+1)} dv_0. \quad (9)$$

If (2b) is substituted in (6) for the $(1 \rightarrow 0)$ transition the result is:

$$n_+(v_0)dv_0 = \frac{\pi}{\sqrt{3}(1-v_0)} dv_0, \quad (10)$$

with $-2 < v_0 = 1 - 3 \cos^2\theta < 1$.

To obtain positive densities, the integration limits must be adjusted correctly under the transformation $\theta \rightarrow v_0$. It is clear that the density is non-zero at $v_0 = \pm 2$ (or $v = v_0 \mp 6v_0$). The density increases without limits as v_0 approaches ± 1 . However, the integral over a frequency range (giving the number of electric field gradients within that range) remains finite. The NMR-components, that correspond to both transitions are shown in fig. 3.

Now, the relative contributions from the two transitions in different regions of v_0 can be calculated. The changes after rf irradiation can be determined and normalized to the original situation with known substate populations. It will be shown that the calibration of the NMR sensitivity is identical for the polarization and the alignment. The NMR intensity I , consisting of the output voltage integrated over the frequency, can be divided into two components I_+ and I_- that originate from the $(1 \rightarrow 0)$ and $(0 \rightarrow -1)$ transitions respectively. These intensities are proportional to the differences of the level populations (using $a_+ \equiv a_1$ and $a_- \equiv a_{-1}$):

$$I_+ = C_{cal}(a_+ - a_0) \quad \text{and} \quad I_- = C_{cal}(a_0 - a_-).$$

In the usual way, the polarization is expressed as a function of I :

$$P = \sum_{m=-1}^1 m a_m = (a_+ - a_0) + (a_0 - a_-) = \frac{I_+ + I_-}{C_{cal}} = \frac{I}{C_{cal}} \quad (11)$$

The calibration constant is determined from a measurement with the spin system in thermal equilibrium (TE) with the lattice:

$$C_{cal} = \frac{I_{TE}}{P_{TE}}. \quad (12)$$

Here, $P_{TE}(T_{TE}, H_{TE})$ is calculated according to the Maxwell-Boltzmann distribution for the known temperature T_{TE} (~ 0.7 K) and magnetic field H_{TE} (~ 2.5 T). Once C_{cal} is determined, for any intensity I the polarization is obtained with (11). The alignment A is defined in terms of the same level populations and is related to the intensities I_+ and I_- using the normalization condition ($\sum_{m=-1}^1 a_m = 1$):

$$A = \left(\sum_{m=-1}^1 3m^2 a_m \right) - 2 = (a_+ - a_0) - (a_0 - a_-) = \frac{I_+ - I_-}{C_{cal}}. \quad (13)$$

No restricting condition is required for a_m to express P and A in terms of I_+ and I_- .

4. Application

For three experiments on rf irradiation of the oriented deuterium nuclei the changes in the polarization and the alignment are calculated in the new formalism. Then, the agreement with the experimental data is discussed. The error of the experimental values for the areas in the NMR spectra, is obtained from the fluctuations in the measurements of the polarization near 0.3 with the sample at a temperature below 0.1 K.

During a period, that is short in comparison with the relaxation time, the difference of two polarization measurements rarely exceeds 0.001. This corresponds approximately to a variation of 0.5 mV MHz in the total area of the NMR spectrum. Therefore, the value of 0.5 mV MHz is adopted as the error of all NMR areas.

4.1 Burning of a pedestal

In fig. 4 the substrate populations are shown for a polarization $P^0 = -0.350$, that is homogeneous over the deuterium spin system. The superscript 0 indicates a value for the original unburnt system. The occupation numbers $a_+^0 = 0.174$, $a_0^0 = 0.302$ and $a_-^0 = 0.524$ represent an alignment $A^0 = 0.094$ according to eq. (13). Applying a saturating rf field on the pedestal of the $(0 \rightarrow 1)$ transition equalizes the substrate populations a_+ and a_0 over the range $2/3 < \cos^2 \theta < 1$. Consequently, the intensity of the other pedestal must increase by an amount that is one half of the intensity that disappeared from the burnt pedestal, as is illustrated in fig. 4:

$$\Delta I_+ \equiv I_+ - I_+^0 = +2\Delta I \quad (19a)$$

$$\Delta I_- \equiv I_- - I_-^0 = -\Delta I \quad (19b)$$

With (11) and (13) the changes in polarization and alignment respectively become:

$$\Delta P = P - P^0 = \frac{\Delta I}{C_{cal}} \quad (20)$$

$$\Delta A = A - A^0 = \frac{3\Delta I}{C_{cal}}, \quad (21)$$

which leads to:

$$\Delta A = 3\Delta P. \quad (22a)$$

For burning of the $(0 \rightarrow -1)$ transition, the sign of the coefficient 3 in

(21) is reversed, leading to:

$$\Delta A = -3\Delta P \quad (22b)$$

Consequently, to increase the alignment the transition with the smaller (absolute) intensity must be burnt for either sign of the polarization P . The fraction of the deuterons, that experience an electric field gradient for $-2 < \nu_0 < -1$, is indicated in fig. 3 and is calculated from (10):

$$2 \int_{-2}^{-1} n_+(\nu_0) d\nu_0 = 4\pi \times 0.184.$$

The factor 2 accounts for the two intervals $(0 < \theta < 0.615)$ and $(\pi - 0.615 < \theta < \pi)$ that must be covered by the integration limits of ν_0 .

The intensity reduction of the $(0 \rightarrow 1)$ transition follows changes in a_+ and a_0 (fig. 4) that are equal in magnitude but have opposite signs:

$$a_+ - a_+^0 = a_0 - a_0^0 = 1/2 \times 0.184(0.302 - 0.174) = 0.012.$$

The modified occupation numbers give a calculated polarization $P = -0.338$ and alignment $A = 0.130$.

Fig. 5 shows that rf burning of a pedestal affects the shape of the NMR spectrum appreciably while the polarization is conserved almost completely. For this set of NMR spectra and another set, pertaining to a deuterium spin system with positive polarization, the partial areas are listed in table 1. The frequency regions for the rf burning were 16.430 MHz to 16.490 MHz for the negative polarization and 16.714 MHz to 16.774 MHz for the positive polarization in a magnetic field of 2.5399 T and at a temperature of 85 mK. The sample was about 1.3 cm³ of deuterated (98%) butanol-D10 spheres, which contained 5% D₂O by volume and 6 × 10¹⁹ EHBA molecules/cm³.

For the system of fig. 5 a polarization $P^0 = -0.335$ and alignment $A^0 = 0.086$ ($a_+^0 = 0.180$, $a_0^0 = 0.305$, $a_-^0 = 0.515$) were obtained. Distribution of the total spectrum area according to the level populations, leads to the intensity values $I_+^0 = 57.61$ mV MHz and $I_-^0 = 97.40$ mV MHz. It is clear that after the burning, the reduction of one pedestal is not equal to double the increase of the other pedestal. This rule is much better satisfied for the areas below and above the center frequency A_L and A_H (fig. 3) which increase by $\Delta A_L = 16.79$ mV MHz and decrease by $\Delta A_H = 9.59$ mV MHz, respectively. Using the $\Delta I_+ = \Delta A_L$ and $\Delta I_- = \Delta A_H$, new occupation numbers follow from the three equations:

$$a_+ - a_0 = \frac{I_+}{I_0} \times (a_+^0 - a_0^0) = -0.089$$

$$a_0 - a_- = \frac{I_-}{I_0} \times (a_0^0 - a_-^0) = -0.231$$

$$a_+ + a_0 + a_- = 1$$

This leads to $P = -32.0$ and $A = 0.142$. With $\Delta A = 0.056$ and $3\Delta P = 0.045$ the condition (22a) is satisfied quite well in view of the applicable errors of about 0.005.

Another check of the formalism is obtained by calculating with (9) and (10) the fractions of I_+^0 and I_-^0 below and above the center frequency of the NMR system:

$$A_L = 0.577 \times I_-^0 + 0.423 \times I_+^0 = -80.58 \text{ mV MHz}$$

$$A_H = 0.423 \times I_-^0 + 0.577 \times I_+^0 = -74.43 \text{ mV MHz}.$$

These results agree well with the measured areas below (-80.50 mV MHz) and above (-74.51 mV MHz) the center frequency.

Fig. 4 applies to positive polarization if the values of a_+ and a_- are interchanged. From table 1(a), the original intensities $I_+^0 = 78.18$ mV MHz and $I_-^0 = 51.25$ mV MHz are obtained by distribution of the total area according to a polarization $P^0 = 0.273$ and the alignment $A^0 = 0.057$ ($a_+^0 = 0.479$, $a_0^0 = 0.314$, $a_-^0 = 0.206$). During the rf burning the changes are $\Delta A_L = 8.00$ mV MHz and $\Delta A_H = -15.52$ mV MHz. Using again $\Delta I_+ = \Delta A_L$ and $\Delta I_- = \Delta A_H$, the result is $a_+ - a_0 = 0.182$ and $a_0 - a_- = 0.075$ which leads to $P = 0.256$ and $A = 0.106$. With $\Delta A = 0.049$ and $3\Delta P = -0.051$ the condition (22b) is satisfied very well.

The formalism is checked by calculating from I_+^0 and I_-^0 the areas $A_L = 62.63$ mV MHz and $A_H = 66.80$ mV MHz. These values agree well with the measurements $A_L = 63.03$ mV MHz and $A_H = 66.40$ mV MHz.

Finally, we discuss another remarkable feature which is the continued fast change of the peak heights after stopping the rf irradiation. This can be explained if the distribution in space of the electric field gradients is examined. The distribution itself is random but this is not the case for the nearest neighbour distribution. If the assumption is made that the field gradients are directed along the C-D or O-D bond and a deuteron is selected in a gradient with $\theta = 0$, then the nearest neighbour within the same molecule experiences a gradient with $\theta = \pi/2$. This implies that cross-relaxation of pedestal deuterons preferably takes place with peak deuterons. In particular $a_0(\theta)$ could be reduced at $\theta = \pi/2$ during the burning process that takes place near $\theta = 0$. Afterwards, the smoothing of $a_0(\theta)$ would account for the intensity increase of the $(1 \rightarrow 0)$ peak. The data in table 1 indicate that this effect is a factor two larger in a magnetic field of 1.25 T than in a field of 2.5 T, although the quadrupole energy is independent of the magnetic field.

4.2. Burning of a peak

If rf irradiation is applied over a frequency range near a peak, both components of the NMR spectrum are burnt, as is indicated in fig. 6. Nevertheless, it is possible to estimate the change of the occupation numbers with the procedure of section 4.1. The fraction of the $(0 + 1)$ transition that disappears is:

$$2 \int_0^{-1} n_+(v_\theta) dv_\theta = 4\pi \times 0.577,$$

which leads to:

$$a_+ - a_+^0 = 1/2 \times 0.577(0.302 - 0.174) = 0.037$$

and the reverse change for a_0 . The influence on the $(-1 + 0)$ transition is:

$$2 \int_0^{-1} n_-(v_\theta) dv_\theta = 4\pi \times 0.239,$$

which gives:

$$a_- - a_-^0 = -1/2 \times 0.239(0.524 - 0.302) = -0.027$$

and again the reverse change for a_0 . The final result ($P=0.286$, $A=0.124$) and the substrate populations are shown in fig. 6. In comparison with pedestal burning, the reduction of the polarization is larger, but the gain in alignment is smaller.

The spectra in fig. 7 were obtained from a sample that consisted of deuterated (99%) 1,2-propanediol-D8 spheres with a diameter of about 1 mm and a doping of 10×10^{19} EHBA molecules/cm³. In the deuterium spin system with negative polarization $P=-0.280$ and alignment $A=0.060$ the $(0 + 1)$ peak has been burnt from 16.250 MHz to 16.350 MHz in a magnetic field of

2.4864 T. It is remarkable that the $(0 + -1)$ pedestal disappeared within 45 minutes after the burning was stopped.

With the occupation numbers $a_+^0=0.203$, $a_0^0=0.313$ and $a_-^0=0.483$ the intensities $I_-^0=-195.76$ mV MHz and $I_+^0=-126.69$ mV MHz are determined from the total area 322.48 mV MHz in the original spectrum. After the burning, the magnitude of the area between 16.150 MHz and 16.250 MHz is increased by 32.10 mV MHz which is not equal to half the decrease 109.83 mV MHz of the magnitude of the area between 16.250 and 16.344 MHz. Therefore, it is estimated conservatively that the alignment producing decrease is equal to double the increase in the lower frequency range or 64.20 mV MHz. This reduction is assigned to each transition according to the original area of I_+^0 and I_-^0 in the burnt frequency range. The separation of the peaks in the NMR spectra is 120 kHz. So, the burning region corresponds to $0 < v_\theta < 1$ for I_+^0 which contains the fraction 0.577 and corresponds to $0 < v_\theta < 1.67$ for I_-^0 with the fraction 0.366. This leads to a transferred area from the $(1 + 0)$ to the $(0 + -1)$ transition of 15.87 mV MHz and from the $(0 + -1)$ to the $(1 + 0)$ transition of 16.23 mV MHz, which makes the net transfer rather small. After the burning, the intensities are:

$$I_+ = I_+^0 + 2 \times 15.89 - 16.21 = -111.12 \text{ mV MHz}$$

$$\text{and } I_- = I_-^0 + 2 \times 16.21 - 15.89 = -179.26 \text{ mV MHz}.$$

Again, the occupation numbers are obtained from the three equations:

$$a_+ - a_0 = \frac{I_+}{I_+^0} \times \frac{a_+^0}{(a_+^0 - a_0^0)} = -0.096$$

$$a_0 - a_- = \frac{I_-}{I_-^0} \times \frac{a_0^0}{(a_0^0 - a_-^0)} = -0.156$$

$$a_+ + a_0 + a_- = 1,$$

which give $P=0.252$ and $A=0.060$.

The measured polarization $P=0.206$ deviates considerably from the value that is estimated in this analysis and consequently, the result for the alignment could be affected by a large systematic error, which might be due to the neglect of the line broadening in this situation.

4.3. RF pumping at 108 MHz

A mixed system of proton and deuteron spins is polarized in a conventional way with microwaves. The deuteron orientation is burnt, giving $P=0$ and $A=0$ to provide a clear initial signal. Irradiation at 108 MHz of the proton system with a positive polarization about 100 kHz below the resonance frequency (inducing removal of energy from the quadrupole reservoir) will increase a_0 in the pedestal region (near $\theta=0$) and increase $a_+ = a_-$ in the peak region (near $\theta=\pi/2$). The consequence for the NMR spectrum of this excess of a_0 on the pedestals (fig. 9) is that photons are absorbed in the $(1+0)$ transition and emitted in the $(0+-1)$ transition. For the peaks a similar scheme applies with reversed signs. This explains why some parts of the rf pumped spectra have a positive and others a negative area. From fig. 2b it is clear that a shift of the frequency above resonance or a negative proton polarization, will reverse the sign of the changes in a_m .

The sample averaged a_m must be obtained from an integration over θ after the distribution of a_m over θ has been determined. In ref. 8 it is checked that a temperature T_Q can be assigned to the quadrupole interaction reservoir (at a certain moment after the irradiation is stopped). The populations of the substates in fig. 1b are obtained with (1):

(1):

$$a_+(\theta) = a_-(\theta) = \frac{\exp[-\delta(3\cos^2\theta-1)/kT_Q]}{\exp[-2\delta(3\cos^2\theta-1)/kT_Q] + 2\exp[-\delta(3\cos^2\theta-1)/kT_Q]} \quad (20a)$$

$$a_0(\theta) = \frac{\exp[-2\delta(3\cos^2\theta-1)/kT_Q]}{\exp[-2\delta(3\cos^2\theta-1)/kT_Q] + 2\exp[-\delta(3\cos^2\theta-1)/kT_Q]} \quad (20b)$$

The integral

$$a_m = \int_0^\pi a_m(\theta) \sin\theta d\theta, \quad (21)$$

is simplified by writing the exponentials as a Taylor series that is truncated after the first order term because the expansion parameter is small. For this parameter the value $\delta/kT_Q=0.1$ is chosen since it represents an alignment of 0.2 and 0.4 for the peaks and pedestals respectively, which described the results in ref. 8 well:

$$a_+(\theta) = a_-(\theta) = \frac{1}{3} \left[1 - \frac{\delta}{kT_Q} (3\cos^2\theta-1) \right] \quad (22a)$$

$$a_0(\theta) = \frac{1}{3} \left[1 + \frac{2\delta}{kT_Q} (3\cos^2\theta-1) \right]. \quad (22b)$$

These occupation numbers are shown in fig. 8 for a temperature $T_Q=6/0.1$ k. After this procedure the polarization is:

$$P = a_+ - a_- = \frac{\int_0^\pi a_+(\theta) \sin\theta d\theta - \int_0^\pi a_-(\theta) \sin\theta d\theta}{\int_0^\pi \sin\theta d\theta} = 0. \quad (23)$$

A is then given by:

$$A = 1 - 3a_0 = 1 - \frac{3 \int_0^\pi a_0(\theta) \sin\theta d\theta}{\int_0^\pi \sin\theta d\theta} \quad (\text{Cont'd})$$

$$= 1 - \frac{3 \int_0^\pi \frac{1}{3} \left[1 + \frac{2\delta}{kT_Q} (3\cos^2\theta - 1) \right] \sin\theta d\theta}{\int_0^\pi \sin\theta d\theta}$$

$$= 0.$$

(24)

This surprising result implies that the pedestal alignment and peak alignment cancel each other completely to first order in the expansion parameter. Macroscopic alignment can be produced by burning both the pedestals which modifies the occupation numbers such that:

$$a_0(\theta) = 1/3 \quad \text{for } -1 < \cos\theta < -\sqrt{2/3}$$

$$a_0(\theta) = 1/3 \left[1 + \frac{2\delta}{kT_Q} (3\cos^2\theta - 1) \right] \quad \text{for } -\sqrt{2/3} < \cos\theta < \sqrt{2/3}$$

$$a_0(\theta) = 1/3 \quad \text{for } \sqrt{2/3} < \cos\theta < 1$$

Substitution in (24) gives $A=0.055$. Although the magnitude of this alignment is considerably smaller than the values that were reported previously [4,8], this procedure can result in negative alignment using the same principle as for positive alignment. This might provide a useful experimental advantage.

In fig. 9 some NMR data are shown that were acquired at a temperature of 90 mK, in a magnetic field of 2.5 T with a sample that consisted of deuterated (98%) and non-deuterated butanol according to the ratio 4/1 with an EHBA concentration of 5×10^{19} molecules/cm³ and without any water. The low polarization (~ 0.15) is attributed to the absence of water in the sample (fig. 9a). The deuterium polarization is burnt to zero (fig. 9b). It was possible to carry out the rf pumping at 108 MHz although the NMR

system resonates at a fixed frequency near 16.6 MHz. Consequently, it is very difficult to determine how much rf power is coupled to the proton spin system at 108 MHz. The decay time of the peaks (figs. 9c, 9d) is 3.7 hrs, which is in good agreement with ref. 4. Next, rf burning was applied to the low-frequency half of the spectrum (fig. 9e). Again, one half of the burnt intensity is added to the corresponding unburnt part of the spectrum. Due to the applicable signs, this constitutes a reduction of the unburnt area. Several remarkable features occur: Firstly, the ratio of the remaining peak intensity and pedestal intensity changes quite clearly. Secondly, a positive area appears just below the center frequency although before the last burning both NMR components change sign at the center frequency [see (22)]. These phenomena can be explained by a fast (minutes) redistribution of each $a_m(\theta)$ as a function of θ , especially a smoothing of the sharp edges in $a_+(\theta)$ and $a_-(\theta)$ at $\cos^2\theta=1/3$ (fig. 8). Thirdly, the absolute values of the intensities increase for a long time (tens of minutes) after the rf field is turned off. This implies an increase of the deviation from equilibrium for the substrate populations and therefore, a decrease of the entropy in the observed spin system, violating the second law of thermodynamics if this is an isolated system. One explanation would be that the NMR system observes only a part of the deuterium spin system with the unobserved part having a different distribution of the substrate populations. However, a similar effect is then expected after the rf burning in fig. 9b. Another explanation is an entropy exchange with either the proton spin system, the electron spin system or the lattice.

5. Relaxation

It has been shown that the electron spin-spin interaction reservoir and the nuclear Zeeman reservoir(s) reach a common temperature within a

time that is short in comparison with the decay time of this temperature towards the lattice temperature (e.g. see the review in ref. [13]). In a partially deuterated sample of 1,2-ethanediol a similar temperature dependence was reported [4] for the relaxation rate of the proton and deuteron Zeeman reservoir. This temperature dependence was also observed for the relaxation of the deuterium quadrupole reservoir after rf pumping. Therefore, it was concluded that the relaxation of the quadrupole reservoir takes place through thermal contact with the electron spin-spin interaction reservoir. The measured values for this relaxation time $\tau(D,D)$ ranged up to 6 hours. For butanol we obtained $\tau(D,D) \approx 4$ hours (see figs. 9c and 9d). During this measurement the proton polarization decayed with a time constant that was larger than 100 hours.

Another method to introduce a deviation from thermal equilibrium in the quadrupole interaction reservoir is by rf burning. The relaxation of this state in a magnetic field of 1.25 T should be governed by a time constant that has a value comparable to $\tau(D,D)$. However, it is obvious from figs. 5c and 5d that the recovery time of the NMR spectrum towards the approximate shape of fig. 5a, is much larger. The ratios of the peak heights in figs. 5a, 5c and 5d is 1.38, 0.87 and 0.91 respectively which indicates a relaxation time $\tau_Q \approx 80$ hours. The same procedure for a measurement with positive deuterium polarization in a magnetic field of 2.5 T resulted in $\tau_Q \approx 55$ hours. The difference between τ_Q and $\tau(D,D)$ is attributed to the proton content that is a factor 10 higher for the material used during rf pumping.

6. Conclusions

A formalism has been developed to analyze NMR spectra that are measured after high intensity rf irradiation of a frozen oriented spin

system of deuterium. It is demonstrated that quantitative estimates can be made which predict the change in the polarization and the alignment with good accuracy. This led to a method for extracting experimental values for these parameters from the measurements. The data, that are obtained after the pedestal burning, follow the predictions very closely. The burning of a peak region is much harder to analyze. The results from the rf pumping make its value for applications questionable. The experimental spectra indicate that the lifetime of the rf induced orientation changes can be longer than 50 hours which is an order of magnitude larger than the values reported in ref. [4].

7. Acknowledgements

The dedication of C. Chan, A. Morgan and the other technicians of the TRIUMF targets group is gratefully acknowledged. Important contributions to the NMR system were made by M. Hayden, J. Cresswell, N. Shiboaka and G. Waters.

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Table 1

Areas of the NMR spectra from the (0 + -1) pedestal burning with decay
in a magnetic field of 2.5 T (a) and from the (1 + 0) pedestal burning
with decay in a magnetic field of 1.25 T (b).

Frequency Range (MHz)	16.425 16.497 16.600 16.703 16.775 to 16.497 16.600 16.703 16.775				
Time	Spectrum type	Area	(mV MHz)		Polarit- zation
(a) 17-9-85	22:01 original	6.80 56.24 62.39 4.01	+0.273		
	23:52 burnt	10.21 60.82 49.94 0.94	+0.257		
	18-9-85 0:03 decay 1	9.95 61.31 49.27 1.20	+0.257		
	1:24 decay 2	9.21 62.40 47.69 1.70	+0.255		
	6:11 decay 3	8.84 60.87 46.83 1.82	+0.249		
	(b) 18-9-85 22:01 original	-5.17 -75.33 -66.27 -8.24	-0.335		
	23:41 burnt	-1.05 -62.66 -71.71 -12.39	-0.319		
	19-9-85 0:11 decay 1	-1.48 -59.17 -73.95 -12.84	-0.318		
	1:06 decay 2	-2.05 -57.45 -75.39 -13.10	-0.319		
	7:36 decay 3	-2.59 -56.45 -70.20 -11.48	-0.304		

Figure Captions

1. a) The energy level shift for deuterium nuclei due to the magnetic dipole and electric quadrupole interaction.
b) The quadrupole shifts only.
2. The energy level schemes show the similarity between (a) the polarizing transitions and (b) the aligning transitions.
3. The NMR line shape of deuterium is shown as a function of the normalized frequency shift ν_Q with the two constituting components. No broadening is taken into account.
4. The change of the substate populations after rf burning of one pedestal ($1 < \nu_Q < 2$) is shown as a function of $\cos^2\theta$. The initial configuration is represented by the dashed lines and the unoriented spin system by the dashed-dotted line.
5. Some NMR spectra are shown for the procedure in which the pedestal of the $(1 \rightarrow 0)$ transition was burnt (b) for 100 minutes. Parts (c) and (d) result from decay in a magnetic field of 1.25 T between the measurements. For each part the polarization P and the time of day is indicated.
6. The change of the fractional substate populations after rf burning of a peak area ($0 < \nu_Q < 1$) is shown as a function of $\cos^2\theta$. The initial configuration is represented by the dashed lines and the unoriented spin system by the dashed-dotted line.
7. Some NMR spectra are shown for the procedure in which the peak of the $(1 \rightarrow 0)$ transition was burnt (b) for 12 minutes. Parts (c) and (d) result from decay in a magnetic field of 2.5 T at a temperature of 75 mK. For each part the polarization P and the time of day is indicated.

8. The fractional substate populations are indicated for a deuterium spin system, that was rf pumped [$a_+(\theta)=a_-(\theta)$] to a peak alignment $A=0.20$ and pedestal alignment $A=-0.40$, as indicated by the dotted lines. Then, the low-frequency half of the spectrum was burnt, giving, $a_+=a_0$ or $a_+=a_0$ depending on θ . The dashed-dotted line represents the unoriented spin system.
9. Some NMR spectra are shown that were measured during an rf pumping and rf burning sequence. The original deuterium polarization $P=0.161$ was burnt completely (b). Then, followed rf pumping at 120 kHz below the proton resonance frequency (c) and a spectrum after 1 hour decay (d). Next, the negative area is burnt off (e) and the consecutive decay is shown (f,g,h). For each part the time of day is indicated.

Fig. 1

Fig. 2

Fig. 4

Fig. 3

Fig. 5