Nuclear magnetic double resonance based on strong rf magnetic-field-induced coupling between spin systems

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(Received 1 July 1974)

The origin of the rf magnetic-field-induced coupling between spin systems is discussed. A new nuclear-double-resonance technique employing this coupling is proposed, which has particular value in measuring pure nuclear-quadrupole-resonance spectra of integer-spin nuclei by nuclear double resonance. The sensitivity of the new technique is discussed for the case of ^1H-^{14}N double resonance in zero static magnetic field, as well as for the case of nuclear double resonance in a strong static magnetic field and the case of nuclear quadrupole double resonance. The technique is illustrated by ^1H-^{14}N double resonance in thymine in zero static magnetic field and by ^{19}F-^{23}Na double resonance in NaF, by ^1H-^{14}N double resonance in $NH_4H_2PO_4$, and by ^1H-^{87}Rb double resonance in RbH_2PO_4 in a strong static magnetic field.

I. INTRODUCTION

Nuclear double resonance as introduced by Hartmann and Hahn[1] and later by Lurie and Slichter[2] is a high-sensitivity technique which detects the weak NMR or nuclear-quadrupole-resonance (NQR) signal of type-B nuclei via their effect on the A-spin system which exhibits a strong NMR signal. The technique is based on the existence of nuclear dipole-dipole coupling between the two spin systems in a frame of reference in which the energy levels of the A and B spins are equally spaced, which makes entropy transport possible.

Double resonance in the laboratory frame of one spin system and in the rotating frame of another spin system has been studied by Slusher and Hahn.[3] It represents an extension of the rotating-frame nuclear double resonance[1,2] to the zero-magnetic-field region.

Dipolar coupling between integer nuclear spins (B-spin system) in an asymmetric electric field gradient and any other nonresonant spins (A-spin system) is, however, highly reduced in zero magnetic field.[4] This effect is usually called spin quenching. The level-crossing technique[5-7] where the A- and B- spin systems couple in a nonzero magnetic field is therefore used to detect pure NQR spectra of integer-spin nuclei by nuclear double resonance.

It is the purpose of this paper to show that the two spin systems couple even though spin quenching occurs when a strong rf magnetic field is applied to the sample with a frequency which is either (a) near to one of the quadrupole transition frequencies of the B nuclei when the sample is in zero magnetic field and the A spins exhibit no quadrupole coupling, or (b) equal to $\omega_A \pm \omega_B$ when the Zeeman or quadrupole coupling of the A and B nuclei is nonzero. Here ω_A is one of the transition frequencies between the energy levels of the A nuclei, and ω_B is one of the transition frequencies between energy levels of the B nuclei.

This effect is one of the forms of the well-known solid effect.[8] It was already observed by Abragam and Proctor[9] in LiF, by Landesman[10] in paradichlorobenzene, and by Koo[6] and Edmonds *et al.*[7] in zero-magnetic-field nuclear-double-resonance detection of ^{14}N nuclei.

A schematic representation of the rf magnetic-field-induced coupling between the A- and B-spin systems as well as a schematic representation of the coupling between the A- and B-spin systems in the case of rotating-frame nuclear double resonance is shown in Fig. 1.

This rf magnetic-field-induced coupling between spin systems enables one to detect resonance frequencies of the B nuclei via the signal of the A nuclei. A new nuclear-double-resonance technique is proposed, based on this coupling, which is of particular importance in detection of pure NQR spectra of integer-spin nuclei, since it can be used in many cases when the level-crossing technique fails.

The double-resonance line shapes obtained by this new technique are evaluated for the case of ^1H-^{14}N double resonance in zero static magnetic field, as well as for the case of nuclear double resonance between two purely magnetic spin systems in a strong static magnetic field and for the case of nuclear quadrupole double resonance.

A theoretical estimate of the sensitivity of this new technique is presented together with some experimental results.

II. ORIGIN OF THE rf MAGNETIC-FIELD-INDUCED COUPLING BETWEEN SPIN SYSTEMS

In this section we are going to describe the physical origin of the rf magnetic-field-induced coupling between spin systems.

In the following description we shall limit our-

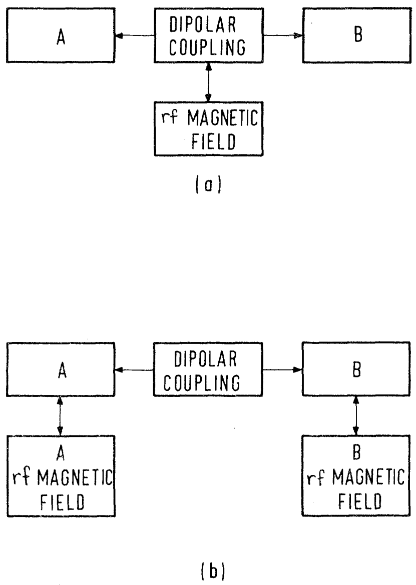

FIG. 1. Dipolar coupling between the A- and B-spin systems in the case of the solid effect (a) and in the case of rotating-frame nuclear double resonance (b).

selves to the case of well-resolved spectra of the A and B nuclei, i.e., to the case when the energy differences between Zeeman, quadrupole, or mixed energy levels of both nuclei are much larger than the resonance linewidths. The case of coupling between purely magnetic A spins and quadrupole B spins in zero magnetic field will be treated at the end of this section.

The A spins precess in a static magnetic field or in local electric field gradients at the A spin sites or in both with their resonance frequencies ω_A. The frequency spectra of the dipolar magnetic fields produced by the A spins consists therefore of discrete peaks at the frequencies ω_A.

Similarly the frequency spectra of the dipolar magnetic fields produced by the B spins consists of discrete peaks at the B-spin resonance frequencies ω_B.

The frequency spectra of the dipolar magnetic fields produced by the A and B spins are shown in Fig. 2(a). Only one resonance frequency of the A spins and one resonance frequency of the B spins are shown.

A strong rf magnetic field $H_1 \cos\omega_0 t$ modulates the precession of the A and B spins. In the frequency spectra of the dipolar magnetic fields new rf magnetic-field-induced peaks appear at the frequencies $\omega_A \pm \omega_0$ and $\omega_B \pm \omega_0$. This situation is shown in Fig. 2(b). These new peaks are weak as compared with the original ones since

$$\gamma_A H_1,\ \gamma_B H_1 \ll \omega_0 , \tag{1}$$

which is usually the case during a double-resonance experiment.

The position of the rf magnetic-field-induced peaks can be changed by changing the rf field frequency ω_0. At some certain frequencies ω_0 the rf magnetic-field-induced peaks in the frequency spectra of the dipolar magnetic fields produced by the A spins match the resonance frequencies of the B spins and vice versa. This happens when

$$\omega_0 = \omega_A \pm \omega_B . \tag{2}$$

When such a situation occurs the A spins driven by the rf magnetic field induce transitions between energy levels of the B spins and at the same time the B spins driven by the rf magnetic field induce transitions between energy levels of the A spins.

Since a quantum of energy $\hbar\omega_0$ gained by the A-spin system from the rf magnetic field is different from a quantum of energy $\hbar\omega_B$ needed to produce a transition in the B-spin system, the energy difference $\pm\hbar\omega_A$ should be absorbed in or emitted from the A-spin system during such a process, depending on whether $\omega_0 = \omega_A + \omega_B$ or $\omega_0 = \omega_A - \omega_B$. Every transition in the B-spin system due to this process is therefore accompanied by a transition in the A-spin system, and similarly every transition in the A-spin system produced by the B spins is accom-

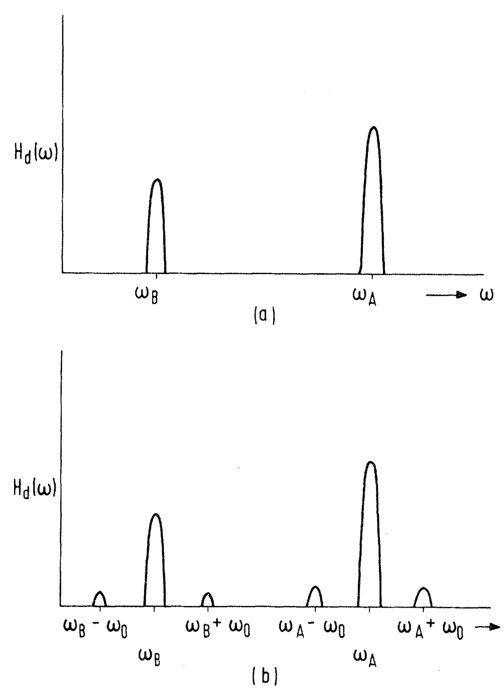

FIG. 2. Frequency spectra of the dipole magnetic fields produced by the A and B spins without (a) and with (b) a rf magnetic field applied.

panied by a transition in the B-spin system. These simultaneous transitions in both spin systems are schematically represented in Fig. 3 for the case of $\omega_0 = \omega_A + \omega_B$ and for the case of $\omega_0 = \omega_A - \omega_B$.

This effect may be interpreted as that in the oscillating frame of reference of the A spins the energy levels of the B spins seem to be $\hbar\omega_A$ apart and thus resonant with the energy levels of the A spins.

Similarly in the oscillating frame of reference of the B spins the energy levels of the A spins seem to be $\hbar\omega_B$ apart.

Under the influence of the rf magnetic field the two spin systems relax to a common equilibrium state with a common spin temperature in a frame of reference in which the energy levels of the A and B spins are equally spaced. Here the spin temperature is defined only over the energy levels touched by the coupling process.

When only two energy levels of the A-spin system and two energy levels of the B-spin system are touched by the coupling process the equilibrium is reached after

$$\begin{aligned} n_{1A}n_{2B} &= n_{2A}n_{1B} \quad \text{for } \omega_0 = \omega_A - \omega_B \, , \\ n_{1A}n_{1B} &= n_{2A}n_{2B} \quad \text{for } \omega_0 = \omega_A + \omega_B \, . \end{aligned} \tag{3}$$

Here n_{1A} is the number of A nuclei on the lower energy level and n_{2A} is the number of A nuclei on the upper energy level. Similarly n_{1B} and n_{2B} are the numbers of B nuclei on the lower and upper energy levels, respectively.

For two purely magnetic spin systems with arbitrary spins in a strong magnetic field the equilibrium is reached when

$$\begin{aligned} T_A/T_B &= -\omega_A/\omega_B \quad \text{for } \omega_0 = \omega_A + \omega_B \, , \\ T_A/T_B &= \omega_A/\omega_B \quad \text{for } \omega_0 = \omega_A - \omega_B \, . \end{aligned} \tag{4}$$

Here T_A and T_B are the spin temperatures, and ω_A and ω_B are the Larmor frequencies of the A- and B-spin systems, respectively.

When a system of purely magnetic A spins is put in zero magnetic field the only motion the spins perform is due to magnetic dipolar coupling between the A spins themselves and between the A spins and any other spins which are not decoupled from the A spins by spin quenching. The frequency spectra of the dipolar magnetic fields produced by the A spins consists of a single peak at zero frequency with a width equal to the A-spin zero-field linewidth $(\Delta\omega)_A$.

The B spins for which we assume nonzero quadrupole coupling precess at their quadrupole resonance frequencies ω_{QB} in the local electric field gradients. The frequency spectra of the dipolar magnetic fields produced by the B spins consist of discrete peaks at the frequencies ω_{QB}.

The rf magnetic field $H_1 \cos\omega_0 t$ induces some extra peaks at the frequencies ω_0 and $\omega_{QB} \pm \omega_0$ in the frequency spectra of the dipolar magnetic fields. The peak at the frequency ω_0 has a width equal to the A-spin zero-field linewidth $(\Delta\omega)_A$, whereas the B-spin resonance linewidths are usually small as compared with the $(\Delta\omega)_A$. The two spin systems couple whenever a quadrupole resonance line lies within the peak at the frequency ω_0. This happens for all frequencies ω_0 in the range

$$|\omega_0 - \omega_{QB}| \lesssim (\Delta\omega)_A \, . \tag{5}$$

For a given frequency ω_0 within this range every transition in the B-spin system with frequency ω_{QB} is accompanied by a transition in the A-spin system with a frequency $\omega_0 - \omega_{QB}$. In this case equilibrium in the common AB-spin system is reached when

$$n_1/n_2 = 1 - \hbar(\omega_{QB} - \omega_0)/kT_A \, . \tag{6}$$

Here n_1 and n_2 are the populations of the two corresponding quadrupole energy levels of the B nuclei with energies $E_1 - E_2 = h\omega_{QB}$, and T_A is the final spin temperature of the A-spin system.

III. THEORY OF THE rf MAGNETIC-FIELD-INDUCED COUPLING BETWEEN SPIN SYSTEMS

In this section we give a theoretical description of the rf magnetic-field-induced coupling between spin systems for the case of two purely magnetic spin systems in a strong static magnetic field. A similar approach can be used for all cases described in this paper.

The Hamiltonian of our system is

$$H = H_{ZA} + H_{ZB} + H_{dAA} + H_{dBB} + H_{dAB} + H_{\mathrm{rf}\,A} + H_{\mathrm{rf}\,B} \, . \tag{7}$$

Here H_{ZA} and H_{ZB} are the Zeeman Hamiltonians of the two spin systems:

$$\begin{aligned} H_{ZA} &= \hbar\omega_A \sum_i I^i_{Az} \, , \\ H_{ZB} &= \hbar\omega_B \sum_k I^k_{Bz} \, . \end{aligned} \tag{8}$$

H_{dAA}, H_{dBB}, and H_{dAB} are the dipole-dipole interactions between the A, B and A and B spins, respectively.

$H_{\mathrm{rf}\,A}$ and $H_{\mathrm{rf}\,B}$ describe the coupling of the A and B spins to the rf magnetic field $H_1 \cos\omega t$:

$$\begin{aligned} H_{\mathrm{rf}\,A} &= \hbar\omega_{1A} \sum_i I^i_{Ax} \cos\omega t \, , \\ H_{\mathrm{rf}\,B} &= \hbar\omega_{1B} \sum_k I^k_{Bx} \cos\omega t \, . \end{aligned} \tag{9}$$

The A and B spins oscillate under the influence of the rf magnetic field. From now on we are going to observe the A-spin system in the frame of reference which oscillates with the A spins and the B-

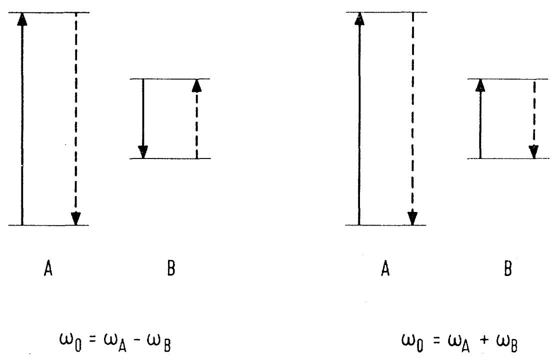

FIG. 3. Mutual spin flips in the A and B spin systems for $\omega_0 = \omega_A + \omega_B$ and $\omega_0 = \omega_A - \omega_B$.

spin system in the frame of reference which oscillates together with the B spins.

The laboratory frame of reference and the oscillating one are connected by the transformation which excludes the term $H_{\mathrm{rf}\,A} + H_{\mathrm{rf}\,B}$ from the Hamiltonian.

Since

$$[H_{\mathrm{rf}\,A}(t) + H_{\mathrm{rf}\,B}(t),\ H_{\mathrm{rf}\,A}(t') + H_{\mathrm{rf}\,B}(t')] = 0\ , \tag{10}$$

the transformation is

$$T = \exp\left(\frac{i}{h}\int (H_{\mathrm{rf}\,A} + H_{\mathrm{rf}\,B})\,dt\right). \tag{11}$$

Performing the transformation one gets the Hamiltonian

$$H^* = H_{ZA} + H_{ZB} + H_{dAA} + H_{dBB} + H_{dAB} \tag{12}$$

plus some terms linear and quadratic in ω_{1A}/ω and ω_{1B}/ω which oscillate with frequencies ω and 2ω.

Since ω_{1A}/ω and ω_{1B}/ω are usually much smaller than unity we shall neglect all these terms except the ones coming from H_{dAB}. These terms couple the two spin systems.

The oscillating terms, coming from H_{dAB}—which does not commute either with H_{ZA} or with H_{ZB}, and which can thus induce simultaneous transitions in both spin systems—are equal to

$$H^{(1)}_{dAB} = 3\,\frac{\omega_{1A}}{\omega}\sum_{i,k} C_{ik} Z_{ik} I^i_{Ay}(Y_{ik} I^k_{By} + X_{ik} I^k_{Bx})\sin\omega t$$
$$+ 3\,\frac{\omega_{1B}}{\omega}\sum_{i,k} C_{ik} Z_{ik} I^k_{By}(Y_{ik} I^i_{Ay} + X_{ik} I^i_{Ax})\sin\omega t\ , \tag{13}$$

$$H^{(2)}_{dAB} = \frac{1}{2}\,\frac{\omega_{1A}\omega_{1B}}{\omega^2}\sum_{i,k} C_{ik} I^i_{Ay} I^k_{By}\cos 2\omega t\ . \tag{14}$$

Here X_{ik}, Y_{ik}, and Z_{ik} are the direction cosines of the distance vector $\vec{r}_{ik}$ between the ith and kth sites and $C_{ik} = \gamma_A\gamma_B\hbar/r^3_{ik}$.

Assuming $\omega_A > \omega_B$ one can divide the term H_{ZA} into two terms:

$$H_{ZA} = \pm\hbar\omega_B \sum_i I^i_{Az} + \hbar(\omega_A \mp \omega_B)\sum_i I^i_{Az}\ . \tag{15}$$

The energy levels of the first term in expression (15) are as equally spaced as the energy levels of H_{ZB}. For the (+) sign their sequence is the same as in the laboratory frame, whereas for the (−) sign it is inverted.

Let us now transform into a frame of reference in which the energy levels of the A- and B-spin systems are equally spaced. This is done by the transformation

$$T = \exp\left(i(\omega_A \mp \omega_B)\sum_i I^i_{Az}\,t\right). \tag{16}$$

The terms in H_{dAB} which can be made static in this frame of reference by proper choice of the rf field frequency are equal to

$$H^{*(1)}_{dAB} = \frac{3}{2}\,\frac{\omega_{1A}}{\omega}\sum_{i,k} C_{ik} Z_{ik}(I^k_{By} Y_{ik} + I^k_{Bx} X_{ik}) I^i_{Ax}$$
$$\times\cos(\omega_A \mp \omega_B - \omega)t$$
$$+\frac{3}{2}\,\frac{\omega_{1B}}{\omega}\sum_{i,k} C_{ik} Z_{ik}(I^i_{Ax} Y_{ik} - I^i_{Ay} Y_{ik}) I^k_{By}$$
$$\times\cos(\omega_A \mp \omega_B - \omega)t\ , \tag{17}$$

$$H^{*(2)}_{dAB} = \frac{1}{4}\,\frac{\omega_{1A}\omega_{1B}}{\omega^2}\sum_{i,k} C_{ik} I^k_{By} I^i_{Ay}\cos(\omega_A \mp \omega_B - 2\omega)t\ . \tag{18}$$

The two spin systems couple when $H^{*(1)}_{dAB}$ or $H^{*(2)}_{dAB}$ is static. This happens (i) when $\omega_A \mp \omega_B = \omega$; in this case a rf magnetic-field-induced peak and an original peak in the frequency spectra of the dipolar magnetic field match. It also occurs (ii) when $\omega_A \mp \omega_B = 2\omega$; in this case two rf magnetic-field-induced peaks match.

The cross relaxation rate W_{AB} is in case (i) approximately equal to[8]

$$W_{AB} \approx (\Delta\omega)_{AB}\,[(\omega_{1A}/\omega)^2 + (\omega_{1B}/\omega)^2]\ , \tag{19}$$

whereas in the case (2) it is approximately equal to

$$W_{AB} \approx (\Delta\omega)_{AB}\,(\omega^2_{1A}\omega^2_{1B}/\omega^4)\ . \tag{20}$$

Here $(\Delta\omega)_{AB}$ is the broadening of the A-spin resonance line due to the B spins.

For a typical case of ^{14}N and ^{1}H spin systems in a static magnetic field of 4 kG with a typical value $(\Delta\omega)_{\mathrm{NH}} = 6$ kHz and for a rf magnetic field amplitude of 100 G, the cross-relaxation rate W_{NH} in case (i) is approximately equal to 0.3 sec, whereas in case (ii) it is of the order of 10^5 sec and is thus negligibly long. For that reason we are considering only case (i) in this article.

The cross-relaxation times in the present case

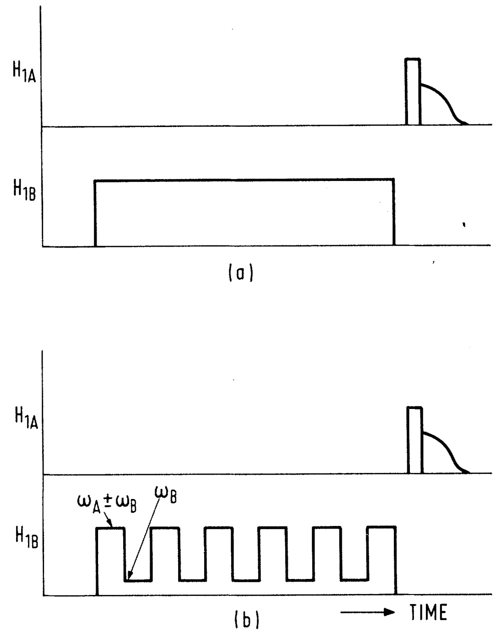

FIG. 4. Schematic representation of the nuclear-double-resonance process in the case of well resolved spectra of the A and B nuclei. (a) Single-coupling process; (b) multiple-coupling process.

are approximately a factor

$$1/(\omega_{1A}^2/\omega^2+\omega_{1B}^2/\omega^2)$$

longer than in the case of rotating-frame nuclear double resonance. This is the main disadvantage of the measuring technique using rf-induced coupling between spin systems. However, in the case of zero-magnetic-field nuclear-double-resonance detection of integer-spin nuclei the presently discussed coupling mechanism is the strongest one because of spin quenching. The measuring technique using this coupling is in this case the only possible double-resonance detection scheme. In other cases the main advantage of the new measuring technique is its simplicity and convenience.

IV. EXPERIMENTAL

A. Case of well-resolved spectra of the A and B spins

The technique described in this section can be used in all cases, whenever the Zeeman, quadrupole, or mixed resonance frequencies of the A and B nuclei are significantly larger than the resonance linewidths.

The experimental procedure is shown in Fig. 4(a). The A and B spins are left until thermal equilibrium of both spin systems with the lattice is reached. At this moment a strong rf magnetic field pulse with frequency ω is applied to the sample. After the end of this pulse a 90° pulse is applied to the A-spin system at some A-spin resonance frequency ω_A and the A-spin free-induction decay amplitude is measured.

Now the whole procedure is repeated without the strong rf magnetic field pulse applied and the A-spin free-induction decay amplitude at frequency ω_A is again measured. The difference between the two free-induction decays, which is called the double-resonance signal, is recorded as a function of frequency ω.

When $\omega=\omega_A\pm\omega_B$, ω_B being a resonance frequency of the B spins, a new state in the A-spin system is reached during the strong rf magnetic field pulse due to the rf magnetic-field-induced coupling between spin systems. This new state results in a changed A-spin free-induction decay amplitude and therefore in a nonzero double-resonance signal. In order to get an optimum double-resonance signal the strong rf field pulse should last several cross-relaxation times.

The sensitivity and the resolution of the technique can be increased by applying a train of strong rf field-coupling pulses at the frequency $\omega_A\pm\omega_B$ with weak rf field pulses at the frequency ω_B in between [Fig. 4(b)] to saturate the particular transition between energy levels of the B spins. The weak rf field pulses at the frequency ω_B can, for example, be obtained by simultaneous attenuation and amplitude or frequency or phase modulation of the carrying signal at the frequency $\omega_A\pm\omega_B$ with the known frequency ω_A. No rf at the frequency ω_A should come to the irradiation coil in order to prevent direct saturation of the A-spin energy levels. The same rf field sequence can be obtained with two signal generators working at two different frequencies which are always ω_A apart.

During the experiment the modulation frequency or the frequency difference is set to the fixed value ω_A and the frequency of the carrier signal is swept.

The double-resonance spectra consists in this case of broad single-coupling lines with strong narrow lines added at the frequencies $\omega_A\pm\omega_B$. The widths of these additional lines are equal to the linewidths of the corresponding B-nuclei resonance lines.

In a multiple-coupling process the thermal equilibrium between the B spins and lattice does not need to be reached. When weak-enough saturating rf field pulses are used the resonance lineshapes of the B nuclei can be measured directly.

B. Double resonance between purely magnetic A spins and quadrupole B spins in zero magnetic field

Here the basic cycle of the new measuring technique is essentially the single-level crossing cycle[5] with strong rf magnetic field applied to the sample

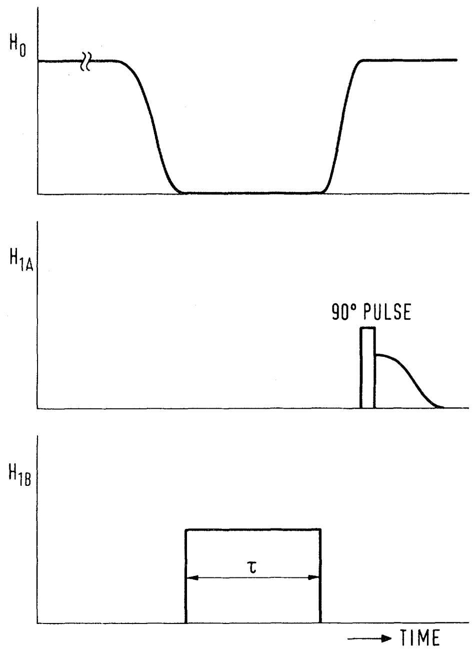

FIG. 5. Field sequence in a zero-magnetic-field nuclear double resonance. Single-coupling process.

in zero static magnetic field.

The procedure is illustrated in Fig. 5. The A-spin system is first polarized in a high magnetic field H_0 and then adiabatically demagnetized by moving the sample out of the magnet. During this process the spin temperature of the A-spin system decreases from the lattice temperature T_L to a rather low value $T_A = T_L(H_L/H_0)$. Here H_L is the local magnetic field at the A-spin sites. The sample is now irradiated with a strong rf magnetic field at a frequency ω for a time τ. After the irradiation the sample is moved back into the magnet and the remaining A-spin magnetization is determined by measuring the A-spin free-induction decay amplitude following a 90° pulse. Then the whole procedure is repeated without the strong rf magnetic field applied. The difference between the A-spin free-induction decay amplitudes with and without the strong rf magnetic field applied is recorded as a function of the rf field frequency ω. It is different from zero when the rf magnetic field couples the two spin systems, i.e., when $\omega \approx \omega_{QB}$. Here ω_{QB} is any of the quadrupole transition frequencies of the B nuclei.

If the B-spin quadrupole-resonance frequencies are lower than the A-spin Larmor frequency in high magnetic field H_0, the two spin systems couple also when their energy levels cross, which has some additional influence on the double-resonance spectra.

The sensitivity and the resolution of the technique is increased when one uses instead of the strong rf magnetic field coupling pulse a train of coupling pulses at a frequency ω near to a quadrupole-resonance frequency ω_{QB} with the weak rf field pulses at the frequency ω_{QB} in between (Fig. 6). The purpose of the weak rf field pulses is to saturate the particular quadrupole transition.

Experimentally a weak rf signal at the frequency ω_{QB} can be obtained from the carrying signal at the frequency ω by its simultaneous attenuation and amplitude or phase or frequency modulation of the carrier signal at the frequency $\omega_M = \omega - \omega_{QB}$. A sideband of the modulated signal is used to saturate the particular quadrupole transition.

During the experiment the modulation frequency ω_M is set to a fixed value and the frequency of the carrier signal is swept through the resonance frequencies ω_{QB}. The double-resonance spectra appear as strong sharp lines at the frequencies $\omega_{QB} \pm \omega_M$ on the broad single-coupling lines. Also in this case the resonance line shapes of the B nuclei can be obtained directly.

V. ANALYSIS OF THE DOUBLE-RESONANCE PROCESS

A. ^{1}H-^{14}N double-resonance spectra

1. Single-coupling process

In this section we present the results of a calculation of the double-resonance spectra for a ^{1}H-^{14}N system in a single level-crossing cycle for the case of an applied strong rf magnetic field. The analogous treatment for the weak rf magnetic field case can be found in Ref. 4. For sake of simplicity spin-lattice relaxation is omitted from the calculation.

The following conditions usually met in a double-resonance experiment have been considered to be valid throughout the calculation. (i) The number $3N$ of nitrogen nuclei per unit volume is much smaller than the number $2n$ of protons per the unit volume. (ii) The nitrogen quadrupole transition frequencies are much lower than the Larmor frequency of protons in the strong static magnetic field H_0 in which the protons are polarized. (iii) An equilibrium in the common NH spin system is reached during every level crossing.

In addition, the cross-relaxation rate W_{NH}, i.e., the rate in which the two spin systems are relaxing towards the common equilibrium state under the influence of a strong rf magnetic field, was assumed to have the Gaussian form

$$W_{NH} = \frac{1}{T_0} \sum_i e^{-(\omega-\omega_{QNi})^2/\omega_L^2} . \tag{21}$$

Here ω is the rf field frequency, T_0 is a constant proportional to $(\gamma_H H_1/\omega)^2$, ω_{QNi} are the nitrogen

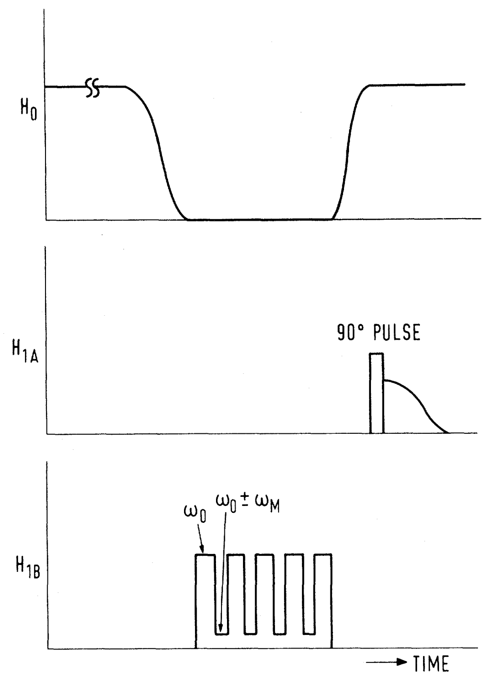

FIG. 6. Field sequence in a zero-magnetic-field nuclear double resonance. Multiple-coupling process.

quadrupole-resonance frequencies, and the proton local frequency $\omega_L = \gamma_H H_L$ measures the proton zero-field linewidth.

The changes in proton magnetization ΔM at the end of the level-crossing cycle due to the double-resonance process are for the three nitrogen quadrupole transitions, to first order in N/n equal to

$$(\Delta M)_1 = M_0 \frac{N}{n} \left(\tfrac{169}{64} + \tfrac{13}{4} x_1 + x_1^2\right) \left[1 - \exp\left(-\frac{\tau}{T_0} e^{-x_1^2}\right)\right],$$

$$(\Delta M)_2 = M_0 \frac{N}{n} \left(\tfrac{25}{64} + \tfrac{5}{4} x_2 + x_2^2\right) \left[1 - \exp\left(-\frac{\tau}{T_0} e^{-x_2^2}\right)\right] \quad (22)$$

$$(\Delta M)_3 = M_0 \frac{N}{n} (1 + 2x_3 + x_3^2) \left[1 - \exp\left(-\frac{\tau}{T_0} e^{-x_3^2}\right)\right],$$

with M_0 being the equilibrium proton magnetization in the static magnetic field H_0, $x_i = (\omega - \omega_{QNi})/\omega_L$ and $\omega_{QN1} > \omega_{QN2} > \omega_{QN3}$. The calculated double-resonance lines are plotted in Fig. 7 for two different ratios τ/T_0.

The double-resonance signals are at $x_i = 0$ for a high enough ratio τ/T_0 equal to the corresponding level-crossing signals.

2. *Multiple-coupling process*

In the calculation of the double-resonance sensitivity we shall in this case completely neglect the level-crossing process, but we can no longer neglect the proton spin-lattice relaxation in zero magnetic field. Spin-lattice relaxation of nitrogens is still assumed to be slow as compared with the double-resonance process.

Assuming that during a single coupling pulse an instantaneous equilibrium in the common NH spin system is reached, the proton spin temperature at the end of the coupling pulse θ_f is related to the proton spin temperature at the beginning of the coupling pulse θ_i through the equation

$$\theta_f = \theta_i (1 + \epsilon) . \quad (23)$$

Here the heat-capacities ratio ϵ is equal to

$$\epsilon = \frac{N}{n} \left(\frac{\omega_M}{\omega_L}\right)^2 , \quad (24)$$

where ω_M is the modulation frequency, i.e., the frequency difference between the corresponding nitrogen quadrupole-resonance frequency and the rf field frequency.

After the nth coupling the final spin temperature of the proton system $\theta_f(n)$ is related to the initial proton spin temperature θ_i through the equation

$$\theta_f(n) = \theta_i (1 + \epsilon)^n \approx \theta_i e^{n\epsilon} . \quad (25)$$

Let τ_1 be the length of a strong rf field pulse, τ_2 the length of a weak rf field pulse, and τ the duration of the whole pulse train.

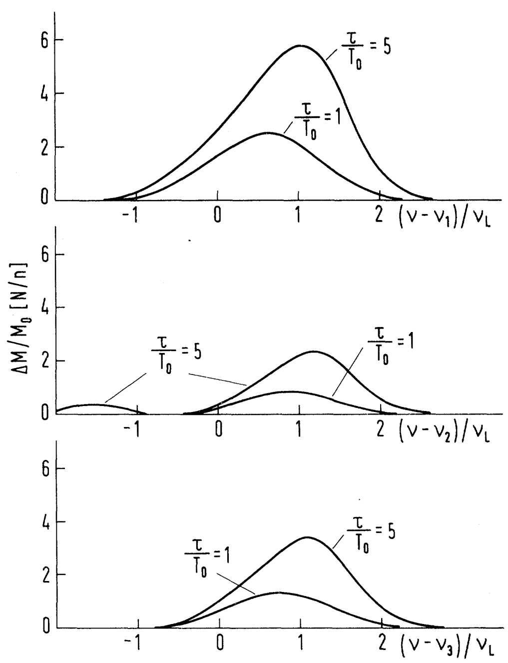

FIG. 7. Calculated [1]H-[15]N double-resonance line shapes obtained by zero-magnetic-field nuclear double resonance in a single-coupling process.

In order to reach an equilibrium in the common NH spin system during each coupling pulse the time τ_1 should be equal to several cross-relaxation times W_{NH}^{-1}. In the following we shall assume $\tau_1 + \tau_2$ to be equal to $3W_{NH}^{-1}$. The number of couplings is thus equal to

$$n = \tau/(\tau_1 + \tau_2) = \tau W_{NH}/3 \ . \tag{26}$$

In addition to the double-resonance process the proton spin temperature raises also because of the spin-lattice relaxation. Both processes are independent. The inverse proton spin temperature which is proportional to the proton magnetization in a high magnetic field is at the end of the irradiation equal to

$$\theta_f^{-1} = \theta_i^{-1} e^{-\epsilon W_{NH}\tau/3 - \tau/T_{1H}} \ . \tag{27}$$

Here T_{1H} is the proton spin-lattice relaxation time in zero magnetic field.

The difference $\Delta\theta_f^{-1}$ between the final inverse proton spin temperature with and without the strong rf magnetic field irradiation is maximum for[11]

$$\tau = T_{1H} \ln(1+x)/x \ , \tag{28}$$

where

$$x = \epsilon W_{NH} T_{1H}/3 \ . \tag{29}$$

In this case the difference $\Delta\theta_f^{-1}$, which is proportional to the double-resonance signal is equal to

$$\Delta\theta_f^{-1} = \theta_i^{-1} x/(1+x)^{1+1/x} \ . \tag{30}$$

The magnitude of the double-resonance signal increases with x. For the assumed Gaussian form of the cross-relaxation rate W_{NH} the maximum double-resonance signals are obtained when $\omega_M = \omega_L$.

Since the cross-relaxation rates W_{NH} are usually, for all three nitrogen quadrupole transitions, approximately equal, the sensitivities of the detection of different nitrogen quadrupole-resonance frequencies by the multiple-coupling technique are also approximately equal.

B. Sensitivity of the nuclear quadrupole double resonance

1. Single-coupling process

In this section we shall calculate the change in the A-spin free-induction decay amplitude following a 90° pulse at frequency ω_{QA} after the sample is irradiated with a strong rf magnetic field pulse at frequency $\omega_{QA} \pm \omega_{QB}$. Here ω_{QB} is one of the quadrupole-resonance frequencies of the B nuclei. We assume the cross relaxation between spin systems to be much faster than the spin-lattice relaxation of both spin systems. We also assume that the rf magnetic field pulse lasts several cross-relaxation times W_{BA}^{-1} so that an instantaneous equilibrium is reached in the common AB-spin system during the pulse.

If the two spin systems are in thermal equilibrium with the lattice before the rf field pulse is applied the A-spin free-induction decay signal S at the end of the rf field pulse will be equal to

$$S = S_0\left(1 - \frac{n_B}{n_A + n_B}\ \frac{\omega}{\omega_{QA}}\right) \ . \tag{31}$$

Here n_A and n_B are the numbers of A and B nuclei touched by the double-resonance process, $\omega = \omega_{QA} \pm \omega_{QB}$, and S_0 is the free-induction decay signal of the A-spin system at the frequency ω_{QA} after thermal equilibrium with the lattice is reached.

It can be easily seen that for $\omega_{QA} \gg \omega_{QB}$ all double-resonance lines have the same intensity, whereas in a general case the double-resonance line at the frequency $\omega_{QA} - \omega_{QB}$ is weaker than the one at the frequency $\omega_{QA} + \omega_{QB}$.

2. Multiple-coupling process

In the analysis of this process we can no longer neglect the spin-lattice relaxation of the A-spin system, but we shall still assume that it is slower than the cross-relaxation between the two spin systems. We shall again neglect the spin-lattice relaxation of the B nuclei.

Let a strong rf field pulse in the train [Fig. 4(b)] last several cross-relaxation times W_{BA}^{-1} and let τ be the duration of a strong plus a weak rf field pulse. Then a train of strong and weak rf field pulses at the frequencies $\omega_{QA} \pm \omega_{QB}$ and ω_{QB}, respectively, lasting for a time t which is longer than the spin-lattice relaxation time T_{1A} of the A nuclei produces a new equilibrium state in the A spin system with the free-induction decay signal at the frequency ω_{QA} equal to

$$S = S_0/(1 + \epsilon T_{1A}/\tau) \ . \tag{32}$$

Here

$$\epsilon = n_B/(n_A + n_B) \ . \tag{33}$$

The double-resonance signals $\Delta S = S_0 - S$ at the frequencies $\omega_{QA} + \omega_{QB}$ and $\omega_{QA} - \omega_{QB}$ have equal intensities. The double-resonance sensitivity increases with increasing T_{1A} and also with increasing t as long $t < T_{1A}$; when $t > T_{1A}$ the sensitivity reaches its maximum value and is independent on further lengthening of t.

C. Nuclear double resonance between two purely magnetic spin systems

1. Single-coupling process

In the analysis of the single-coupling process we shall again neglect the spin-lattice relaxation of both spin systems. Before the strong rf field pulse is applied the spin temperatures of both spin systems are equal to the lattice temperature T_L

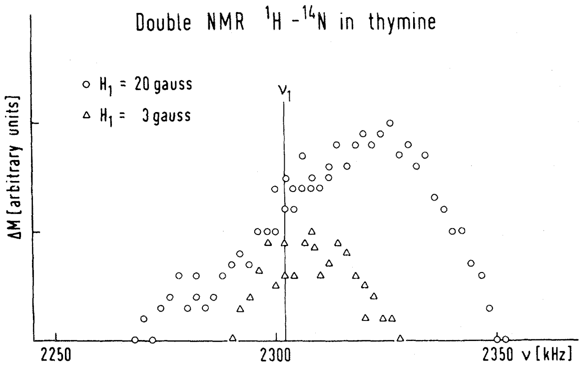

FIG. 8. Measured ^{1}H-^{14}N double-resonance line shape of the highest-frequency ^{14}N NQR transition in thymine.

and the A-spin magnetization is equal to the equilibrium A-spin magnetization M_{AO} at the temperature T_L. After the coupling pulse at the frequency $\omega_A \pm \omega_B$ is applied, which lasts several cross-relaxation times, the magnetization of the A-spin system changes to

$$M_A = M_{AO}(1-\epsilon) , \tag{34}$$

where

$$\epsilon = \frac{n_B I_B(I_B+1)(1 \pm \omega_B/\omega_A)}{n_A I_A(I_A+1) + n_B I_B(I_B+1)} . \tag{35}$$

Here n_A and n_B are the numbers, ω_A and ω_B are the Larmor frequencies, and I_A and I_B are the spins of the A and B nuclei, respectively. Again the double-resonance signal $\Delta M = M_{AO} - M_A$ at the frequency $\omega_A + \omega_B$ is stronger than the one at the frequency $\omega_A - \omega_B$.

2. *Multiple-coupling process*

Similarly as in the case of ^{1}H-^{14}N double resonance and in the case of nuclear quadrupole double resonance we shall in the analysis of this process neglect the spin-lattice relaxation of the B nuclei, but we shall no longer neglect the spin-lattice relaxation of the A nuclei.

Before every coupling pulse the spin temperature of the B-spin system is infinite due to the direct saturation of the B-spin energy levels by the weak rf pulse.

After a train of strong and weak rf field pulses at the frequencies $\omega_A \pm \omega_B$ and ω_B, respectively, which lasts longer than the spin-lattice relaxation time T_{1A} of the A system, the magnetization of the A spins changes from M_{AO} to M_A,

$$M_A = \frac{M_{AO}}{1+\epsilon T_{1A}/\tau} . \tag{36}$$

Here

$$\epsilon = \frac{n_B I_B(I_B+1)}{n_A I_A(I_A+1) + n_B I_B(I_B+1)} \tag{37}$$

and τ is the duration of a weak plus a strong rf field pulse. Also in this case the double-resonance sensitivity increases with T_{1A}.

VI. EXPERIMENTAL RESULTS

The new technique has been experimentally tested:

(a) In the case of zero-magnetic-field nuclear double resonance between ^{1}H and ^{14}N nuclei in thymine: The double-resonance line shape of the highest-frequency ^{14}N quadrupole transition was measured at two different rf magnetic field amplitudes. The single-coupling technique was used. The results are shown in Fig. 8. The meausred line shape qualitatively agrees with the calculated one. When a rf magnetic field intensity of 30 G was used the cross-relaxation time was found to be approximately 10 msec, which is well below our shortest experimentally obtainable time for which the sample stays in zero magnetic field.

(b) In the case of nuclear double resonance between purely magnetic ^{23}Na and ^{19}F spins in NaF

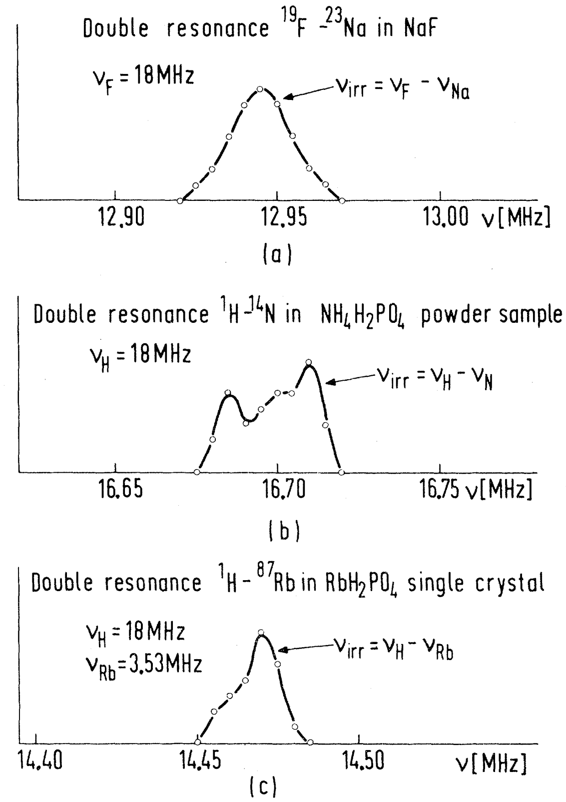

FIG. 9. Measured nuclear-double-resonance spectra in a strong static magnetic field. (a) ^{19}F-^{23}Na double resonance in NaF; (b) ^{1}H-^{14}N double resonance in $NH_4H_2PO_4$; (c) ^{1}H-^{87}Rb double resonance in RbH_2PO_4.

in a strong static magnetic field. The double-resonance line shape at the frequency $\omega_F - \omega_{Na}$ in a single-coupling process was measured. The result is shown in Fig. 9(a). The rf field amplitude was approximately 80 G and the irradiation time was 1 sec. The Larmor frequency of ^{19}F was 18 MHz. In this case the cross-relaxation time was found to be 150 msec.

(c) In the case of ^1H-^{14}N double resonance in a $NH_4H_2PO_4$ powder sample: The double-resonance line shape at the frequency $\omega_H - \omega_N$ was measured. The proton Larmor frequency was 18 MHz, the irradiation time was 1 sec and the rf magnetic field amplitude was 80 G. The results are shown in Fig. 9(b). The unusual double-resonance line shape is due to the nuclear quadrupole broadening of the ^{14}N resonance lines.

(d) In the case of ^1H -^{87}Rb double resonance in a RbH_2PO_4 single crystal: The experimental conditions were the same as in (c). The ^{87}Rb resonance line at the frequency 3.53 MHz was chosen. The results are shown in Fig. 9(c).

All these results present various applications of the new double-resonance technique in the single-coupling case. The multiple-coupling technique had so far not been used.

VII. DISCUSSION

A new nuclear-double-resonance technique based on strong rf magnetic-field-induced coupling between spin systems has been presented. It has been analyzed (a) in the case of zero-field nuclear-double-resonance detection of ^{14}N NQR spectra through the proton signal; (b) in the case of nuclear quadrupole double resonance; and (c) in the case of nuclear double resonance between two purely magnetic spin systems in a strong static magnetic field.

In the case (a) the sensitivity of the new technique is higher than the sensitivity of the level-crossing technique which can be used for the same purpose. The new technique is of particular importance in some cases when the level-crossing signals cannot be obtained. This is the case when (i) the spin-lattice relaxation time of the B-spin system is much shorter than the time for which the sample stays in zero static magnetic field; (ii) when the level-crossing times are too short for sufficient energy exchange between the two spin systems; and (iii) when the quadrupole-resonance frequencies of the B nuclei are too high for the level crossing to occur. In all these cases the new technique is useful complementary tool to the level-crossing technique.

In the cases (b) and (c) the cross-relaxation times are longer than the cross-relaxation times in the case of rotating-frame nuclear double-resonance, resulting in a lower sensitivity. The main advantage of the new technique is in these cases the very simple experimental arrangement needed to obtain the double resonance signals. It can be also used to detect pure NQR spectra of integer-spin nuclei by nuclear quadrupole double resonance, when the spin quenching makes the rotating-frame nuclear double resonance impossible.

The double-resonance linewidths are in the single-coupling case mostly determined by the A-spin resonance linewidth which is usually broad. Therefore the single-coupling technique can be used for fast searching of unknown resonance frequencies of the B nuclei. The toll is a lower resolution.

This last disadvantage can be removed by the application of the multiple-coupling technique where the double-resonance spectra include also lines of the same linewidth as the corresponding resonance lines of the B nuclei. The multiple-coupling technique is even suited for a direct line-shape measurement of the B-nuclei resonance lines.

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