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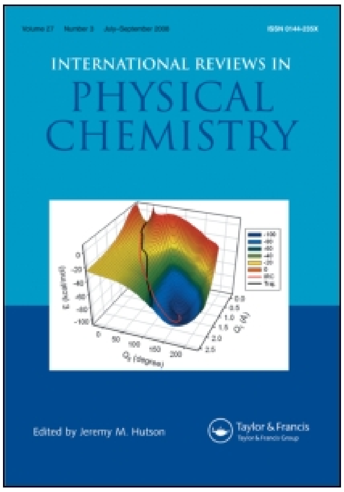

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RECENT ADVANCES IN HIGH SENSITIVITY NUCLEAR QUADRUPOLE RESONANCE

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ABSTRACT

The field of nuclear quadrupole resonance has been transformed recently by the invention of double-resonance techniques which are applicable to powdered solids or frozen liquids. The spectra of light elements such as ^{2}H, ^{14}N, ^{17}O and ^{23}Na are now detected with ease and with a sensitivity such that ^{17}O, or even ^{2}H, may be measured in its natural abundance. The review describes four of these techniques, namely double resonance with level crossing (DRLC), double resonance with continuous coupling (DRCC), double resonance in the laboratory frame (DRLF) and double resonance with coupled multiplets (DRCM).

The treatment relies on physical models where possible and is aimed at the practical experimenter who may not be a specialist in the thermodynamics of nuclear spin systems.

I. INTRODUCTION

A *Nuclear quadrupole double resonance*

Recently there has been a rapid expansion in the quantity of nuclear quadrupole resonance (NQR) data that has become available. Not only has its volume increased but high-resolution NQR spectra of light elements in powdered samples are published as routine today which would have been impossible only 10 years ago. The reason for the change has been the advent and development of nuclear quadrupole double resonance (NQDR) which detects the NQR of one set of spins (Q spins) by observing the effect upon a second set of spins (P spins) of thermal coupling between the two spin assemblies.

The ability to detect the NQR of light elements is important for two particular reasons.

1. These light elements such as ^{2}H (substituting for ^{1}H), ^{14}N, ^{17}O and ^{23}Na often play important roles in the binding and function of chemically and biologically interesting molecules.
2. The simple electronic structure of light elements holds out the promise of rapid advance in the theoretical understanding of electric field gradients in molecules which would unlock the vast store of structural information that NQR spectra contain.

In a recent review (Edmonds, 1977) of NQDR particular emphasis was laid upon double resonance with level crossing (DRLC) which is to date the most widely applicable technique. However, DRLC demands that the number of Q spins whose resonance is to be detected does not fall below about 5% of the number of P spins which register the Q spin resonance. This review concentrates upon techniques which may be thought of as developments of DRLC (although in fact one predates DRLC) and which have very much higher sensitivities than DRLC. For example, in suitable samples the resonance of ^{17}O in its natural abundance of 0.037% or ^{2}H in its natural abundance of 0.016% may be detected with ease using inexpensive apparatus.

The importance of NQDR lies in the information gained about the electronic structure of the molecules to which it is applied, while the various techniques merely provide a means toward that end. However, it is sometimes necessary to have an understanding of the techniques in order to maximize the information obtainable. This review describes the techniques in physical rather than in purely mathematical terms and with the viewpoint of the practical experimenter in mind. The theoretical foundations of the subject may be found in Slichter (1978) or the specialist texts of Abragam (1961) and Goldman (1970).

Also with an emphasis on practicality, only those methods applicable to powdered solids or frozen liquids are discussed and any requiring single crystals are ruled out, as crystals of the requisite size are seldom available. This means that NQR is always detected in zero or small applied field so that all the techniques involve field cycling as first proposed by Ramsey and Pound (1951). The remainder of section I deals briefly with some relevant general topics.

B *A spin-spin coupling mechanism considered classically*

Two of the very high sensitivity NQDR methods considered, namely double resonance in the laboratory frame (DRLF) and double resonance by the solid state effect (DRSS), employ a particular spin-spin coupling mechanism. It was discovered by Redfield (1955) and by Hartmann and Hahn (1962) and enables a nucleus precessing at a high frequency ω_Q to make thermal contact (by exchange of resonant photons) with a P spin or assembly of P spins with much smaller precession frequencies of order $\omega_P \ll \omega_Q$.

Let us consider a Q spin with spin I situated at 0 and a P spin with spin S situated at P, where P is related to 0 by co-ordinates R and θ as in *Figure 1*. We first consider the system classically with the magnetic moment M of the Q spin precessing about the z axis with angular frequency ω_Q as in *Figure 2a*. This could be due to the presence of a magnetic field B_0 along the z axis so that $\omega_Q = -\gamma_Q B_0$ where γ_Q is the magnetogyric ratio of the Q spins. The components of the magnetic moment along the three axes in $oxyz$ are given by

$$M_x = M_\perp \cos \omega_Q t \qquad M_y = M_\perp \sin \omega_Q t \qquad M_z = M_\parallel \tag{1}$$

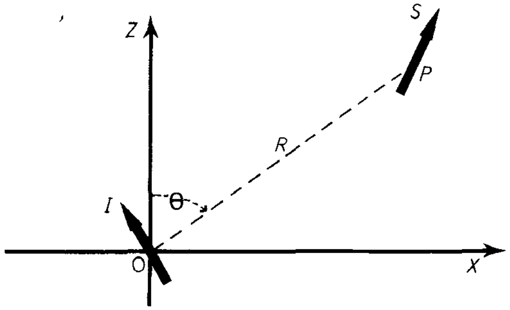
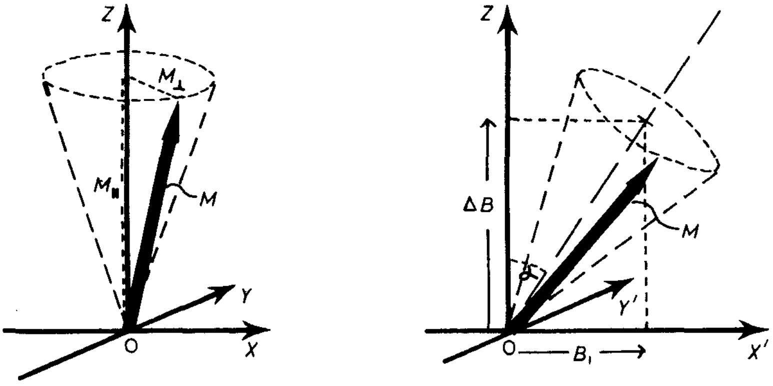


FIG. 1. The position of a P spin with spin S relative to a Q spin with spin I.



(a) (b)

FIG. 2. (a) The precession of a Q spin of magnetic moment M viewed in the laboratory frame oxy in the absence of an applied radio-frequency magnetic field. (b) The precession of a Q spin viewed in a frame $ox'y'z$ rotating with an applied radiofrequency magnetic field B_1.

If we view this motion in a new set of axes $ox'y'z$ with the same origin as $oxyz$ and rotating about the z axis with angular frequency ω the components of M in $ox'y'z$ become

$$M'_x = M_\perp \cos \Delta\omega t \qquad M'_y = M_\perp \sin \Delta\omega t \qquad M'_z = M_\parallel \tag{2}$$

with $\Delta\omega = \omega_Q - \omega$. In this frame it is as if the magnetic field B_0 has been replaced by a smaller field ΔB such that $(\Delta B/B_0) = (\Delta\omega/\omega_Q)$ with M precessing about ΔB with angular frequency $\Delta\omega = -\gamma_Q \Delta B$. We may write the reduced field as

$$\Delta B = (B_0 + \omega/\gamma_Q)$$

It should be clear that, just because we have chosen to observe the precession of M from such a bizarre viewpoint in the rotating set of axes, the fluctuating field at the P spin due to the precession of M has in no way changed. This field has components which fluctuate at frequencies 0 and ω_Q as given in Eq.(1) and, for example, there are no components fluctuating at frequency $\Delta\omega$.

Let us now apply to the Q spins a second magnetic field $B_1 \ll B_0$ directed along the x' axis of $ox'y'z$ so that in the laboratory frame $oxyz$ it rotates about oz with angular frequency ω and lies in the xy plane. In the set of axes $ox'y'z$ there is a fixed field B_1 along ox' and a reduced field ΔB along oz. These may be combined to produce an effective field B_E which is static in $ox'y'z$. Within these axes we may expect M to precess about B_E with angular frequency $\omega_E = -\gamma_Q B_E$. The magnitude and direction of B_E in $ox'y'z$ are defined by

$$B_E = (\Delta B^2 + B_1^2)^{1/2} \text{ or } \omega_E = (\Delta\omega^2 + \omega_1^2)^{1/2} \text{ and } \tan\alpha = (\omega_1/\Delta\omega)$$

as shown in *Figure 2b*. In $ox'y'z$ the components of M become

$$\begin{aligned} M'_x &= M_\parallel \sin\alpha + M_\perp \cos\alpha . \cos\omega_E t \\ M'_y &= M_\perp \sin\omega_E t \\ M'_z &= M_\parallel \cos\alpha + M_\perp \sin\alpha . \cos\omega_E t \end{aligned} \tag{3}$$

In the laboratory frame *oxyz* the components become

$$\begin{aligned} M_x &= M'_x \cos \omega t - M'_y \sin \omega t \\ &= M_{\parallel} \sin \alpha \cos \omega t + \tfrac{1}{2} M_{\perp}(\cos \alpha + 1) \cos(\omega + \omega_E)t + \tfrac{1}{2} M_{\perp}(\cos \alpha - 1) \cos(\omega - \omega_E)t \\ M_y &= M'_y \cos \omega t + M'_x \sin \omega t \qquad (4) \\ &= M_{\parallel} \sin \alpha \sin \omega t + \tfrac{1}{2} M_{\perp}(\cos \alpha + 1) \sin(\omega + \omega_E)t + \tfrac{1}{2} M_{\perp}(\cos \alpha - 1) \sin(\omega - \omega_E)t \\ M_z &= M'_z = M_{\parallel} \cos \alpha + M_{\perp} \sin \alpha \cos \omega_E t \end{aligned}$$

If $\omega \sim \omega_Q$ then ω_E is small in comparison with ω_Q and there is a component of M along the z axis which fluctuates at frequency ω_E. All components of M in the xy plane fluctuate with high frequencies of order ω_Q. The low-frequency component may be associated with the precession of M about B_E. The rotating frame chosen allows us to view this precession very simply as B_E is fixed in $ox'y'z$.

The amplitude of the low-frequency component of M_z is proportional to $\sin \alpha = \omega_1/(\Delta\omega^2 + \omega_1^2)^{1/2}$. It depends on B_1 through ω_1 and is only large when $\Delta\omega$ is small, that is when $\omega \sim \omega_Q$. A fluctuating moment $M_{\perp} \sin \alpha \cos \omega_E t$ along the z axis, through the magnetic dipole interaction, will cause a magnetic field along the x axis at P given by

$$B_{1P} = (3\mu_0/4\pi R^3) \sin \theta \cdot \cos \theta \cdot M_{\perp} \sin \alpha \cos \omega_E t \qquad (5)$$

If the P spin is precessing about oz with angular frequency $\omega_P (\omega_P \ll \omega_Q)$, then B_{1P} will induce transitions in the P spin provided that $\omega_E \sim \omega_P$.

This is the essence of DRLF or DRSS coupling whereby a spin precessing at a high frequency ω_Q may exchange photons with a neighbouring spin precessing at a much lower frequency ω_P and thus exchange energy with it. The reciprocal interaction may be thought of as the precessing P spin causing a field fluctuating at ω_P along oz at the Q spin which causes the Q spin to flip from parallel-to-B_E to antiparallel-to-B_E or vice versa, if $\omega_P \sim \omega_E$. When $\omega_1 \ll \Delta\omega$ so that $\omega_E \approx \Delta\omega$ it is customary to call this solid state effect coupling whereas DRLF coupling usually refers to the situation $\Delta\omega \sim 0$ so that $\omega_E \sim \omega_1$. Note that the probability of a P spin flip, assumed proportional to the square of B_{1P} depends upon ω_1 and $\Delta\omega$ as

$$\sin^2 \alpha = \omega_1^2/(\Delta\omega^2 + \omega_1^2) \qquad (6)$$

Thus the solid state regime referred to above with $\omega_1 \ll \Delta\omega$ results in much weaker coupling than does DRLF with $\Delta\omega \sim 0$, so that $\sin \alpha \sim 1$.

C *The spin coupling mechanism using quantum mechanics*

Let us consider two Q spin states $|A\rangle$ and $|B\rangle$ separated in energy by $\hbar\omega_Q$ and two P spin states $|+\rangle$ and $|-\rangle$ separated in energy by $\hbar\omega_P$. We assume the two spins to be disposed in space and having spins I and S as depicted in *Figure 1*. The magnetic dipole–dipole interaction between the two spins is given (Slichter, 1978) by the usual Van Vleck terms

$$\begin{aligned} \mathscr{H}_{PQ} = {} & L(I_z S_z) + M(I_+ S_- + I_- S_+) + N(I_z S_+ + I_+ S_z) + N(I_z S_- + I_- S_z) \\ & + V(I_+ S_+ + I_- S_-) \qquad (7) \end{aligned}$$

where $L = \beta(1 - 3\cos^2\theta)$; $M = -(\beta/4)(1 - 3\cos^2\theta)$; $N = -(3\beta/2)\sin\theta\cos\theta$; $V = -(3\beta/4)\sin^2\theta$; $\beta = (\mu_0/4\pi R^3)\gamma_P\gamma_Q\hbar^2$ and $S_+ = S_x + jS_y$ etc, with $j = \sqrt{-1}$.

As a zero-order approximation we may use product states such as $|A\rangle \cdot |+\rangle$ to represent the state with the Q spin in state $|A\rangle$ and the P spin in state $|+\rangle$. However, $\mathscr{H}_{PQ}$ admixes these simple states so that, using the first-order perturbation theory result

$$|M\rangle' = |M\rangle + \sum_N [\mathscr{H}_{NM}/(E_M - E_N)] \cdot |N\rangle$$

in an obvious notation we obtain

$$\begin{aligned} |A, +\rangle' = |A\rangle \cdot |+\rangle &+ [\langle + | \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle/\hbar\omega_P]|A\rangle \cdot |-\rangle \\ &+ [\langle + | \cdot \langle A|\mathscr{H}_{PQ}|B\rangle \cdot |+\rangle/\hbar\omega_Q]|B\rangle \cdot |+\rangle \\ &- [\langle + | \cdot \langle A|\mathscr{H}_{PQ}|B\rangle \cdot |-\rangle/(\hbar\omega_P + \hbar\omega_Q)]|B\rangle \cdot |-\rangle \end{aligned} \qquad (8)$$

with similar admixtures in the other states. As $\mathscr{H}_{PQ}$ is linear in both I_x, I_y, I_z and S_x, S_y, S_z, the matrix elements of $\mathscr{H}_{PQ}$ consist of simple products. For example, if $|B\rangle = |\frac{1}{2}\rangle$, $|A\rangle = |3/2\rangle$, $|+\rangle = |\frac{1}{2}\rangle$ and $|-\rangle = |-\frac{1}{2}\rangle$ then

$$\langle + | \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle = N\langle \tfrac{1}{2}|\mathrm{S}_+| - \tfrac{1}{2}\rangle\langle 3/2|I_z|3/2\rangle = (3/2)N$$

with N given by Eq. (7).

If we apply resonant frequency magnetic fields to the spins, the state admixtures due to $\mathscr{H}_{PQ}$ allow us to induce normally forbidden transitions, such as that between $|B,-\rangle'$ and $|A,+\rangle'$. In fact

$$\begin{aligned} \langle -,B|'\Delta|A,+\rangle' = &[\langle + | \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle/\hbar\omega_P]\langle - | \cdot \langle B|\Delta|A\rangle \cdot |-\rangle \\ &- [\langle - | \cdot \langle B|\mathscr{H}_{PQ}|B\rangle \cdot |+\rangle/\hbar\omega_P]\langle + | \cdot \langle B|\Delta|A\rangle \cdot |+\rangle \end{aligned} \qquad (9)$$

where Δ represents the applied radiofrequency magnetic field. We have assumed $\omega_P \ll \omega_Q$ so that we have ignored terms in $(1/\omega_Q)$ in comparison with those in $(1/\omega_P)$. The matrix elements of Δ on the right-hand side of Eq. (9) represent normally allowed $\Delta I_z = \pm 1$ transitions of the Q spin. Thus it is seen that, by irradiating the Q spins at frequencies around $\omega_Q \pm \omega_P$ we can, through the medium of the dipolar coupling $\mathscr{H}_{PQ}$, induce spin flips of the P spins. The transition probability of a forbidden transition is seen to be that of an allowed transition multiplied by a factor F^2 where $F \ll 1$ and is given by

$$\begin{aligned} F \sim \langle + | \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle/\hbar\omega_P &= KN/\hbar\omega_P \\ &= K(\mu_o/4\pi R^3)\hbar^2\, \gamma_Q \gamma_P (3/2) \sin\theta \cos\theta (1/\hbar\omega_P) \end{aligned}$$

where K is a number of order unity. F is seen to be the ratio $(\gamma_P B_{1P}/\gamma_Q B_1)$ in the classical derivation of the coupling, if we take the limit $\omega_1 \ll \Delta\omega$.

D *Spin temperature in the rotating frame*

Here we will illustrate the principles by discussing a particular simple example. For a more thorough treatment reference should be made to Redfield (1955) or a particularly lucid treatment in Slichter (1978). Consider a spin 3/2 nucleus situated in an electric field gradient that is axially symmetric about the z axis, so that $\eta = 0$, with a radio frequency magnetic field $2B_1 \cos\omega t$ applied along the x axis. The Hamiltonian may be written

$$\mathscr{H}_Q = \tfrac{1}{2}\hbar\omega_Q[I_z^2 - \tfrac{1}{3}I(I+1)] + 2\hbar\omega_1 I_x \cos\omega t$$

with $\hbar\omega_Q = e^2qQ/2$ and $\omega_1 = -\gamma_Q B_1$. The eigenfunctions are $|3/2\rangle$, $|\frac{1}{2}\rangle$, $|-\frac{1}{2}\rangle$ and $|-3/2\rangle$ written in terms of the expectation value of I_z. The first term in $\mathscr{H}_Q$ leads to the states represented by $|+3/2\rangle$ and $|-3/2\rangle$ being degenerate with eigenvalue $+\frac{1}{2}\hbar\omega_Q$ and $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ degenerate with eigenvalue $-\frac{1}{2}\hbar\omega_Q$. The second term in $\mathscr{H}_Q$ leads to off-diagonal matrix elements

$$\langle \pm 3/2 | \mathscr{H}_Q | \pm \tfrac{1}{2} \rangle = \langle \pm \tfrac{1}{2} | \mathscr{H}_Q | \pm 3/2 \rangle = (\sqrt{3}/2)\hbar\omega_1 \cos \omega t$$

and

$$\langle \pm \tfrac{1}{2} | \mathscr{H}_Q | \mp \tfrac{1}{2} \rangle = \hbar\omega_1 \cos \omega t.$$

We are interested in the system when $\omega \sim \omega_Q$ so that this simple laboratory frame representation is clearly not satisfactory. The presence of large amplitude matrix elements connecting $|\pm 3/2\rangle$ and $|\pm\frac{1}{2}\rangle$ which oscillate at frequency ω, when the $|3/2\rangle$ and $|-3/2\rangle$ states are separated in energy from the $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ states by $\hbar\omega_Q \sim \hbar\omega$, means that the system is continuously switching between these states. For example, it would not be possible to define a temperature for an assembly of such systems.

It is well known that we may remove the troublesome time-dependent matrix elements by transforming to a new representation. The transformation is brought about by multiplying the wavefunctions of the system ψ by a unitary transformation T

$$\psi_Q = \mathrm{T}\psi, \text{ with } T = \exp[+\tfrac{1}{2}j\omega t(I_z^2 - \tfrac{1}{3}I(I+1))]$$

The Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \mathscr{H}\psi$$

becomes

$$i\hbar \frac{\partial}{\partial t}(T^{-1}\psi_Q) = \mathscr{H}T^{-1}\psi_Q$$

or

$$i\hbar \frac{\partial \psi_Q}{\partial t} = \left\{ T\mathscr{H}T^{-1} - i\hbar T \frac{\partial T^{-1}}{\partial t} \right\} \psi_Q$$

so that the effective transformed Hamiltonian is

$$\mathscr{H}_Q^* = T\mathscr{H}T^{-1} - (\hbar\omega/2)(I_z^2 - \tfrac{1}{3}I(I+1))$$

$\mathscr{H}_Q^*$ still contains time dependent off-diagonal terms which oscillate at frequencies ω and 2ω but they connect states in the new representation separated by energies very much less than $\hbar\omega$ so that they are quite ineffective in inducing transitions and may be safely discarded. The remaining time independent Hamiltonian may be written

$$\mathscr{H}_Q'^* = (\tfrac{1}{2})(\hbar\omega_Q - \hbar\omega)(I_z^2 - \tfrac{1}{3}I(I+1)) + \hbar\omega_1 \mathscr{I}_x$$

The matrix representing $\mathscr{I}_x$ is identical to the normal matrix representing I_x with the two matrix elements $\langle -\frac{1}{2}|I_x|\frac{1}{2}\rangle$ and $\langle \frac{1}{2}|I_x|-\frac{1}{2}\rangle$ set to zero. The eigenvectors and eigenvalues of $\mathscr{H}_Q'^*$ are shown in *Figure 3*. Note particularly that two pairs of degenerate states remain, which is also the case in the more complicated situation with η non-zero.

Viewed in the transformed representation with time-independent Hamiltonian $\mathscr{H}'^*$ we may expect an assembly of such spin 3/2 nuclei, if allowed to interact even slightly, to reach an equilibrium condition describable by a spin temperature θ_Q. In particular we expect the magnetization to point in the direction of the effective magnetic field B_E acting, and to obey the Curie Law

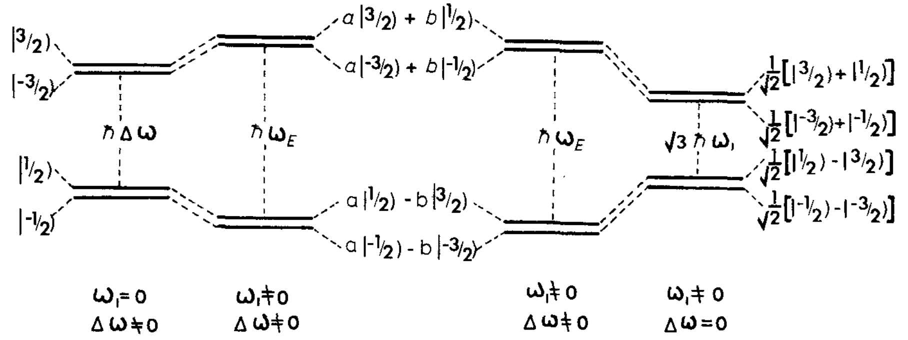


FIG. 3. The eigenvalues and eigenfunctions of the essentially time-independent (interaction representation) Hamiltonian $\mathscr{H}_Q^*$ of a spin 3/2 nucleus situated in an axially symmetric electric field gradient and subject to a large applied radio frequency field.

$$M = C\, B_E/\theta_Q, \qquad C = N_Q\, \gamma_Q^2\, \hbar^2\, I(I+1)/\mu_0 \cdot 3k_B$$

The quantum-mechanical transformation represented by T is equivalent in many ways to the classical transformation we performed in section IB to the rotating frame. In fact for spins experiencing a Zeeman interaction the equivalence is exact and the equivalent Zeeman transformation T_z, given by

$$T_z = \exp(j\omega t\, I_z)$$

is a rotation about oz with frequency ω. For the quadrupolar interaction, T does not represent any simple transformation of axes. Strictly speaking T represents a transformation to an interaction representation but it is most often called a transformation to the rotating frame.

E *Spin quenching*

It can be shown that the expectation value of any component of the angular momentum operator is zero in a singlet state produced by an electric field acting upon an integer spin system. This is known as spin quenching. It can also be shown that systems with half-integer spins (3/2, 5/2 . . .) have energy levels produced by electric fields which are always at least doubly degenerate and thus not quenched. We have attempted to derive these results elsewhere (Edmonds, 1977). Also, these results and some consequences for NQR are clearly discussed by Leppelmeier and Hahn (1966).

A much simplified physical picture is as follows. An electric field, derived say from static electric charges, is clearly not affected if we were to reverse time. Thus a state created by an electric field should in no way be affected by time reversal. But, if associated with that singlet state there were a finite expectation value for I_x we would expect this to reverse sign under time reversal. Therefore any singlet state invariant under time reversal must have zero expectation values for the components of angular momentum. The doubly degenerate states of half-integer spins escape the consequences of this argument as the two degenerate states could have equal and opposite expectation values of I_x. The pair is thus invariant under time reversal without either state having a zero expectation value of I_x.

Thus if $|A\rangle$ represents a singlet state of an integer spin nucleus in an electric field gradient we expect

$$\langle A|I_x|A\rangle = \langle A|I_y|A\rangle = \langle A|I_z|A\rangle = 0$$

This leads to a drastic reduction of any spin-spin coupling. As an example we consider the effect upon the DRLF or DRSS coupling that we have discussed. If we examine the expression given in Eq. (8) for possible admixtures into the state $|A\rangle \cdot |+\rangle$ due to the dipolar coupling Hamiltonian $\mathscr{H}_{PQ}$, we have

$$\langle +| \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle = \langle +| \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |+\rangle = \langle -| \cdot \langle A|\mathscr{H}_{PQ}|A\rangle \cdot |-\rangle = 0$$

as $\mathscr{H}_{PQ}$ is linear in I_x, I_y and I_z. This eliminates all admixture coefficients with $\hbar\omega_P$ in the denominator. As matrix elements of I_x, I_y, and I_z between quenched states are in general not zero, so that for example $\langle A|\mathscr{H}_{PQ}|B\rangle \neq 0$, we still retain the admixture coefficient in Eq.(8) with denominator $\hbar\omega_Q$. Thus for non-degenerate states of integer spin nuclei we expect the Q to P spin coupling to be reduced by a factor $\sim (\omega_P/\omega_Q)^2$.

For integer spin nuclei with small quadrupole splittings $\hbar\omega_Q$ or for a nucleus such as ^{14}N with $I = 1$ but with $\eta \approx 0$, so that at least one quadrupole splitting is small, the techniques of DRLF and DRSS may still be possible. However, in general they are not very effective for integer spin nuclei as $(\omega_P/\omega_Q)^2$ is often 10^{-4} or less. The application of a magnetic field, which changes sign under time reversal, is effective in reducing the effects of quenching. However, this is seldom possible when NQDR is applied to a polycrystalline specimens, as a magnetic field sufficient to reduce appreciably the effects of quenching leads to an unacceptable broadening of the NQR spectrum.

II DOUBLE RESONANCE WITH LEVEL CROSSING (DRLC)

A *The method*

Double resonance with level crossing (DRLC) is not one of the very high sensitivity methods with which we will be primarily concerned. However, it may be considered as the basic technique from which the more advanced techniques develop so that we will briefly describe it here (see also Edmonds, 1977).

DRLC was first described in the unpublished PhD thesis of J. Koo, a student of Professor E. L. Hahn (Koo, 1969). The powdered solid specimen needs to include the quadrupolar Q nuclei of interest and also an abundant and easily detected assembly of P nuclei which are nearly always protons. The experiment proceeds in cycles with each cycle divided into three phases. During the polarization phase the sample resides in a large steady magnetic field ($\sim$ 1 T) and after a time of the order of the spin-lattice relaxation time the P nuclei become partially polarized. The sample is then moved to a region of zero field at the same temperature. During the transit the P nuclei become adiabatically demagnetized to a low spin temperature. The Q nuclei become partially polarized by the P spins when a given pair of quadrupolar split Q energy levels have an energy separation equal to the reduced energy splitting of the P spins, as the field is reduced to zero. This PQ spin coupling by exchange of resonant photons is known as level crossing coupling. For simplicity at this stage we assume both P and Q spin-lattice relaxation times are long in comparison with the time the specimen spends out of the large magnetic field.

During the irradiation phase spent in zero applied magnetic field the Q spins are irradiated at frequency ν in an attempt to detect an allowed transition among their quadrupole split energy levels. The P spins are not heated by the irradiation as their energy levels are split only by spin-spin coupling and by much less than $h\nu$.

During the final detection phase the specimen is returned to the large field during which transit further level crossing occurs. The final spin temperature of the P spins in the large field is sampled by applying a single 90° pulse to the *P* spins and monitoring the amplitude of the resultant free induction decay. The whole cycle is then repeated with a different value of ν until the desired region of the spectrum has been swept. If during the irradiation phase, the radiation at ν does appreciably heat the *Q* spins, some of this energy will be passed back to the *P* spins by level crossing during the detection phase and the final free induction decay signal of the *P* spins will be reduced.

No matter which quadrupolar *Q* spin system is studied the measurement is always of the *P* spin free induction decay. Thus a simple fixed frequency spectrometer that can deliver a single 90° pulse to the *P* spins each cycle is all that is required. A detailed description of the simple apparatus required is given elsewhere (Edmonds, 1977). The sensitivity is largely independent of the *Q* spin quadrupole splitting studied, so that, for example, for ^2H a good signal-to-noise ratio is attainable at around 100 kHz. The technique is equally applicable to integer and half integer nuclear spins as the *PQ* thermal contact by level crossing occurs in an appreciable magnetic field, which removes the quenching effects mentioned in section IE. The major limitation of the method is that the low field spin-lattice relaxation time of the *P* spins must be a few seconds or longer so that they do not depolarize during the irradiation phase. This limitation may often be overcome by reducing the specimen temperature sufficiently, although this may necessitate long cycle times in order that the high field polarization phase is sufficiently long to polarize initially the *P* spins.

Finally the reason that NQDR and in particular DRLC has been so successful in detecting previously undetected resonances is the ability of the *P* spins to record the cumulative effect of the irradiation of many *Q* spin resonances during a single cycle. If instead of irradiating at a single frequency ν the irradiation is swept during the irradiation phase from ν_1 to ν_2 then, by studying the size of the *P* spin free induction decay at the end of a single cycle, it is possible to state whether or not there are any *Q* spin resonances between ν_1 and ν_2. In this manner *Q* spin resonances may be rapidly located. Unlike continuous wave NQR, saturation of a resonance does not make it impossible to detect. On the contrary the use of excessive power merely broadens the line which may help its detection. A final spectrum obtained with low irradiation power, and thus no saturation, reveals the true width and accurate frequency position of the line.

Most of these advantages of DRLC apply to all the very high sensitivity methods we will discuss. The exception is the freedom DRLC enjoys from adverse effects due to quenching.

B *Sensitivity limitations of DRLC*

In DRLC the *P* spins, during the detection phase, are affected by the energy which the *Q* spins can gain from the applied radiation and store, during the irradiation phase. Consider two quadrupole split energy levels of the *Q* spins separated in zero field by an energy $h\nu$. A population difference between these two energy levels is created by the level crossing with the *P* spins that occurs during specimen transit to zero magnetic field at the completion of the polarization phase. If the specimen in zero field is irradiated at frequency ν energy is absorbed until saturation occurs so that the population difference is reduced to zero. After that, no further energy can be absorbed by the *Q* spin levels no matter how intense or prolonged the irradiation. Thus, as is explained (Edmonds, 1977), the sensitivity of DRLC depends upon

1. How much polarization is passed to the *Q* spins.
2. The number of *Q* spins relative to the number of *P* spins.

In practice a Q spin to P spin number ratio of about 1 to 20 is as low as can be tolerated.

In order to invent much higher sensitivity methods, mechanisms for the continuous transfer of energy between Q and P spins during the irradiation phase must be devised. In this way the same few Q spins may continuously pass energy to the P spins when the Q spins are irradiated and the cumulative total of the energy transferred is limited only by the duration of the irradiation phase. This in turn is usually limited by the zero-field spin-lattice relaxation time of the P spins, $T_{1P}(0)$.

III DOUBLE RESONANCE WITH CONTINUOUS COUPLING

Double resonance with continuous coupling (DRCC) is by far the simplest very high sensitivity NQDR method so that we describe it first. It was first employed by Edmonds and Mailer (1977) and it is applicable to low frequency (<500 kHz) spectra. It is particularly suited to the detection of the NQR spectra of the deuteron and will even do so in suitable specimens (Edmonds and Mailer, 1978) with the deuteron in its natural abundance of 0.016%.

The DRCC experiment is identical to the DRLC experiment we have described except that during the irradiation phase the Q spins are continuously coupled to the P spins rather than the two spin assemblies being isolated as in DRLC. The coupling mechanism employed is best understood by reference to a particular example illustrated in ***Figure 4***. The dots show the effect of direct absorption by the protons (P spins) during a DRLC experiment performed on formic acid at 77 K. The spin-spin coupled protons (the proton bath) are seen to have energies that extend upward to frequencies as high as 80 kHz. The two deuteron NQR spectral lines for HCOOD are shown as two arrows around 120 kHz. The separation in frequency between the high frequency tail of the proton bath and deuteron quadrupole energy splittings ensures no coupling between Q and P spins in zero applied magnetic field. However, it is well known (Wright, 1949; Anderson, 1962) that if a small steady magnetic field is applied, the frequencies that characterize the proton bath will increase. For formic acid it was shown (Edmonds and

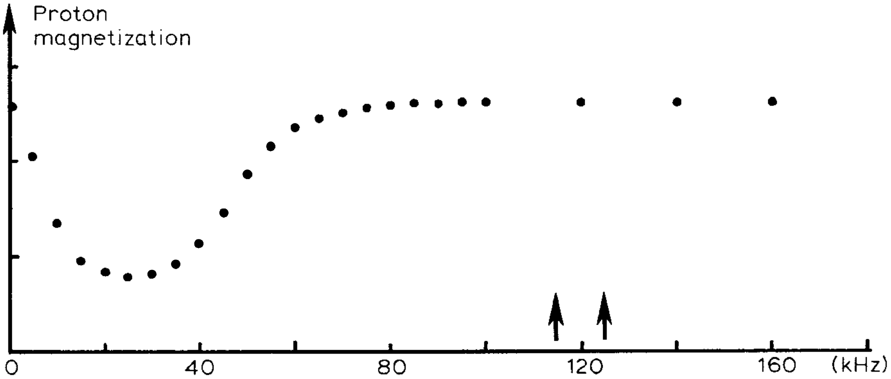


FIG. 4. The dipolar coupled proton bath absorption measured in a DRLC experiment performed on formic acid at 77 K. The cycle time was 60 s, the irradiation time was 4 s and the rotating amplitude of the applied irradiation field B_1 was 10^{-6} T. The positions of the deuteron NQR lines of HCOOD dilute in HCOOH are shown by arrows.

Mailer, 1977) that an applied field of 5×10^{-4} T (5 gauss) is sufficient to cause overlap of the deuteron NQR frequencies by the high frequency tail of the proton bath and thus ensure *PQ* coupling.

In zero applied field an attempt to detect the deuteron NQR spectra of HCOOH enriched with HCOOD is characteristic of DRLC. The intensity of the detected spectral lines is small and increasing the irradiation power leads to no increase in intensity but merely in line broadening. If the same experiment is repeated with a steady field of 5×10^{-4} T applied during irradiation, the detected spectral lines are much more intense and grow if the irradiation amplitude or duration are increased. It is now found that the spectrum can be measured with an arbitrarily small (or zero) isotopic enrichment of HCOOH provided the *P* spin zero field spin lattice relaxation time $T_{1P}(0)$ allows a sufficiently prolonged irradiation time. This is now characteristic of DRCC. The steady field applied is chosen to be sufficiently large to allow adequate *PQ* spin coupling but not so large that direct *P* spin absorption from the irradiation swamps the absorption through the *Q* spins. For nuclei such as deuterons with small (<500 kHz) quadrupole splittings, even fields of order 5×10^{-4} T are capable of removing quenching effects sufficiently for fast *PQ* coupling, which is why DRCC works well for integer spin nuclei like the deuteron.

An alternate method (Edmonds and Mailer, 1977) of performing DRCC is to arrange that during the irradiation phase the specimen is alternately irradiated in zero applied steady field and then subject to the steady field while the irradiation is switched off. This method has the added advantages that no line broadening occurs due to detection of the NQR while a steady field is applied and also that direct absorption by the *P* spins is avoided completely. The alternating method of DRCC is like DRLC with multiple level crossing before final detection of the cumulative effect on the *P* spin temperature. The steady field that is repetitively applied may, however, be much smaller than resonant level crossing would demand.

Finally, many apparently DRLC experiments performed upon specimens such as ice, are in fact DRCC experiments. In ice the proton-proton separation is so small that the *P* spin bath overlaps the deuteron splitting with no applied field and this accounts for the very high sensitivities attained (Edmonds and Mailer, 1977). In fact for nearly all deuteron spectra the lowest frequency ν_0 NQR spectral line lies at a frequency within those spanned by the *P* bath which has a marked effect upon the relative sensitivities with which the other lines in the deuteron spectrum are detected.

An example of the NQR spectrum of deuterium obtained by DRLC enhanced by DRCC is shown in *Figure 5*. This was obtained by Davidson *et al.* (1979) from a frozen liquid mixture of water and pyridine (C_5H_5N) in the molecular ratio of 4:1. The water was isotopically enriched to 10% D_2O. The displayed spectrum takes the form of a chart recorder trace which is the analogue output of an automated NQDR spectrometer. Each box-like excursion of the chart recorder pen measures the amplitude of the free induction decay of the protons at the end of an experimental cycle. A single frequency of irradiation is applied to the sample while it is momentarily in zero applied steady magnetic field during each cycle and, in the spectrum displayed, this frequency was stepped from 127 kHz to 190 kHz in steps of 250 Hz.

By varying the ratio of water to pyridine and measuring the NQR spectra it was possible to deduce that a complex of 4 water molecules and 1 pyridine molecule is formed when a mixture of the two liquids is cooled. The slight reduction in the off-resonance signal at the lowest frequencies results from direct absorption by the proton bath and indicated that the deuterium NQR detection sensitivity is enhanced by DRCC.

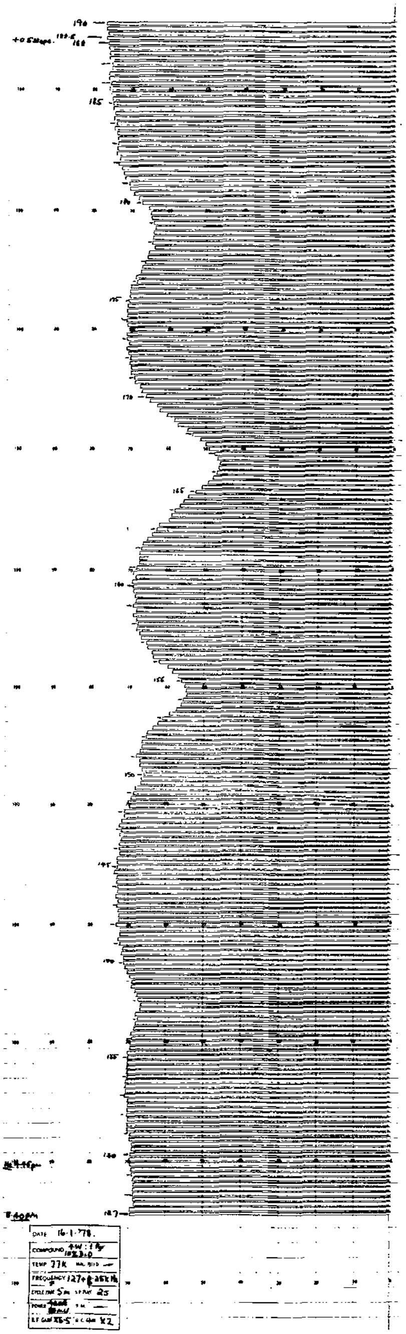


FIG. 5. The analogue output of an automated NQDR spectrometer displaying the deuterium NQR spectrum of a frozen mixture of water, 10% enriched in deuterium, and normal pyridine. The frequency of irradiation was stepped from 127 kHz to 190 kHz in steps of 250 Hz. The spectrum was measured at 77 K, the cycle time was 300 S, the irradiation time was 2 s and the linear peak to peak amplitude of the irradiation field was 16×10^{-6} T.

IV DOUBLE RESONANCE IN THE LABORATORY FRAME AND DOUBLE RESONANCE BY THE SOLID STATE EFFECT

Double resonance in the laboratory frame (DRLF) and double resonance by the solid state effect (DRSS) use the same *PQ* spin coupling mechanism we have discussed in sections IB and IC. DRLF was first applied to detect NQR in polycrystalline solids by Redfield (1963) and by Slusher and Hahn (1968) while DRSS has been used to this end by Minier (1969), Seliger *et al.* (1975) and Poplett and Smith (1979). Experiments which detect proton satellite lines flanking quadrupole spectral lines are also properly included in this category (Edmonds *et al.*, 1973). So too is double transition quadrupole resonance (Edmonds and White, 1978), useful in the assignment of NQR spectra, in which two magnetically coupled quadrupole nuclei undergo simultaneous transitions to absorb a single input photon.

Once again the experiment is exactly as DRLC except for the form of irradiation. At the start of the irradiation phase the specimen resides in zero applied field with the *P* spins adiabatically demagnetized to a low spin temperature. For definiteness and to use the calculation of section ID we will consider a set of $I = 3/2$ nuclei situated in identical axially symmetric crystalline electric fields ($\eta = 0$) for the supposedly rare *Q* spins. We perform DRLF and apply a radiofrequency magnetic field $2B_1 \cos\omega t$ to such a *Q* spin perpendicular to the axis of symmetry of the electric field gradient and with $\omega = \omega_Q$. Following sections IB, IC and ID we expect strong *PQ* coupling provided that $\sqrt{3}\,\omega_1 \approx \omega_P$, so that some of the energy gained by the *Q* spins from the presence of B_1 is transferred to the cold *P* spins. The coupling may be explained by stating that the effective quadrupole splitting of the *Q* spin energy levels in the rotating frame (*see Figure 3*) is equal to a characteristic *P* spin splitting $\hbar\omega_P$, due to spin-spin coupling in the *P* spin bath. In fact the expected energy transfer does occur but stops after a very short time and no appreciable further transfer occurs no matter how prolonged the irradiation. To understand this we must invoke the concept of a spin temperature in the rotating frame as briefly discussed in section ID. This is complicated in detail and we will present a simplified picture sufficient for the design of experiments using DRLF and DRSS. For a more complete treatment the original papers and the textbooks quoted in section IA should be consulted.

Before B_1 is applied the magnetization of each *Q* spin is directed parallel or antiparallel to the *z* axis. When B_1 is suddenly applied the magnetization of each *Q* spin is perpendicular to it, resulting in a rotating frame Zeeman energy $\boldsymbol{M}_Q \cdot \boldsymbol{B}_1 = 0$. As these hot *Q* spins are coupled to the cold *P* spins, energy flows from the *Q* spins to the *P* spins but stops when the *Q* spins come to the same spin temperature in their rotating frame as the *P* spin bath has in the laboratory frame. The *Q* spin state now corresponds to an appreciable *Q* spin magnetization pointing in the direction of B_1 so that $-(\boldsymbol{M}'_Q \cdot \boldsymbol{B}_1) < 0$. If the number of *Q* spins relative to the number of *P* spins is small then the temperature rise of the *P* spin bath resultant from this single transient coupling is very small. For the technique to be effective in indicating a *Q* spin resonance when $\omega \sim \omega_Q$, methods of repetitively heating the *P* bath via the *Q* spins must be found. To date four different methods have been used.

1. In the first method used by Hartmann and Hahn (1962), the radio frequency applied field $2B_1 \cos\omega t$ is periodically and abruptly phase shifted by 180° at intervals τ comparable to the *PQ* heat transfer time τ_{PQ}. This has the effect of reversing the direction of B_1 in the rotating frame. The *Q* spins having been cooled by contact with the *P* spins to have a Zeeman energy $-\boldsymbol{M}'_Q \cdot \boldsymbol{B}_1$ in the rotating frame, have this energy

abruptly increased to $+\boldsymbol{M}'_Q \cdot \boldsymbol{B}_1$ by a phase shift. Once again the Q spins cool by transferring energy to the P spins only to be reheated by the next phase shift.

2. The second technique (Redfield, 1963) involves irradiation simultaneously by two radiofrequency fields $2B_1 \cos(\omega_Q + \delta\omega)t$ and $2B_1 \cos(\omega_Q - \delta\omega)t$. In a frame rotating at ω_Q these are two contra-rotating fields rotating at frequencies $+\delta\omega$ and $-\delta\omega$. In the frame rotating at ω_Q they may be summed to produce a linear field which oscillates in amplitude from positive to negative with a period $(2\pi/\delta\omega)$. This is equvialent to a periodic harmonic phase shift of the B_1 field effective in the rotating frame rather than the periodic square wave modulation of phase in the first method.
3. In the third method the applied field is frequency modulated at frequency ω_M with frequency deviation $\Delta\omega$ so that it may be written

$$2B_1 \cos(\omega_Q + \Delta\omega \cos \omega_M t)t = 2B_1 \cos[\omega_Q t + (\Delta\omega/\omega_M) \sin \omega_M t]$$

Regarded as a perturbation it may be shown (Slusher and Hahn, 1968) that the modulation induces $\Delta I_z = 0$ transitions between the energy levels of the Q spins in the rotating frame (*see Figure 3*) provided that $\omega_M = \sqrt{3}\omega_1$. The modulation may be considered as producing an extra effective field of amplitude proportional to $\Delta\omega$ which oscillates at frequency ω_M along the z axis. This induces transitions of the Q spins from parallel to B_1 to antiparallel to B_1 in the rotating frame, thus heating them. It is seen as an ingenious method for rotary saturation (Redfield, 1955) in which an effective field is caused to act along the z axis in the rotating frame but not in the laboratory frame. Any real field of frequency ω_M applied along the z-axis in the laboratory frame would of course result in large direct absorption by the P spins as $\omega_M \sim \sqrt{3}\omega_1 \sim \omega_P$ which would destroy the detection of NQR. This technique has the additional advantage that if the rotating amplitude of B_1 is known, then γ_Q is measurable through $\omega_M = |\gamma_Q B_1|$ for maximum heating. In fact if ω_M is too large two NQR lines may be observed (Slusher and Hahn, 1968) each separated from the true NQR line position by $\Delta\omega$ so that

$$\omega_1 < \omega_M = (\omega_1^2 + \Delta\omega^2)^{1/2} = \omega_E$$

which is understood as the resonant Q spin magnetization precessing about B_E rather than B_1 in the rotating frame.
4. The fourth heating technique is an exception to the rule that long spin-lattice relaxation times are advantageous for NQDR and relies upon a short Q spin relaxation time T_{1Q}. This was first employed for quadrupole nuclei by Goldman and Landesman (1963), not as a method of detecting NQR, but as a method of producing polarized protons using a large quadrupole splitting. They show that under the influence of T_{1Q} an equilibrium temperature T_Q is established in the rotating frame given by

$$\frac{T_L}{T_Q} \approx \frac{\omega_Q \Delta\omega}{\Delta\omega^2 + \omega_1^2}$$

where T_L is the lattice temperature. We have simplified their expression by assuming B_1 much greater than any local fields acting. $(1/T_Q)$ is zero far from resonance and also exactly on resonance, positive when $\Delta\omega > 0$ and negative when $\Delta\omega < 0$. The role of T_{1Q} may be thought of as scattering spins out of their coherent state in the rotating frame to alignment along the z-axis. For DRLF with $\Delta\omega = 0$ this is from along B_1 to perpendicular to B_1 or from a negative Zeeman energy to zero Zeeman energy, $\boldsymbol{M}_Q \cdot \boldsymbol{B}_1 = 0$ or $T_Q = \infty$. This is seen to be effective in continually heating the Q spins. Were ω_Q produced by the Zeeman interaction then T_{1Q} preferentially scatters spins along the positive z-axis which corresponds to a positive projection on B_E ($T_Q > 0$) for $\Delta\omega > 0$ and a negative projection ($T_Q < 0$) for $\Delta\omega < 0$. This model is useful for illustrating the Goldman and Landesman (1963) result for DRSS with $\Delta\omega \neq 0$ for Zeeman split Q nuclei. For quadrupole split Q nuclei a model may be constructed with two contra-rotating reference frames but it is too complicated to give much insight. Note that this technique can produce either cooling $\Delta\omega > 0$ or heating $\Delta\omega < 0$ of the P spins, which can lead to complicated line-shapes. Its main defect relative to the first three heating techniques, relying on applied radio frequency fields, is its lack of flexibility in that $(1/T_{1Q})$ may only be controlled by variation of the lattice temperature. Against this, as an equilibrium is reached with the near infinite lattice heat bath, there is no need for a polarization phase and the experiment may start in zero field and involve only one sample transit.

That DRLF is most effective in detecting the NQR of naturally abundant ^{17}O was first demonstrated by Hsieh *et al.* (1972). In *Figure 6* taken from their paper, we show the NQR lines obtained from naturally abundant ^{17}O in 2,5-dichloro-*p*-benzoquinone. The high sensitivity obtained using powdered specimens proved for the first time the usefulness and practicality of double nuclear resonance methods in the detection of NQR spectra.

If DRLF has a major drawback it is that the applied field B_1 is used both to heat the Q spins and to ensure good PQ coupling so that

$$\omega_1 = -\gamma_Q B_1 \sim \omega_P = -\gamma_P B_L$$

Although it is shown (Lurie and Slichter, 1964) that smaller values of B_1 do lead to appreciable coupling, being resonant with smaller P bath energy splittings, the efficiency of heat transfer does drop quite sharply with B_1. Even for ^{17}O a rotating B_1 of amplitude 20 to 50 $\times$ 10^{-4} T (20 to 50 gauss) may be required, depending upon B_L. This corresponds to an applied field with linear peak to peak amplitude of 80–200 $\times$ 10^{-4} T which is experimentally inconvenient and which may lead to appreciable NQR line broadening. For nuclei such as ^{25}Mg, ^{33}S, ^{41}K and ^{43}Ca with small magnetogyric ratios the required B_1 is even larger.

V DOUBLE RESONANCE WITH COUPLED MULTIPLETS

Double resonance with coupled multiplets (DRCM) takes advantage of the energy splitting that occurs in quadrupole energy levels due to the proximity of a neighbouring nucleus or set of nuclei. It was first described by Brosnan and Edmonds (1980a). In *Figure 7a* two degenerate doublets of a half-integer nucleus with a quadrupole moment, split in energy by $\hbar\omega_Q$ due to the presence of an electric field gradient are shown. In *Figure 7b* the effect of magnetic interaction with a neighbouring $S = \frac{1}{2}$ nucleus to produce two multiplets is shown. Because of their small size and large magnetic moment, protons are particularly effective in this role and may produce overall multiplet splittings of 100 kHz or more. If the energy splittings within a multiplet are comparable with P spin bath splittings ω_P then, given magnetic dipole coupling between the two spin system and the P spin bath, the populations of levels within a given multiplet will correspond to equilibrium at the P spin bath temperature T_P. The populations of energy levels are represented by their length in *Figure 7b*. As $\hbar\omega_Q$ is assumed much larger than any P spin bath energy splitting, the bath is quite incapable of causing transitions between one multiplet and another. On the other hand transitions between one multiplet and another are easily induced by applying a small radio frequency field B_1 at

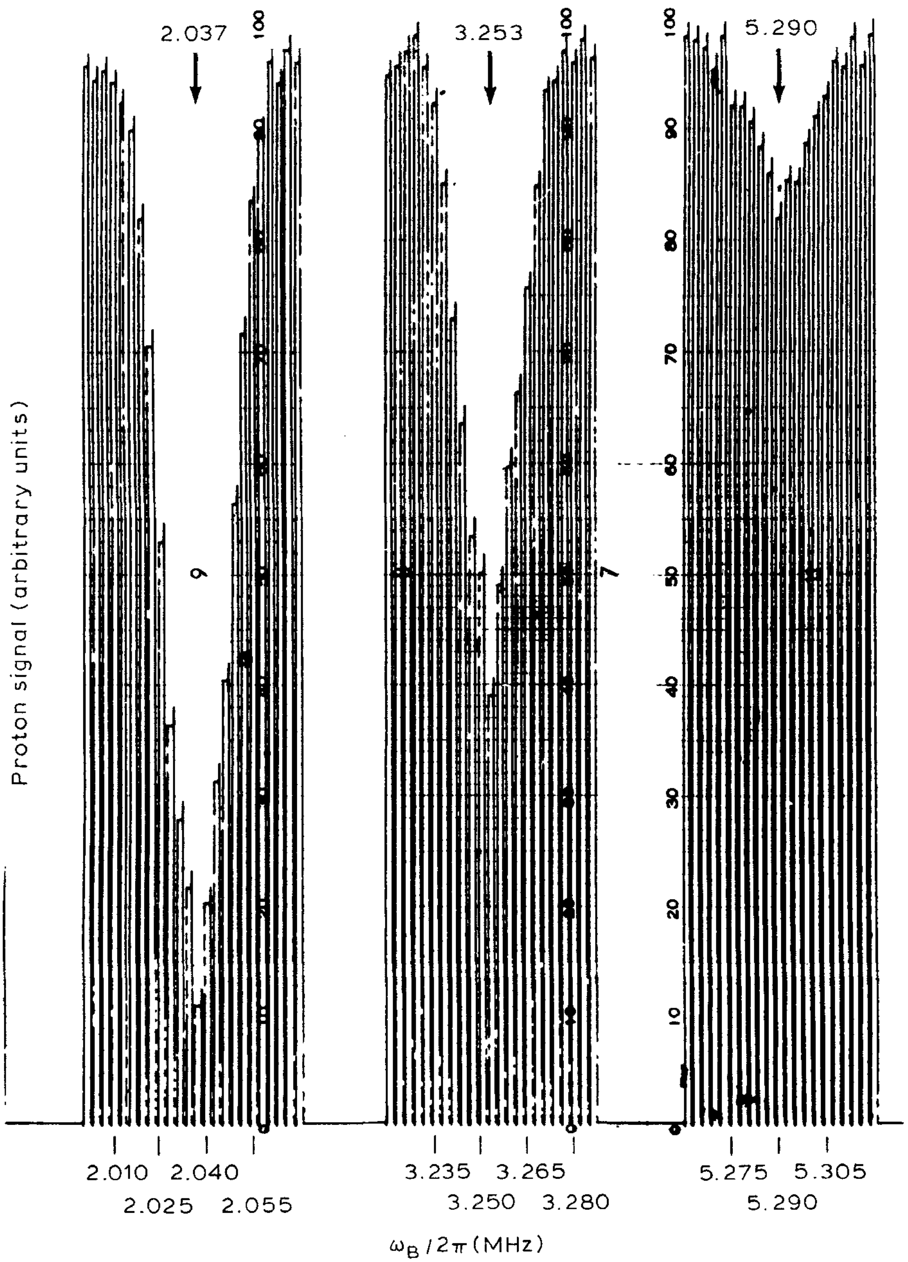


FIG. 6. From left to right are displayed the 3/2 ↔ 1/2, 5/2 ↔ 3/2 and 5/2 ↔ 1/2 NQR spectral lines of ^{17}O naturally abundant in 2,5-dichloro-*p*-benzoquinone. The spectra were measured at 77 K and the irradiation frequency was advanced between cycles by 3 kHz.

frequencies in the vicinity of ω_Q. *Figure 7c* shows the effect we would expect to result from the saturation of a single allowed inter-multiplet transition. The two energy levels connected by the applied radiation have equal populations (saturation) but the populations within each multiplet are still characterized by equilibrium at a spin

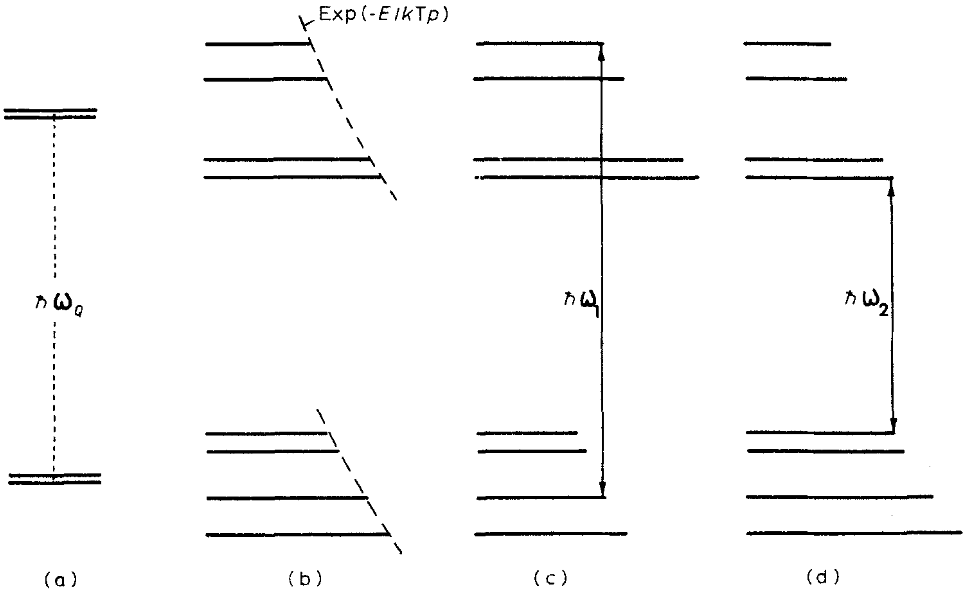


FIG. 7. (a) A sketch of two degenerate doublets of a half-integer ($I > \frac{1}{2}$) spin nucleus in an electric field gradient. (b) Shows the formation of two multiplets due to interaction with a neighbouring $S = \frac{1}{2}$ nucleus. The energy level populations within the multiplets resultant from their magnetic interaction with the P spin bath at temperature T_p are indicated by the lengths of the lines representing energy levels. (c) and (d) show the effects upon the level populations of saturating each of two different allowed intermultiplet transitions.

temperature T_p. The required adjustment of populations of levels within a multiplet is brought about by thermal contact with the P spin bath. If the number of Q spins is small very few intermultiplet transitions need occur before saturation occurs. After saturation no further intermultiplet transitions can occur. However, subsequent saturation at a second allowed intermultiplet transition results in a different saturation condition as shown in *Figure 7d*, requiring another interchange of energy with the P spin bath. It is easily shown (Brosnan and Edmonds, 1980a) that a sequential pair of saturations necessarily heats the P spin bath (provided $T_p > 0$) and that the energy transferred is proportional to

$$N_Q \hbar^2(\omega_1 - \omega_2)^2/kT_p$$

where N_Q is the number of Q spins and ω_1 and ω_2 are the two saturating irradiation frequencies.

Consider now the case in which the specimen is irradiated simultaneously by two radio frequency magnetic fields of frequencies ω_1 and ω_2. In the usual high temperature approximation the population difference between any energy level in the lower multiplet and the corresponding level in the upper multiplet separated from it by an energy $\hbar\omega_1$ may be shown (Brosnan and Edmonds, 1981a) to be constant and to be given by

$$\Delta = \frac{N_Q}{(N_o + M_o)}\left(\frac{P_2}{P_1 + P_2}\right)\left(\frac{\hbar\omega_1 - \hbar\omega_2}{kT_p}\right)$$

N_Q is the number of Q spins, N_o and M_o are the total degeneracies of the lower and upper multiplets and P_1 and P_2 are the total transition probabilities per unit population difference induced between the two multiplets by the irradiation at ω_1 and ω_2 respectively. If $\omega_1 > \omega_2$ then Δ is positive ($T_p > 0$) and ω_1 induces a net transition rate from lower to upper multiplet, while ω_2 induces a net transition rate from upper to lower multiplet. The Q spins are thus caused by the two irradiation fields to cycle between the two multiplets each time passing heat to the P spin bath. The rate of energy transfer is given by

$$R = \frac{N_Q}{(N_o + M_o)} \left(\frac{P_1 P_2}{P_1 + P_2}\right)\left(\frac{(\hbar\omega_1 - \hbar\omega_2)^2}{kT}\right)$$

which is independent of the sign of $(\hbar\omega_1 - \hbar\omega_2)$.

An interesting effect is observed if T_{1Q}, the spin-lattice relaxation time of the Q spins in zero applied steady magnetic field, is short. In these circumstances it is possible to observe the *NQR* of naturally abundant ^{17}O using only a single irradiation to scan the spectrum. The quadrupole relaxation takes the place of the second irradiation to ensure that the Q spins cycle between the two multiplets so that DRCM is observed (Brosnan and Edmonds, 1981a).

Assuming that the magnetic dipole coupling between the spin pair and the P spin bath is comparable to that found in most organic compounds, DRCM is much more efficient (Brosnan and Edmonds, 1980a) than DRLF in heat transfer for small values of the B_1, the applied radiofrequency field amplitude. This is because in DRLF the size of the photon transferred, $\hbar\omega_1$, depends on B_1 (*see Figure 3*) and is such that $\omega_1 \sim -\gamma_Q B_1$ whereas in DRCM the size of the photon transferred $\hbar(\omega_1 - \omega_2)$ depends upon the interaction of the Q spin with its neighbour and $\hbar(\omega_1 - \omega_2)$ may be very much bigger than $|\gamma_Q B_1|$.

To detect NQR by DRCM an experiment like DRLC is performed except that during the irradiation phase the specimen is sequentially or simultaneously irradiated at two frequencies ω_1 and ω_2. A preliminary scan through the spectrum is usually performed with two frequencies $\omega + \omega_M$ and $\omega - \omega_M$ applied simultaneously by multiplying the stepped synthesiser frequency ω with a modulation frequency ω_M in a double balanced modulator. Provided the two frequencies overlap two allowed intermultiplet transitions a large absorption is detected in the vicinity of the quadrupole resonance frequency. To detect (Brosnan and Edmonds, 1980a and 1981a) the full fine structure, ω_1 is fixed in frequency to irradiate one allowed transition, while ω_2 is stepped between DRLC cycles to sweep the spectrum. Because of the factor $P_1P_2/(P_1 + P_2)$ that occurs in the expression for the energy transfer rate R the best resolution of the fine structure is obtained (Brosnan and Edmonds, 1981a) with $P_1 \gg P_2$. This condition may be realized by adjusting the amplitude of irradiation at ω_1 to be sufficiently much larger than the amplitude of irradiation at ω_2. In any NQR experiment in which two frequencies ω_1 and ω_2 are applied simultaneously one must check that amplifier distortion does not generate significant power at $(\omega_1 - \omega_2)$ as this is directly absorbed by the P spin bath. In DRCM with ω_1 fixed and ω_2 swept it is wise to verify the spectrum by sequential rather than simultaneous irradiation to eliminate any direct mixing of ω_1 and ω_2.

In *Figure 8* we display the unpublished results of Davidson and Edmonds showing one multiplet in the ^{17}O NQR spectrum of naturally abundant H_2SO_4 at 77 K. The long arrows indicate the fixed frequency ω_1 employed in each scan. Each spectrum is the result of a single scan through the spectrum with no averaging. The thick arrows at the bottom of *Figure 8* indicate the deduced main spectral lines that compose the multiplet.

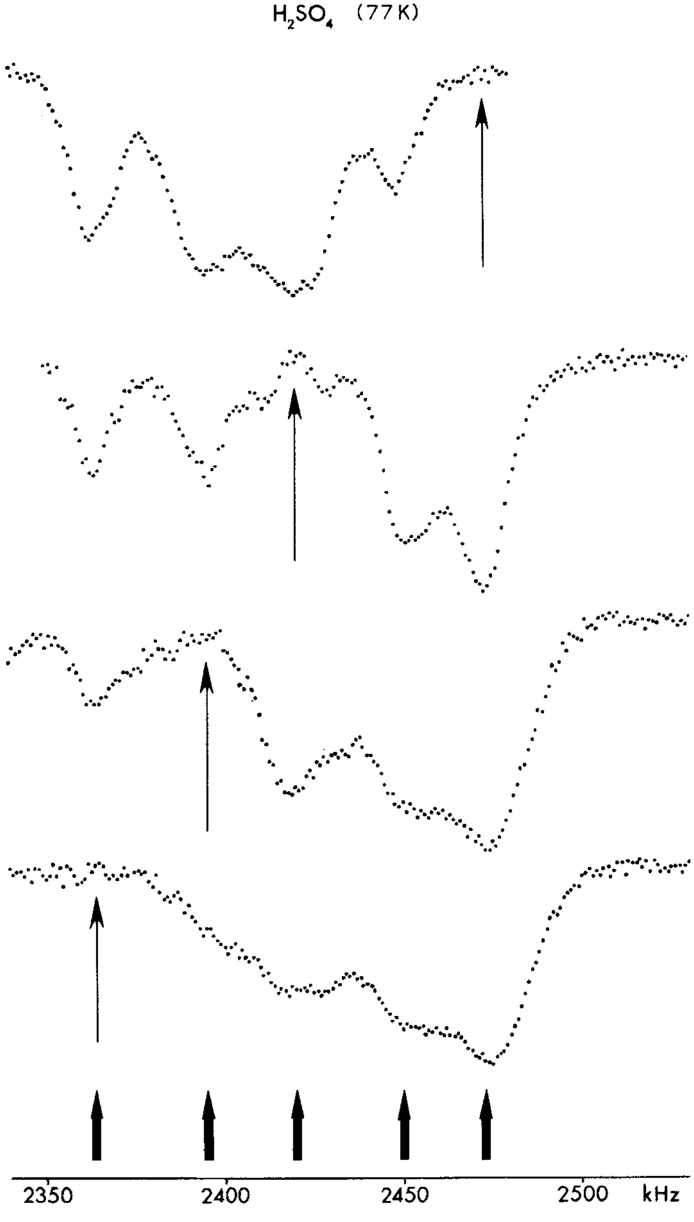


FIG. 8. Fine structure on one of the spectral lines using DRCM on ^{17}O naturally abundant in H_2SO_4 at 77 K. Each spectrum was obtained by simultaneously irradiating the specimen at a fixed frequency ω_1 indicated under each spectrum by a long arrow and at a second frequency ω_2 which was stepped between experimental cycles to scan the spectrum. The cycle time was 300 s, the irradiation time was 20 s and each of the applied radio-frequency fields had a rotating amplitude of 10^{-4} T. The thick arrows indicate the main components of the fine structure measured in this manner.

Note that at the low irradiation power used there is no evidence of absorption when $\omega_2 \approx \omega_1$ such as would result from DRLF. To date published data from DRCM are only available for ^{17}O naturally abundant in COH (Brosnan and Edmonds, 1980a and 1981a; Brosnan *et al.*, 1981; Poplett and Smith, 1981), POH (Brosnan and Edmonds, 1981b), H_2O (Brosnan and Edmonds, 1980b), H_3O^+ (Poplett, 1981) and C=O (Brosnan *et al.*, 1981) groups but in these cases well resolved fine structure is detected. Should such fine structure be measurable for other nuclei in other molecular groups, the power of NQR as a structural tool will increase markedly.

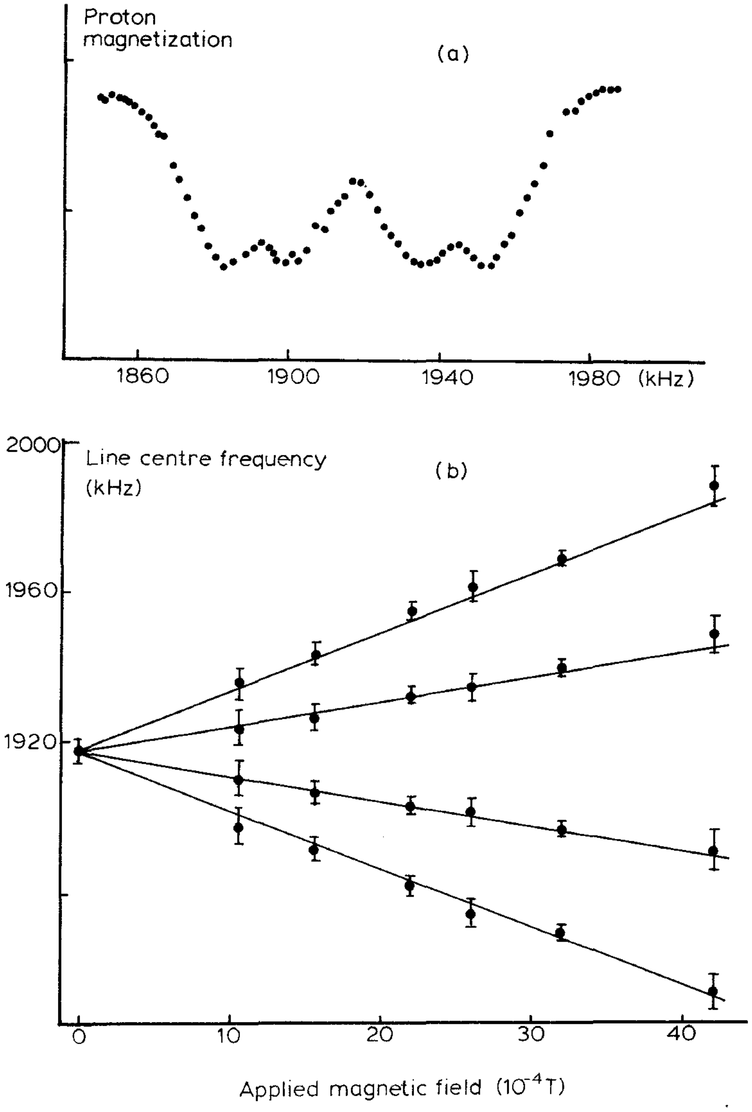


FIG. 9. (a) The NQR spectrum of ^{23}Na in NaOH at 77 K with a steady magnetic field of 23×10^{-4} T applied parallel to the radio frequency field of linear peak to peak amplitude of 10^{-5} T. The cycle time was 300 and the irradiation time was 3 s. (b) A plot of multiplet component frequency as a function of steady applied field.

VI CONCLUSIONS

NQR has a considerable advantage over nuclear magnetic resonance (NMR) in that high resolution spectra displaying fine structure may be obtained from powdered solids and frozen liquids which possess no long range order. This is because the field which produces the energy splittings detected is the electric field gradient built into the molecule studied in NQR rather than the externally imposed magnetic field, as in NMR. Thus NQR is one of the few truly microscopic structural analytical techniques.

The major reason that NQR was not much used in the past was the experimental difficulty of obtaining the spectra of the lighter elements of most interest chemically and biologically. This review is an attempt to demonstrate that the experimental hurdle has been largely surmounted. Furthermore the equipment required is simple, easily automated and cheap by today's standards. The fixed magnetic field can be provided by a permanent iron magnet of no great homogeneity and the pulsed NMR spectrometer needs only a fixed frequency and the ability to apply one radio-frequency pulse to excite the free induction decay.

The new techniques allow two classes of experiment to be performed.

1. The first extends to lighter elements the range of NQR experiments previously possible only for heavier elements such as ^{35}Cl.
2. The second introduces entirely new experiments only possible because of the very high sensitivities now achieved.

An example of the first class is the study of Zeeman splittings of NQR spectral lines produced by the application of small steady magnetic fields during irradiation. In *Figure 9a* the splitting of a ^{23}Na NQR spectral line in powdered NaOH at 77 K when 23×10^{-4} T is applied parallel to the radio frequency field direction is displayed (Edmonds and Mailer, 1979). In *Figure 9b* the splitting of the four component multiplet as a function of the steady field applied is shown. This allows (Morino and Toyama, 1961; Brooker and Creel, 1974) both the quadrupole coupling constant and the anisotropy constant to be determined from the single NQR line of a spin 3/2 nucleus.

Examples of the entirely new types of experiment now possible are those that involve magnetic dipolar coupling between adjacent light nuclei leading to extra spectral lines. Poplett (1980) has recently reviewed these effects. One instance is double transition quadrupole resonance, which is the detection of the absorption of a single input radiofrequency photon by the simultaneous transitions of two magnetically coupled quadrupolar nuclei (Edmonds and White, 1978). As only tightly coupled and therefore close nuclei can so respond, the effect is of considerable use in the assignment of spectral lines to particular nuclei. *Figure 10* shows the spectrum of such double transitions (Davidson *et al.*, 1979) within a frozen deuterated water and pyridine mixture like that whose simple single transition NQR spectrum is shown in *Figure 5*. The heavy, light and broken arrows show the predicted frequencies of the most intense, less intense and weakest double transition spectral lines based on a particular assumed assignment of the single transition spectrum.

A second example of the novel application of NQR is the detection of proton motion in a para-electric from a study of the fine structure in the NQR spectrum of ^{17}O revealed by DRCM. In KH_2PO_4 the proton in one oxygen to oxygen hydrogen bond is static at temperatures below T_c, the ferro-electric transition temperature, so that a conventional $O{-}H\cdots O$ bond exists. At temperatures above T_c the proton hops rapidly between two symmetrical positions (Slater, 1941) so that a $O \cdots H \leftrightarrow H \cdots O$ bond is formed. In

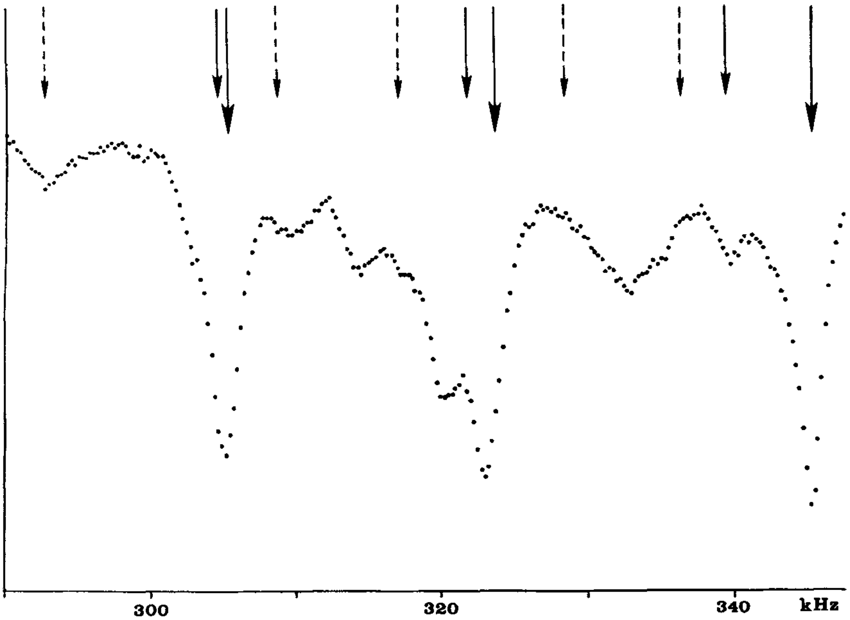


FIG. 10. The double transition quadrupole resonance spectrum of deuterium for a complex of 4 D_2O molecules to 1 pyridine molecule formed by freezing the liquid mixture to 77 K. The cycle time was 300 s the irradiation time was 20 s and the linear peak to peak amplitude of the irradiation field was 5.2×10^{-4} T. The arrows show the predicted line positions based upon a particular assignment of the single transition NQR spectrum shown in *Figure 5*.

Figure 11a a single NQR spectral line of naturally abundant ^{17}O measured in a O—H bond is shown as dots (Brosnan and Edmonds, 1981b). In *Figure 11b* the partially collapsed proton fine structure of an ^{17}O NQR line observed at $T > T_c$ is shown. The crosses give the prediction of a theoretical model to determine O—H distances together with the quadrupole coupling constant, including its sign which can not normally be determined by NQR in powders. The analysis confirms that the mobile proton does occupy a double well potential and in the paraelectric state it hops between the two wells spending negligible time in transit. The direction of the electric field gradient principal axes are determined for ^{17}O and are shown to tip by 5 to 10 degrees when the proton jumps.

Turning finally to the choice between the various NQDR techniques described in this review, they can be seen to be complementary rather than competitive. If the quadrupole nuclei are sufficiently abundant then DRLC should be employed as it is simple and applicable to integer and half-integer spin nuclei. If the quadrupole nuclei are rare and $\nu_Q < 500$ kHz then DRCC has no serious competitor, particularly for the deuteron. If the quadrupole frequency is higher and there is appreciable multiplet splitting due to near-neighbour interaction then DRCM is very effective and allows the fine structure to be measured. If there is inadequate or zero multiplet splitting and the quadrupole nucleus has half-integer spin and a sufficiently large γ_Q then DRLF is most effective. If T_{1Q} is short then this relaxation may substitute for one of the radio-frequency irradiations in some versions of DRLF, DRSS or indeed DRCM.

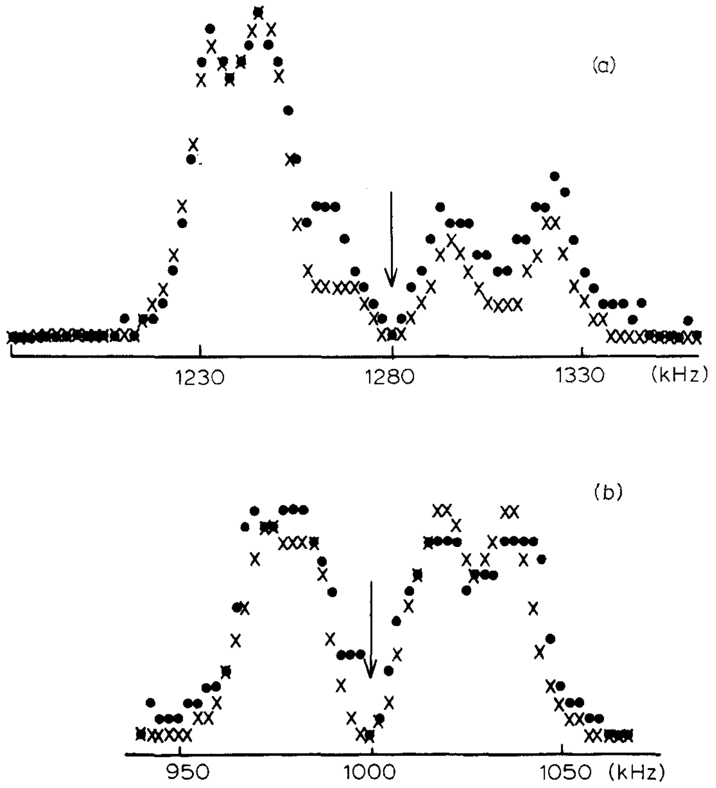


FIG. 11. (a) The dots give the measured DRCM spectrum of one NQR line of naturally abundant ^{17}O in a P—O—H bond in KH_2PO_4 at 77 K. (b) The dots give the spectrum of another ^{17}O NQR line at 160 K. In both cases the cycle time was 200 s the irradiation time was 10 s and the fixed frequency of the second irradiation is indicated by the arrow. The crosses show the best theoretical fit to the spectra.

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