

## NMR double-quantum spin decoupling in solids

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The problem of spin-decoupling spin  $I = 1$  nuclear with large quadrupolar splittings  $\omega_Q$  (e.g. deuterium) from dilute  $S$  spins via double-quantum transitions is dealt with. The normal two-spin-1/2 single-quantum decoupling problem ( $I = 1/2, S = 1/2$ ) is first dealt with as a reminder of the coherent averaging approach and to understand the dependence of the  $S$ -resonance linewidth on the  $I$  rf field intensity ( $\omega_1$ ) and resonance offset ( $\Delta\omega$ ). The double-quantum problem ( $I = 1, S = 1/2$ ) is then treated analogously by introducing fictitious spin-1/2 operators for the  $I$  double-quantum transition. The decoupling condition is found to be very sensitive to the spin- $I$  resonance condition and to go as  $\sim 1/\omega_1^4$  with the spin- $I$  rf field intensity at resonance in the double-quantum regime ( $\omega_1 \ll \omega_Q$ ). Experimental examples on heavy ice, dimethylsulfoxide- $d_6$  and benzene- $d_6$  are presented verifying the quantitative theoretical predictions. Extensions to higher-order multiple-quantum effects for spin  $I > 1$  and for several coupled spin-1/2 nuclei are discussed.

### I. INTRODUCTION

The application of heteronuclear spin decoupling has made an important contribution to solid-state NMR. In its most common form we have a sample with abundant spins  $I$  and dilute spins  $S$ . By strongly irradiating the  $I$  spins with a radio-frequency field near their Larmor frequency we can spin decouple them from the  $S$  spins<sup>1</sup> allowing the observation of a high-resolution spectrum. Figure 1 depicts this approach in simple schematic terms, showing the  $S$  free-induction decay while continuously irradiating the  $I$  spins. This has been applied to NMR of <sup>13</sup>C and other nuclei in solids.<sup>2</sup>

A potentially useful candidate for such experiments is the case deuterium ( $I$ ), proton ( $S$ ). By spin-decoupling the deuterium in a  $\approx 99\%$  deuterated sample we could directly observe a high-resolution proton spectrum. Figure 2 indicates the difficulty of such an approach. The deuterium nucleus has spin 1 and the interaction of the quadrupole moment with electric-field gradients causes a splitting of the spectrum into lines (two allowed transitions) separated by  $2\omega_Q$ , where  $\omega_Q$  denotes a quadrupolar frequency. Typically, the splitting can be high,  $\nu_Q \equiv \omega_Q/2\pi \sim 100$  kHz. Thus, it might appear that the deuterium decoupling rf field intensity must be sufficient to cover the entire quadrupolar spectrum, i.e.,

$$\omega_1 \gtrsim \omega_Q, \quad (1)$$

where  $\omega_1$  is the intensity of the rf field. The situation appears particularly acute in the case of a polycrystalline sample where all the orientations of the electric-field gradients give a continuous distribution of  $\omega_Q$ . The deuterium NMR spectrum expected for such a case is shown in Fig. 3 for an axially symmetric field gradient. Figure 4

shows an example of 99% deuterated dimethylsulfoxide (DMSO- $d_6$ ) showing the center portion of such a spectrum. The maximum splitting is  $2\nu_Q \approx 88$  kHz which makes it difficult for our decoupling transmitter to cover the full spectral range.

It was realized a few years ago by Meiboom and co-workers<sup>3</sup> in their liquid-crystal work that deuterium spin decoupling might take place via deuterium double-quantum transitions, i.e., rapid transitions between the  $m = \pm 1$  levels. Since the  $m = 0$  level does not affect the  $S$  spin this should indeed suffice. Furthermore, although this is a second-order process it is resonant for all spins (the  $m = \pm 1$  splitting is  $2\omega_Q$  independent of  $\omega_Q$  to first order) and might provide a better mechanism for decoupling than the strongly off-resonant allowed transitions. In fact, Meiboom *et al.* were able to decouple deuterium in oriented molecules in liquid-crystal solution, where  $2\omega_Q$  is a few kHz, with moderate rf fields. Very recently, we

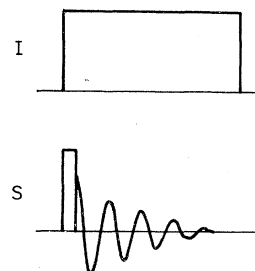


FIG. 1. Schematic description of spin decoupling. We wish to observe spins  $S$  whose resonance is broadened by interaction with spins  $I$ . Irradiation of the  $I$  spins with near-resonant rf radiation under the appropriate conditions serves to decouple them from the  $S$  spins giving a lengthened free-induction decay following the  $S$  pulse.

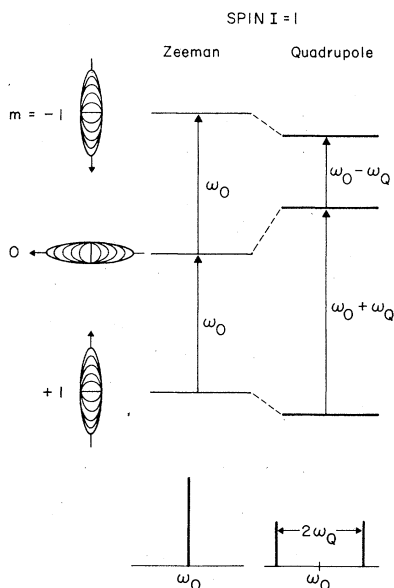


FIG. 2. Spin  $I=1$  in high magnetic field. The degenerate allowed transitions are split by the quadrupolar interaction into two lines separated by  $2\omega_Q$ . For deuterium the quadrupolar coupling parameter is typically of the order of  $\omega_Q/2\pi \sim 100$  kHz. Thus it is difficult to "cover" the allowed  $I$  transitions with practical values of  $\omega_1$ .

extended this to solids and showed that even in 99% deuterated ice where  $2\omega_Q \sim 230$  kHz a field of  $\nu_1 \equiv \omega_1/2\pi \sim 20$  kHz sufficed for spin decoupling.<sup>4</sup> Using second-order perturbation theory, we estimated that instead of (1), the criterion for the onset of spin decoupling via double-quantum transitions is actually much less stringent:

$$\omega_1 \gtrsim (\omega_Q D)^{1/2}, \quad (2)$$

where  $D$  roughly characterizes the  $I$ - $S$  dipolar coupling.

Various schemes for deuterium spin decoupling have been proposed as indicated schematically in

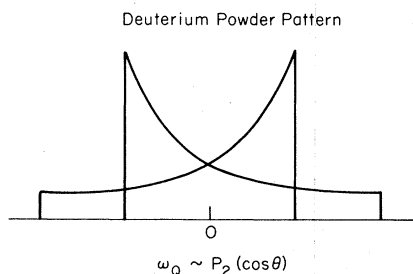


FIG. 3. Expected spectrum for polycrystalline arrangement of deuterium spins with axially symmetric electric-field-gradient tensor. For deuterium the maximum width of such a spectrum is typically of the order of  $\sim 100$  kHz.

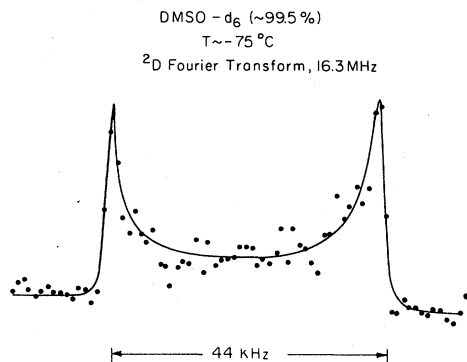


FIG. 4. Center portion of deuterium Fourier-transform NMR spectrum of solid DMSO- $d_6$ . The total width of the spectrum is 88 kHz.

Fig. 5. Except for special cases, the third approach of double-quantum decoupling appears to be the simplest and has the most promise in terms of utilization of the rf power. The purpose of the present paper is to present a more quantitative analysis and set of experiments of spin decoupling for spin- $I$ . We shall see that the result (2) is indeed borne out by a more rigorous analysis. The effects of frequency offset of the rf irradiation on the  $I$  spins are also accounted for. The approach adopted is to calculate the effects of the quadrupolar and rf irradiation fields on the  $I$ - $S$  dipolar-coupling Hamiltonian  $\mathcal{H}_{IS}$  and to find the conditions for making the effective  $\mathcal{H}_{IS}$  vanish.

In Sec. II we outline the well-known and simple problem of spin decoupling when both  $I$  and  $S$  are spins- $\frac{1}{2}$  so no quadrupolar splitting is involved.

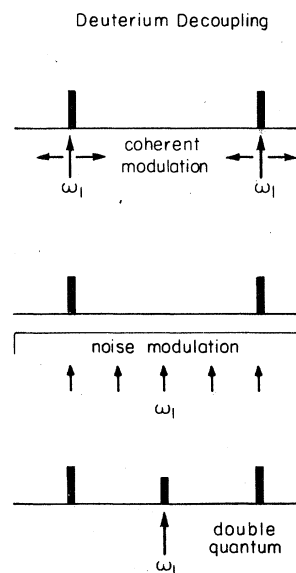


FIG. 5. Possible schemes for deuterium spin decoupling.

This serves to introduce the form of the Hamiltonian and to illustrate the approach for calculating the effective  $\mathcal{H}_{IS}$  when rf irradiation is applied to the  $I$  spins, using coherent averaging theory.<sup>5</sup> This yields the expected condition for normal single-quantum spin decoupling. The asymptotic dependence of the  $S$  linewidth on the  $I$  resonance offset and on  $\omega_1$  for large  $\omega_1$  is also estimated theoretically. In Sec. III the  $I$  spin is taken as spin-1 with quadrupolar coupling parameter  $\omega_Q$ . We introduce fictitious spin- $\frac{1}{2}$  operators used previously to describe double-quantum coherence.<sup>6,7</sup> In the practically interesting case  $D \ll \omega_1 \ll \omega_Q$  the system is formally identical to a fictitious spin- $\frac{1}{2}$  coupled to the  $S$  spin and we derive the double-quantum decoupling condition for the effective  $\mathcal{H}_{IS}$ . Again the asymptotic dependence of the  $S$  linewidth on  $\omega_1$  and  $\Delta\nu$  is calculated.

In Sec. IV experimental results are presented illustrating the deuterium spin decoupling in solids and showing the behavior as a function of deuterium rf field  $\omega_1$  and resonance offset  $\Delta\omega$  and comparison with theory. We conclude in Sec. V with an extension to two coupled spin- $\frac{1}{2}$   $I$  spins where double-quantum effects can also be observed and a brief discussion of higher-order multiple-quantum effects for spin  $I = \frac{1}{2}n$  or  $n$ -coupled spins- $\frac{1}{2}$ .

## II. SPIN DECOUPLING FOR SPINS- $\frac{1}{2}$

This section is intended to serve as an introduction to notation and background for the subsequent application to the novel double-quantum effects. The coherent averaging treatment for normal single-quantum decoupling outlined here has been utilized previously.<sup>5</sup>

### A. Hamiltonian

The situation of interest here is depicted schematically in Fig. 6. Spins  $I = \frac{1}{2}$  interact with spins  $S = \frac{1}{2}$  and are subjected to rf irradiation near their Larmor frequency and we neglect  $I$ - $I$  and  $S$ - $S$  couplings. The effects of many-body  $I$ - $I$  interactions have been treated elsewhere.<sup>2</sup> We shall be interested in what follows in coherent  $I$  interactions due to quadrupolar couplings or a small number of dipolar interactions which lead to multiple-quantum effects and where the calculation can be done exactly. Thus the neglect of many-body  $I$ - $I$  interactions is justified. This is especially so for 99% deuterated material, where the deuterium-deuterium coupling is not normally larger than deuterium-proton coupling, so the effects of  $I$ - $I$  interactions on the spin decoupling are expected to be weak, and we need only to

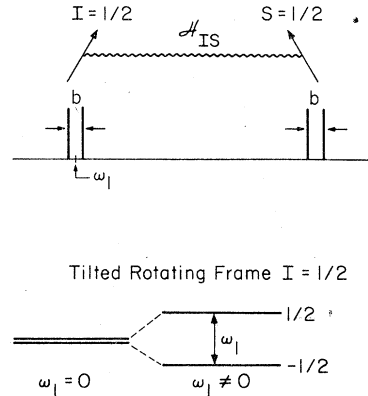


FIG. 6. Spin-decoupling case when  $I = \frac{1}{2}$ ,  $S = \frac{1}{2}$  showing coupled spins, typical spectrum, and  $I$  energy levels. Applying a resonant rf field of intensity  $\omega_1$  to the  $I$  spins splits the  $\pm \frac{1}{2}$  levels in the rotating frame by  $\omega_1$ , thus causing inversions of the  $I$  spins at a rate  $\omega_1$  relative to the  $S$  spins. The tilted rotating frame refers to the rotating frame and then to a tilt which diagonalizes the Hamiltonian putting  $z$  along  $\omega_1$ .

overcome the  $I$ - $S$  interactions.<sup>2</sup> We consider that  $I$  are abundant and  $S$  dilute, so several  $I$  spins interact with  $S$  of which only one is shown in Fig. 6.

The spin Hamiltonian for this system in high magnetic field is given in angular velocity units by

$$\mathcal{H} = -\omega_{OI}I_z - \omega_{OS}S_z - 2\omega_1I_x \cos\omega t + \mathcal{H}_{IS}, \quad (3)$$

where  $\omega_{OI}$  and  $\omega_{OS}$  are the  $I$  and  $S$  Larmor frequencies,  $\omega_1$  is the intensity of the  $I$ -rf field at frequency  $\omega$  near  $\omega_{OI}$ , and  $\mathcal{H}_{IS}$  is the truncated  $I$ - $S$  dipolar interaction Hamiltonian

$$\mathcal{H}_{IS} = S_z \sum_j b_j I_{jz}. \quad (4)$$

The parameters  $b_j$  characterize the  $I$ - $S$  dipolar coupling:

$$b_j = -2\gamma_I\gamma_S\hbar P_2 \cos\theta_j / r_j^3, \quad (5)$$

where  $\gamma_I$  and  $\gamma_S$  are magnetogyric ratios,  $r_j$  is the distance between  $S$  and  $I$  spin  $j$ , and  $\theta_j$  is the angle between the  $S$ - $I$  vector and the magnetic field.

In the rotating frame at frequency  $\omega$  for  $I$  and  $\omega_{OS}$  for  $S$ , (3) is transformed to

$$\mathcal{H} = -\Delta\omega I_z - \omega_1 I_x + \mathcal{H}_{IS}, \quad (6)$$

where

$$\Delta\omega = \omega_{OI} - \omega \quad (7)$$

and the counterrotating rf terms have been ignored. We shall henceforth remain in the rotating frame.

### B. Spin-decoupling conditions

The Hamiltonian in (6) contains three terms: a resonance offset  $\Delta\omega$ , an rf field  $\omega_1$ , and the  $I$ - $S$  coupling. It is the third term  $\mathcal{H}_{IS}$  that is responsible for the splitting and broadening of the  $S$  resonance. We now calculate the effect of the first two terms on  $\mathcal{H}_{IS}$  using coherent averaging theory.<sup>5</sup> This is done conveniently by applying a tilt ( $T$ ) transformation to a new frame with the operator

$$T_y = \exp(i\theta I_y), \quad (8)$$

such that the effective field in the rotating frame defined by  $\Delta\omega$  and  $\omega_1$  is along the new  $z$  axis. The Hamiltonian in this tilted frame has the form

$$\mathcal{H}' = -\omega_e I_z + \mathcal{H}'_{IS}, \quad (9)$$

where

$$\overline{\mathcal{H}'_{IS}} = \frac{-i}{6t_c} \int_0^{t_c} dt \int_0^t dt' \int_0^{t'} dt'' (\{\tilde{\mathcal{H}}'_{IS}(t), [\tilde{\mathcal{H}}'_{IS}(t'), \tilde{\mathcal{H}}'_{IS}(t'')]\} + \{\tilde{\mathcal{H}}'_{IS}(t'')[\tilde{\mathcal{H}}'_{IS}(t'), \tilde{\mathcal{H}}'_{IS}(t)]\}), \quad (16)$$

and we neglect higher-order terms.  $t_c$  and  $\tilde{\mathcal{H}}'_{IS}(t)$  are defined as

$$t_c = 2\pi/\omega_e \quad (17)$$

and

$$\tilde{\mathcal{H}}'_{IS}(t) = e^{i t \omega_e I_z} \mathcal{H}'_{IS} e^{-i t \omega_e I_z}. \quad (18)$$

We find by explicit evaluation, inserting (18) and (10) into (14)–(16),

$$\overline{\mathcal{H}'_{IS}}^{(0)} = \cos\theta S_z \sum_j b_j I_{jz}, \quad (19)$$

$$\overline{\mathcal{H}'_{IS}}^{(1)} = \sin\theta \frac{1}{\omega_e} S_z^2 \sum_j b_j^2 (\cos\theta I_{jx} - \frac{1}{2} \sin\theta I_{jz}), \quad (20)$$

$$\overline{\mathcal{H}'_{IS}}^{(2)} = \sin\theta \frac{1}{\omega_e^2} S_z^3 \sum_j b_j^3 [P_2(\cos\theta) I_{jx} - \sin\theta \cos\theta I_{jz}]. \quad (21)$$

The expressions (19)–(21) summarize the desired result, namely, the leading terms in the interaction between  $I$  and  $S$  spins. We have gone to  $\overline{\mathcal{H}'_{IS}}^{(2)}$  and not stopped at  $\overline{\mathcal{H}'_{IS}}^{(1)}$  since we find easily that

$$[\overline{\mathcal{H}'_{IS}}^{(1)}, S_x] = 0 \quad (22)$$

and thus  $\overline{\mathcal{H}'_{IS}}^{(1)}$  does not directly affect the  $S$  spectrum. Thus in the case that  $\overline{\mathcal{H}'_{IS}}^{(0)} = 0$  we must go to the next contributing term  $\overline{\mathcal{H}'_{IS}}^{(2)}$ . Decoupling will be efficient when  $\overline{\mathcal{H}'_{IS}}^{(0)}$  and  $\overline{\mathcal{H}'_{IS}}^{(2)}$  become small. From (19) this means, first of all,

$$\cos\theta \sim 0, \quad (23)$$

$$\mathcal{H}'_{IS} = S_z \sum_j b_j (I_{jz} \cos\theta - I_{jx} \sin\theta) \quad (10)$$

and  $\omega_e$ , and  $\theta$  are given by

$$\omega_e = (\Delta\omega^2 + \omega_1^2)^{1/2}, \quad (11)$$

$$\theta = \tan^{-1}(\omega_1/\Delta\omega). \quad (12)$$

We now calculate the effect of  $\omega_e I_z$  on  $\mathcal{H}'_{IS}$  assuming  $\omega_e \gg |\overline{\mathcal{H}'_{IS}}|$  by calculating the average  $I$ - $S$  Hamiltonian  $\overline{\mathcal{H}'_{IS}}$  due to coherent averaging by  $\omega_e I_z$  at frequency  $\omega_e$ :

$$\overline{\mathcal{H}'_{IS}} = \overline{\mathcal{H}'_{IS}}^{(0)} + \overline{\mathcal{H}'_{IS}}^{(1)} + \overline{\mathcal{H}'_{IS}}^{(2)} + \dots, \quad (13)$$

where

$$\overline{\mathcal{H}'_{IS}}^{(0)} = \frac{1}{t_c} \int_0^{t_c} dt \tilde{\mathcal{H}}'_{IS}(t), \quad (14)$$

$$\overline{\mathcal{H}'_{IS}}^{(1)} = \frac{-i}{2t_c} \int_0^{t_c} dt \int_0^t dt' [\tilde{\mathcal{H}}'_{IS}(t), \tilde{\mathcal{H}}'_{IS}(t')], \quad (15)$$

i.e., from (12) the onset of decoupling occurs when  $\omega_1$  starts to get larger than  $\Delta\omega$ ,

$$\omega_1 \gtrsim \Delta\omega; \quad (24)$$

from (21) this means, second, using (23) and (11), i.e., taking  $\theta = 90^\circ$ ,

$$\omega_1 \gtrsim D, \quad (25)$$

where  $D$  roughly characterizes the strength of the dipolar coupling and can be written as the square root of the second moment of the line due to the operator part of (21) with  $\theta = 90^\circ$ :

$$D^2 = \frac{1}{2} (\text{Tr}[S_z^3 \sum_j b_j^3 I_{jx}, S_x]^2 / \text{Tr} S_x^2)^{1/2}. \quad (26)$$

Equations (24) and (25) express what we expect: that  $\omega_1$  must cover both the resonance offset  $\Delta\omega$  and the dipolar broadening (namely, the larger of the two) for the onset of spin decoupling.

### C. Asymptotic behavior of $S$ linewidth

The asymptotic functional dependence of the  $S$  linewidth for large  $\omega_1$  on  $\Delta\omega$  and  $\omega_1$  can also be extracted and we do so for two experimental situations.

#### 1. Off-resonance decoupling

Assume the rigid  $S$  half linewidth at half height with no  $I$  irradiation is given by  $\delta_0$ , and the  $S$  half linewidth at half height with decoupling is given by  $\delta$ . We investigate how  $\delta/\delta_0$  depends on

$\Delta\omega$  for large  $\omega_1$ . Since  $\omega_1$  is large and we take  $\Delta\omega \neq 0$ , the leading term in  $\overline{\mathcal{H}}_{IS}^{\prime}$  is given by (19). Thus, we see immediately

$$\delta/\delta_0 = \cos\theta \quad (27)$$

and from (12) this means

$$\delta/\delta_0 = \Delta\omega/(\omega_1^2 + \Delta\omega^2)^{1/2}. \quad (28)$$

Thus, for small  $\Delta\omega$  the asymptotic large  $\omega_1$  dependence of  $\delta/\delta_0$  on  $\Delta\omega$  is given by

$$\delta/\delta_0 \sim \Delta\omega/\omega_1, \quad \Delta\omega \neq 0, \quad \omega_1 \text{ large.} \quad (29)$$

### 2. On-resonance decoupling

In this case we assume  $\Delta\omega = 0$  and investigate the asymptotic behavior of  $\delta/\delta_0$  as a function of  $\omega_1$  for large  $\omega_1$ . The leading term in the S linewidth is assumed to arise from  $\overline{\mathcal{H}}_{IS}^{(2)}$  given by (21) since  $\overline{\mathcal{H}}_{IS}^{(0)} = 0$  and from (22)  $\overline{\mathcal{H}}_{IS}^{(1)}$  can only contribute in higher order via cross terms. We assume in this case the S linewidth to be proportional to the square root of its second moment, which is reasonable for a Gaussian-like line shape:

$$\delta/\delta_0 = (\text{Tr}[\overline{\mathcal{H}}_{IS}^{(2)}, S_x]^2 / \text{Tr}[\mathcal{H}_{IS}, S_x]^2)^{1/2}, \quad (30)$$

which can be calculated from (21) for the case that  $\theta = 90^\circ$ :

$$\frac{\delta}{\delta_0} = \frac{1}{8\omega_1^2} \left( \sum_j b_j^6 / \sum_j b_j^2 \right)^{1/2}. \quad (31)$$

Assuming a Gaussian-like shape for the S line we take for the rigid half linewidth

$$\delta_0 = 1.18 M_2^{1/2}, \quad (32)$$

where  $M_2$  is the rigid second moment given by

$$M_2 = \frac{1}{3} I(I+1) \sum_j b_j^2. \quad (33)$$

Using (31)–(33) and defining a dimensionless parameter  $\mu$  which depends on the lattice

$$\mu = \sum_j b_j^6 / \left( \sum_j b_j^2 \right)^3, \quad (34)$$

we find finally, for the asymptotic behavior of  $\delta/\delta_0$ ,

$$\delta/\delta_0 = C\mu^{1/2} (\delta_0^2/\omega_1^2), \quad \Delta\omega = 0, \quad \omega_1 \text{ large,} \quad (35)$$

where  $C$  is a numerical constant easily evaluated from (31)–(34). Note that  $\delta_0$  is related to the parameter  $D$  in (26) and for our assumption of a Gaussian line

$$D \sim \delta_0, \quad (36)$$

so that the rigid linewidth  $\delta_0$  can be used as the parameter for the decoupling criterion, i.e.,

$$\omega_1 \gtrsim \Delta\omega, \delta_0. \quad (37)$$

We note here that physically, the decoupling occurs because the applied perturbation  $\omega_1 I_x$  is vectorially orthogonal to the coupling operator  $I_z$  and causes it to rotate and average to zero. We now apply these considerations to the case of double-quantum effects for spin  $I=1$  where we hope that we can find similar orthogonal vector operators.

### III. DOUBLE-QUANTUM EFFECTS

In this section we treat the theoretical problem of central interest in this paper, namely, that of spins  $I=1$  coupled to our S spin. This is depicted schematically in Fig. 7. The Hamiltonian in the rotating frame is the same as that of Eq. (6) with the addition of the  $I$ -spin quadrupolar interaction

$$\mathcal{H} = -\Delta\omega I_z - \omega_1 I_x + \frac{1}{3}\omega_Q [3I_z^2 - I(I+1)] + \mathcal{H}_{IS}, \quad (38)$$

where we assume that

$$\Delta\omega, \omega_1 \ll \omega_Q, \quad (39)$$

i.e., we irradiate near the center of the quadrupolar spectrum with an  $\omega_1$  much smaller than  $\omega_Q$ . We next show that in the limit  $\omega_1/\omega_Q \ll 1$  the problem of decoupling  $\mathcal{H}_{IS}$  reduces to a spin- $\frac{1}{2}$  problem.

#### A. Fictitious spin- $\frac{1}{2}$ operators

Following the theory of double-quantum NMR,<sup>6</sup> we define the following nine fictitious spin- $\frac{1}{2}$  operators<sup>8</sup>  $I_{p,i}$  in terms of the spin-1 angular

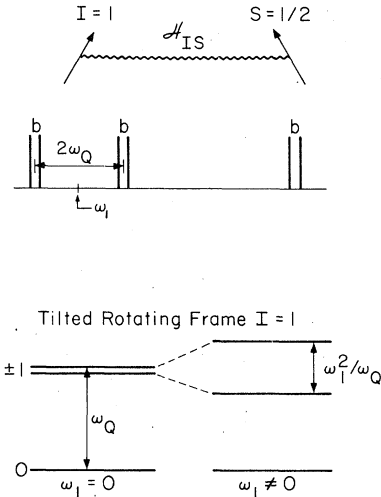


FIG. 7. Spin-decoupling case when  $I=1$ ,  $S=\frac{1}{2}$  showing coupled spins, typical spectrum and  $I$  energy levels. Applying a resonant rf field of intensity  $\omega_1$  to the  $I$  spins such that  $\omega_1 \ll \omega_Q$  splits the  $\pm 1$  levels in the rotating frame by  $\omega_1^2/\omega_Q$  thus causing inversions of the  $I$  spins at a rate  $\omega_1^2/\omega_Q$  relative to the S spins.

momentum operators  $I_p$ :

$$\begin{aligned} I_{p,1} &= \frac{1}{2} I_p, & I_{p,2} &= \frac{1}{2} (I_q I_r + I_r I_q), \\ I_{p,3} &= -\frac{1}{2} (I_q^2 - I_r^2), & p, q, r &= x, y, z, \end{aligned} \quad (40)$$

or cyclic permutation.

The usefulness of these operators derives from the fact that for each  $p$  ( $p = x, y, z$ ) the  $I_{p,i}$  fulfill spin- $\frac{1}{2}$  angular momentum commutation relations:

$$[I_{p,i}, I_{p,j}] = i I_{p,k}, \quad i, j, k = 1, 2, 3, \quad (41)$$

or cyclic permutation.

Thus each  $p$  describes a fictitious two-level spin- $\frac{1}{2}$  subspace with three orthogonal vector operators. Each is an SU(2) subgroup of the full SU(3) group. We term the subspace corresponding to  $p$  the " $p$  space." In particular, the  $I_{z,i}$  operators have matrix elements only between the  $I = 1$  levels  $m = \pm 1$  and thus correspond to double-quantum transitions. They are termed double-quantum operators and the  $z$  space is often called the double-quantum frame.<sup>8</sup> In many cases, the frames are uncoupled from each other, i.e., the evolution of the operators does not involve changes in  $p$ , only independent rotations in each  $p$  space. We shall see shortly that such is the case for double-quantum irradiation and we shall thus have found the orthogonal operators required for double-quantum spin decoupling.

Note that we can equally well use the fictitious spin- $\frac{1}{2}$  operators in the  $I_z$  basis described by Vega and by Ernst *et al.*<sup>7</sup> in all that follows by making the correspondence

$$-I_{z,3} \rightarrow I_x^{1-3}, \quad I_{z,2} \rightarrow I_y^{1-3}, \quad I_{z,1} \rightarrow I_z^{1-3},$$

where  $I_p^{i-j}$  means a  $\sigma_p$  Pauli spin operator between levels  $i$  and  $j$ .

Rewriting the Hamiltonian (38) in terms of the spin- $\frac{1}{2}$  operators (40) we have

$$\mathcal{H} = -2\Delta\omega I_{z,1} - 2\omega_1 I_{z,1} + \frac{2}{3}\omega_Q (I_{x,3} - I_{y,3}) + \mathcal{H}_{IS}, \quad (42)$$

where

$$\mathcal{H}_{IS} = 2S_z \sum_j b_j I_{jz,1}. \quad (43)$$

We now apply a transformation to a tilted frame with the operator

$$T_{x,2} = e^{i\psi_x I_{x,2}}, \quad (44)$$

where

$$\psi_x = \tan^{-1}(2\omega_1/\omega_Q). \quad (45)$$

Remembering that  $\omega_1 \ll \omega_Q$  from (30), i.e.,  $\psi_x \sim 0$ , the transformed Hamiltonian in this new frame can be written to a good approximation as<sup>6</sup>

$$\mathcal{H} \approx -2\Delta\omega I_{z,1} - (\omega_1^2/\omega_Q) I_{z,3} + \frac{2}{3}\omega_Q (I_{x,3} - I_{y,3}) + \mathcal{H}_{IS}. \quad (46)$$

The third term  $\frac{2}{3}\omega_Q (I_{x,3} - I_{y,3})$  commutes with all the other terms in the Hamiltonian and can be dropped since it will have no effect on the decoupling. We thus obtain finally

$$\mathcal{H}_{DQ} \approx -2\Delta\omega I_{z,1} - (\omega_1^2/\omega_Q) I_{z,3} + \mathcal{H}_{IS}, \quad (47)$$

with  $\mathcal{H}_{IS}$  given by (43). The subscript DQ is placed to denote double quantum, since only  $I_{z,i}$  (or  $I_p^{1-3}$  in the alternative notation) operators appear in the effective Hamiltonian. The operator  $(\omega_1^2/\omega_Q) I_{z,3}$  is an effective rf field operator which induces transitions between  $m = \pm 1$  and was used to explain our Fourier transform double-quantum NMR experiments and double-quantum spin locking.<sup>9</sup> Figure 8 depicts the double-quantum transition schematically.

Equation (47) is now formally identical to Eq. (6) for the spin- $\frac{1}{2}$  case. We identify  $I_z$  and  $I_x$  in the latter case with our  $I_{z,1}$  and  $I_{z,3}$  double-quantum operators, respectively, and  $\Delta\omega$  and  $\omega_1$  with  $2\Delta\omega$  and  $\omega_1^2/\omega_Q$ , respectively.  $\mathcal{H}_{IS}$  also has the same form with  $I_{jz}$  replaced by  $2I_{jz,1}$  according to (40). Thus, the system behaves like a fictitious spin- $\frac{1}{2}$  case in double-quantum space with effective resonance-offset field  $2\Delta\omega$  along the  $z, 1$  axis and effective rf field  $\omega_1^2/\omega_Q$  along the  $z, 3$  field. Figure 9 summarizes this section by depicting the double-quantum frame Hamiltonian schematically.

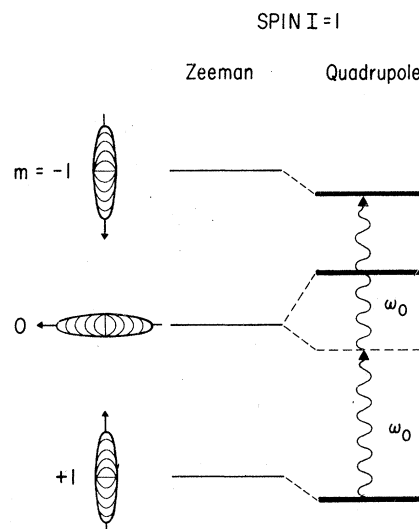


FIG. 8. Schematic description of double-quantum transitions at exact Larmor frequency  $\omega_0$  causing  $\pm 1$  inversions with no appreciable effect on  $m = 0$ .

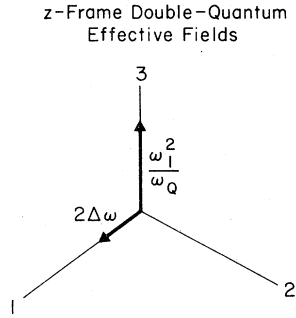


FIG. 9. Schematic description of effective fields in double-quantum frame. The operators  $I_{z,1}$ ,  $I_{z,2}$ , and  $I_{z,3}$  (axes 1, 2, 3) can be replaced by  $I_x^{1-3}$ ,  $I_y^{1-3}$ , and  $I_z^{1-3}$  to conform to the more general definitions and notation of Ref. 7.

### B. Double-quantum decoupling

The Hamiltonian in Eq. (47) contains three terms: a resonance offset  $2\Delta\omega$ , an effective rf field  $\omega_1^2/\omega_Q$ , and the  $I$ - $S$  coupling. We now wish to calculate the effect of the first two terms in (47) on the third,  $\mathcal{H}_{IS}$ , which is responsible for the broadening of the  $S$  line. Equation (41) ensures that the operator  $I_{z,1}$  will precess about the effective field defined by the first two terms in (47) depicted in Fig. 9. This will cause a coherent averaging of  $\mathcal{H}_{IS}$ . We have solved exactly this problem in Sec. II B, and we proceed by analogy here, first by transferring to a tilted frame defined so that the effective field is along the  $z, 1$  axis in the double-quantum frame. The transformation operator is, by direct analogy to (8),

$$T_{z,2} = \exp(-i\theta_D I_{z,2}), \quad (48)$$

where

$$\theta_D = \tan^{-1}(\omega_1^2/2\Delta\omega\omega_Q); \quad (49)$$

and from (47) the transformed Hamiltonian is, by direct analogy with (9),

$$\mathcal{H}'_{DQ} = -\omega_e I_{z,1} + \mathcal{H}'_{IS}, \quad (50)$$

where

$$\omega_{eD} = [(2\Delta\omega)^2 + \omega_1^4/\omega_Q^2]^{1/2}. \quad (51)$$

Again the subscript  $D$  on  $\theta_D$  and  $\omega_{eD}$  serves to indicate that this is the double-quantum case, distinguished from the  $\theta$  and  $\omega_e$  in the spin- $\frac{1}{2}$  case.

Now applying coherent averaging theory, assuming  $\omega_e \gg \|\mathcal{H}'_{IS}\|$ , we obtain, by analogy with (19) and (21) using (43) for  $\mathcal{H}_{IS}$ ,

$$\overline{\mathcal{H}'_{IS}}^{(0)} = 2 \cos\theta_D S_z \sum_j b_j I_{jz,1}, \quad (52)$$

$$\overline{\mathcal{H}'_{IS}}^{(1)} = 4 \sin\theta_D \frac{1}{\omega_{eD}} S_z^2 \sum_j b_j^2 (\cos\theta_D I_{jz,3} - \frac{1}{2} \sin\theta_D I_{jz,1}), \quad (53)$$

$$\begin{aligned} \overline{\mathcal{H}'_{IS}}^{(2)} &= 8 \sin\theta_D \frac{1}{\omega_{eD}^2} S_z^3 \\ &\times \sum_j b_j^3 [P_2(\cos\theta_D) I_{jz,3} - \sin\theta_D \cos\theta_D I_{jz,1}]. \end{aligned} \quad (54)$$

The decoupling conditions for the double-quantum case can now be written easily. We need to make  $\overline{\mathcal{H}'_{IS}}^{(0)}$  and  $\overline{\mathcal{H}'_{IS}}^{(2)}$  small, so we demand from (52),

$$\cos\theta_D \sim 0 \quad (55)$$

and from (54), together with (49), (51), and (55),

$$\omega_1^2/\omega_Q \gtrsim D. \quad (56)$$

Thus, we arrive at the condition for double-quantum decoupling stated previously in Eq. (2) and derived loosely in Ref. 4.

We now follow Sec. II C and derive the quantitative behavior of the  $S$  linewidth for large  $\omega_1^2/D\omega_Q$  on the  $I$  spins in the double-quantum case.

#### 1. Off-resonance double-quantum decoupling

We assume a large  $\omega_1^2/\omega_Q$  off resonance in analogy to Sec. II C.1. In this case, the residual  $I$ - $S$  coupling is dominated by  $\overline{\mathcal{H}'_{IS}}^{(0)}$  in (52) yielding for the linewidth  $\delta$ , relative to the full undecoupled linewidth  $\delta_0$  of the  $S$  spins,

$$\frac{\delta}{\delta_0} = \cos\theta_D = \frac{2\Delta\omega}{[(2\Delta\omega)^2 + \omega_1^4/\omega_Q^2]^{1/2}}. \quad (57)$$

For large  $\omega_1$  such that  $\omega_1^2 \gg 2\Delta\omega\omega_Q$  the asymptotic behavior is

$$\delta/\delta_0 \sim 2\Delta\omega\omega_Q/\omega_1^2, \quad \Delta\omega \neq 0, \quad \omega_1 \text{ large}. \quad (58)$$

Note the extreme predicted sensitivity of the double-quantum decoupling to the resonance condition, due to the large  $\omega_Q$  multiplying  $\Delta\omega$ , in contrast to the normal single-quantum decoupling case, Eq. (28) and (29). This sensitivity to resonance was observed by Meiboom *et al.*<sup>3</sup> in liquid-crystal deuterium decoupling, and is borne out by our experiments on solids described in Sec. IV.

#### 2. On-resonance double-quantum decoupling

We now have  $\Delta\omega = 0$ , so  $\overline{\mathcal{H}'_{IS}}^{(0)} = 0$  and since  $\overline{\mathcal{H}'_{IS}}^{(1)}$  is ineffective we calculate  $\delta/\delta_0$  using the residual term  $\overline{\mathcal{H}'_{IS}}^{(2)}$  with  $\theta_D = 90^\circ$ . Again, assuming for simplicity that the  $S$  linewidth is proportional to the square root of its second moment, we can use Eq. (30) which gives, in this case,

$$\frac{\delta}{\delta_0} = \frac{\omega_Q^2}{2\omega_1^4} \left( \frac{\sum_j b_j^6}{\sum_j b_j^2} \right)^{1/2} \quad (59)$$

We have used the fact that for  $\Delta\omega = 0$

$$\omega_{eD} = \omega_1^2/\omega_Q \quad (60)$$

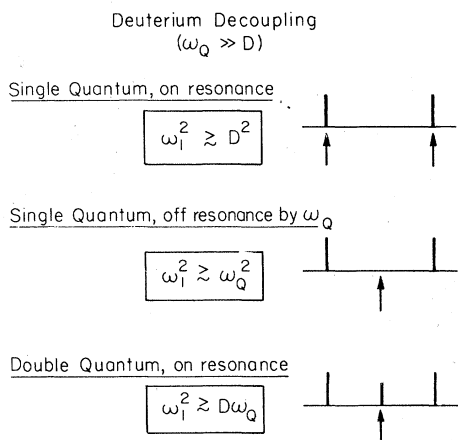


FIG. 10. Summary of spin-decoupling conditions for deuterium with large quadrupole splitting  $\omega_Q$  coupled weakly ( $D \sim b$ ) to spins  $S$ .

from Eq. (51). Assuming a Gaussian line shape we obtain, in analogy to Eq. (32)–(35),

$$\delta/\delta_0 = C_D \mu^{1/2} (\delta_0^2 \omega_Q^2 / \omega_1^4), \quad (61)$$

where  $C_D$  is a numerical constant and  $\mu$  is given by (34).  $C_D$  is easily evaluated from (32), (33), and (59).  $\delta_0$  is the rigid  $S$  line half width at half height with no  $I$ -spin decoupling. We therefore predict a more drastic dependence of  $\delta/\delta_0$  on  $\omega_1$ ,

$$\delta/\delta_0 \sim 1/\omega_1^4, \quad (62)$$

than in the single-quantum case which depends on  $1/\omega_1^2$  as in Eq. (35). A summary of the decoupling conditions appears in Fig. 10 showing the relaxed  $\omega_1$  requirement for double-quantum decoupling.

## IV. EXPERIMENTS

### A. Experimental details

Experiments were done on samples of DMSO- $d_6$ , deuterated benzene ( $C_6D_6$ ), and heavy water ( $D_2O$ ). In all cases the samples were deuterated to >99% and the residual <1% protons were observed while decoupling the deuterium under different conditions. Since all these materials are liquids at room temperature, they were cooled by gaseous nitrogen for the solid-state work. The most appealing way to do the experiments would be to use single crystals with well defined  $\omega_Q$  values. However, as seen in Figs. 3 and 4, even in a powder most of the deuterium spectral intensity is concentrated in a small region of  $\omega_Q$  values near the singularities. This is especially so in the present case where the electric-field-gradient tensors are close to axially symmetric. Thus, we take these to be the effective  $\omega_Q$  values in all our samples. For DMSO  $2\omega_Q$  is 44 kHz and for benzene  $2\omega_Q$  is 70 kHz, giving us two independent values on which to check our theory.

The spectrometer used in these experiments was similar to that described previously for our  $^{13}C$  work,<sup>10</sup> modified for deuterium-proton double resonance. The deuterium decoupling amplifier was a modified amateur radio transmitter producing several hundred watts of rf power at 16.3 MHz. A schematic diagram of the spectrometer and the home built probe are shown in Fig. 11. Calibration of the rf fields  $\omega_1$  was performed both by normal single-quantum experiments on the liquid samples and by double-quantum rotary decays on the solid samples.<sup>9</sup>

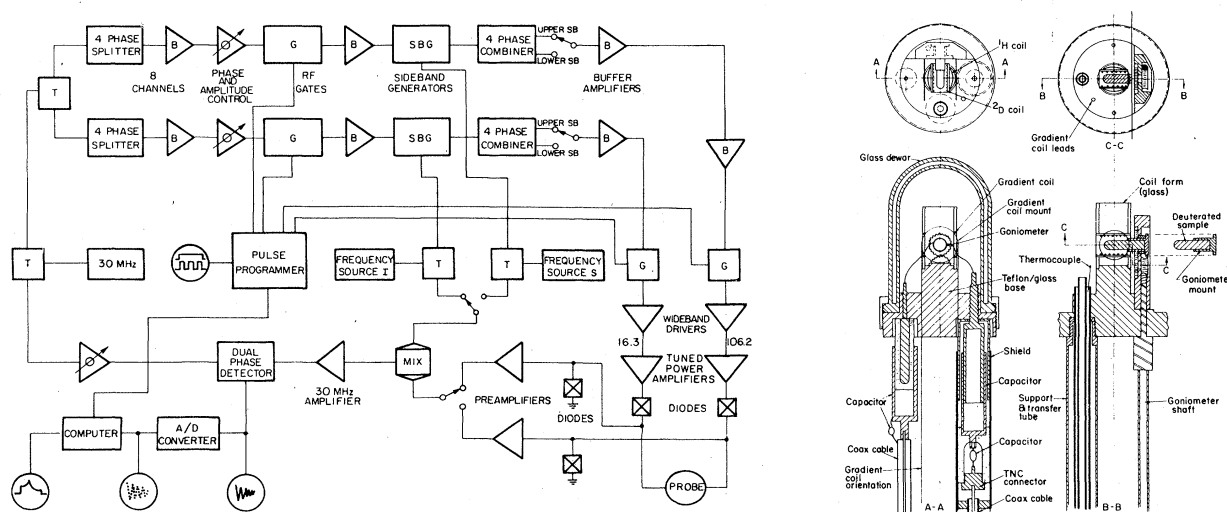


FIG. 11. Schematic of spectrometer used for some of the  $^2D$ - $^1H$  experiments.



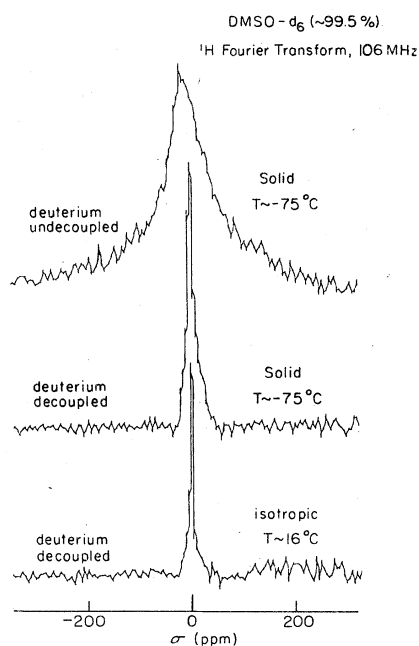


FIG. 12. Demonstration of double-quantum spin decoupling in solid. The residual protons in perdeuterated DMSO- $d_6$  are observed, top with no deuterium irradiation. At center is the spectrum when the deuterium spins are irradiated at resonance with a moderate ( $\nu_1 \sim 10$  kHz) rf field. The deuterium spectrum is much wider than 10 kHz as shown in Fig. 4.

### B. Deuterium decoupled spectra

As a qualitative introduction to the type of spectra observed experimentally with deuterium decoupling we show some simple illustrative examples. Figure 12 shows three spectra indicating the effect of double-quantum decoupling on the residual protons in a perdeuterated ( $\sim 99.5\%$  deuterium) sample of DMSO. In the solid, the deuterium quadrupolar broadening is large, as indicated in Fig. 4. The effect of a moderate rf field on the deuterium with  $\omega_1 \ll \omega_Q$  is sufficient to effect spin decoupling. As expected for the double-quantum process, this is very sensitive to deuterium frequency and is discussed in more detail in Sec. IV C. Also shown is an isotropic liquid spectrum of the same sample for comparison.

The onset of double-quantum decoupling is shown in more detail in Fig. 13. At an rf intensity of  $\nu_1 = 10.4$  kHz the residual  $^1\text{H}$  spectrum is completely decoupled and a further increase in rf intensity to  $\nu_1 = 46.5$  kHz serves only to induce an appreciable Bloch-Siegert shift.<sup>11</sup> The  $^1\text{H}$  linewidth under decoupling conditions is determined by a combination of  $^1\text{H}$ - $^1\text{H}$  dipolar coupling and by anisotropy of the bulk magnetic susceptibility.<sup>12</sup>

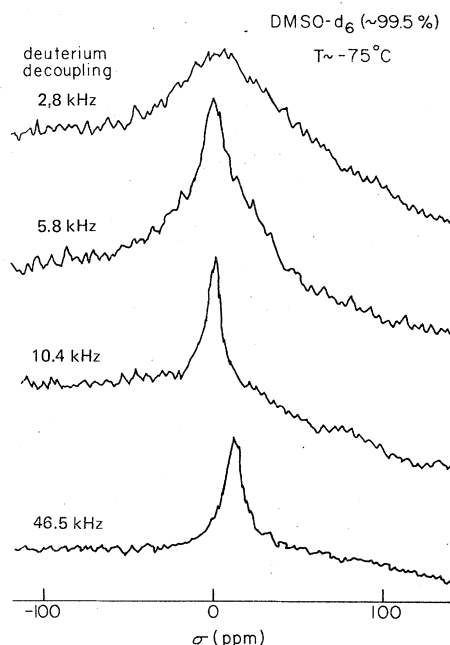


FIG. 13. Dependence of residual proton spectrum in solid DMSO- $d_6$  on intensity  $\nu_1 = \omega_1/2\pi$  of deuterium rf irradiation. At  $\nu_1 \sim 10$  kHz the spins are essentially completely decoupled and a further increase in  $\omega_1$  causes only an appreciable Bloch-Siegert shift.

One of the potential applications of double-quantum deuterium decoupling is the resolution of  $^1\text{H}$ - $^1\text{H}$  dipolar couplings in selectively doped proton groups in a deuterated host. For example, the study of quantum-mechanical tunneling in methyl groups at low temperatures would benefit from this.<sup>13</sup> Figure 14 indicates that indeed fine structure is apparent in the residual  $^1\text{H}$  spectrum when 10% protonated DMSO is doped into a deuterated host. The additional peaks arise from intramolecular dipolar couplings.

As a final example of the resolution obtained by double-quantum decoupling we depict in Fig. 15 the residual  $^1\text{H}$  spectra obtained in deuterated ice and presented in our preliminary communication.<sup>4</sup> This constitutes the first measurement of the proton chemical-shift anisotropy in ice, a material in which there is a great deal of interest and for which many other measurements and calculations have been made.<sup>14</sup> Of particular interest are the atomic and molecular motions in ice, which are responsible for various relaxation mechanisms. By studying the  $^1\text{H}$  line shape as a function of temperature, we have been able to separate out and characterize clearly for the first time that component of the relaxation arising from proton motion amongst sites related by tetrahedral symmetry.<sup>15</sup> The value of  $\Delta\sigma = 34 \pm 4$  ppm for the

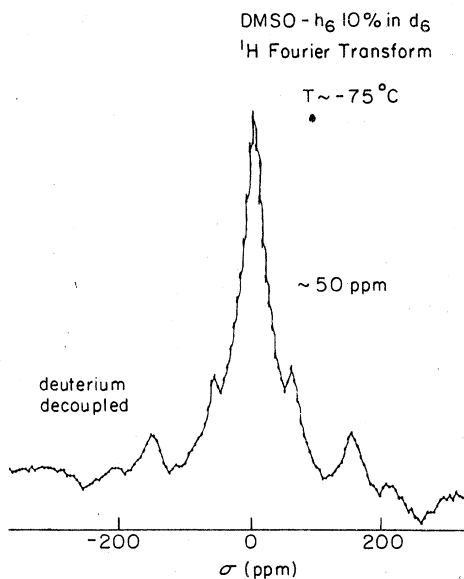


FIG. 14. Resolution of  $^1\text{H}$ - $^1\text{H}$  dipolar coupling fine structure in solid  $\text{DMSO}-h_6$  doped 10% into a lattice of  $\text{DMSO}-d_6$ .

chemical shift is similar to that obtained recently using a multiple pulse technique.<sup>16</sup>

#### C. Dependence on rf intensity and resonance offset

In this section we present experimental results designed to investigate the sensitivity of the double-quantum decoupling to the  $I$  resonance condition [Eq. (48)] and the  $1/\omega_1^4$  dependence on rf intensity [Eq. (52)]. First, the resonance-offset behavior was investigated on perdeuterated dimethylsulfoxide at  $-75^\circ\text{C}$ . The extra linewidth of

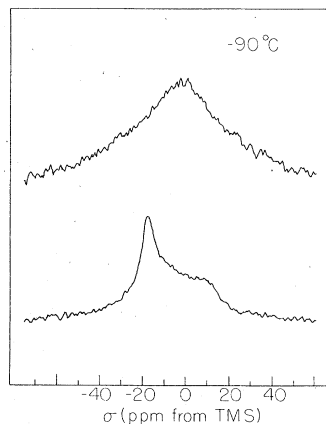


FIG. 15. Resolution of the chemical-shift spectrum for residual protons in heavy ice without (top) and with (bottom) deuterium double-quantum spin decoupling. The deuterium spectral width in this case is  $\sim 230$  kHz. (TMS, Tetramethylsilane).

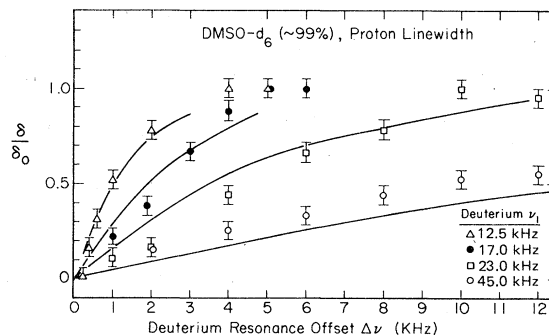


FIG. 16. Behavior of the excess proton linewidth in  $\text{DMSO}-d_6$  at  $-75^\circ\text{C}$  caused by deuterium dipolar coupling as the deuterium spins are irradiated at various frequencies  $\Delta\nu$  from resonance. Note the sensitivity of the decoupling condition to the  $I$  resonance condition, a characteristic of the double-quantum decoupling process. The solid lines are theoretical calculated in the text.

the residual protons due to  $^2\text{D}$  coupling was observed as the  $^2\text{D}$  spins were irradiated with a constant rf field ( $\nu_1$ ) at several frequencies. The dependence of the excess proton linewidth as a function of the offset from deuterium resonance for four values of  $\nu_1$  is shown in Fig. 16. The calculated solid curves are from Eq. (57) with no adjustable parameters. Similar behavior is observed in a completely different sample, perdeuterated benzene at  $-35^\circ\text{C}$  as shown in Fig. 17 for a  $\nu_1$  of  $\sim 10$  kHz. Note in both cases the good agreement between theory and experiment with no adjustable parameters, and the sensitivity of the decoupling to the deuterium resonance condition.

The dependence of the decoupling on rf field intensity  $\nu_1$  was checked on the same two samples. In Fig. 18 the dependence of residual proton linewidth is shown as a function of deuterium  $\nu_1$  applied at resonance in  $\text{DMSO}-d_6$ . The solid line is the asymptotic  $1/\nu_1^4$  dependence from Eq. (61).

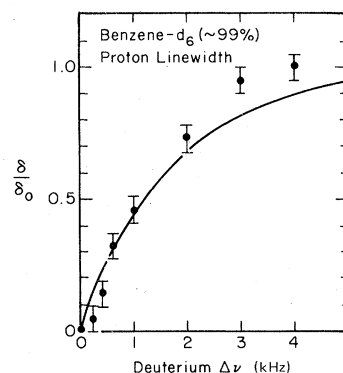


FIG. 17. Same as Fig. 16 for residual protons in solid perdeuterated benzene at  $-35^\circ\text{C}$ .

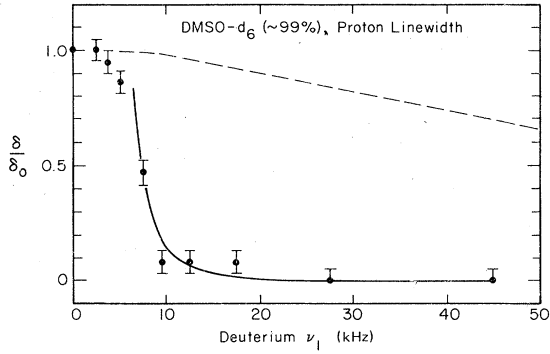


FIG. 18. Behavior of the excess proton linewidth in DMSO- $d_6$  at  $-75^\circ\text{C}$  as the deuterium spins are irradiated at resonance with various values of  $\omega_1$  to induce double-quantum decoupling. The solid line shows the asymptotic  $1/\omega_1^4$  behavior expected from theory as explained in the text. The dashed line shows the expected behavior if double-quantum transitions did not occur.

The dashed line indicates the behavior we would expect if the decoupling had to proceed through the allowed single-quantum transitions. Figure 19 shows analogous results for benzene- $d_6$ . In both cases we get excellent agreement between experiment and the behavior predicted for pure double-quantum effects both for the onset of decoupling and for the asymptotic  $1/\nu_1^4$  behavior.

#### D. Line shapes and linewidths

In the previous sections we were interested in the S-line-width dependence on  $\Delta\nu$  and  $\nu_1$  (for large  $\nu_1$ ) of the  $I$  spin. It is possible to be somewhat more precise and here we make some brief comments about the S line shape and about the  $\nu_1$  dependence for finite  $\nu_1$ . The S line shape is given by the Fourier transform of the free-induction decay function<sup>17</sup>

$$G(t) = \text{Tr}(e^{-i\mathcal{H}t} S_x e^{i\mathcal{H}t} S_x) / \text{Tr} S_x^2, \quad (63)$$

where  $\mathcal{H}$  is the spin Hamiltonian. In the case that  $I$  is a spin- $\frac{1}{2}$  the appropriate  $\mathcal{H}$  in the rotating

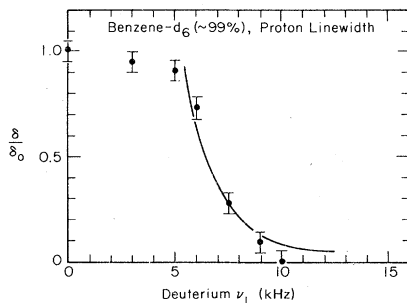


FIG. 19. Same as Fig. 18 for residual protons in solid perdeuterated benzene at  $-35^\circ\text{C}$ .

frame is given by Eq. (6). If we do not decouple, i.e.,  $\omega_1=0$ , then the trace in (63) can be evaluated explicitly, yielding

$$G(t) = \prod_j \cos(\frac{1}{2} b_j t), \quad I = \frac{1}{2}, \quad \omega_1 = 0. \quad (64)$$

If the  $I$  spins are irradiated off resonance by  $\Delta\omega$  with a large  $\omega_1$  then the appropriate Hamiltonian is that in Eq. (19) and again the trace can be evaluated explicitly by replacing  $b_j$  in (64) with  $\cos\theta b_j$ , where  $\theta$  is given by (12):

$$G(t) = \prod_j \cos(\frac{1}{2} \cos\theta b_j t), \quad I = \frac{1}{2}, \quad \text{large } \omega_1. \quad (65)$$

Thus, we see that in the case of single-quantum decoupling the S line shape does not change as the large- $I$   $\omega_1$  is shifted off resonance and only scales in width as  $\cos\theta$ .

What happens in the case of  $I$  being spin-1 and subject to double-quantum decoupling? The appropriate Hamiltonian is given in Eqs. (42) and (43). Again, for no irradiation on  $I$  the trace in (63) is explicitly evaluated as

$$G(t) = \prod_j \frac{1}{3} (1 + 2 \cos b_j t), \quad I = 1, \quad \omega_1 = 0. \quad (66)$$

If the  $I$  spins are now irradiated at  $\Delta\omega$  from resonance with a large  $\omega_1^2/\omega_Q$ , then the appropriate Hamiltonian is given by Eq. (52) and thus evaluation of the trace in (63) is the same as (66) with replacement of  $b_j$  by  $\cos\theta_D b_j$ , where  $\theta_D$  is defined in (49):

$$G(t) = \prod_j \frac{1}{3} [1 + 2 \cos(\cos\theta_D b_j t)]. \quad (67)$$

We have not verified this double-quantum line shape and scaling effect quantitatively, but it certainly would be interesting to do so.

Finally, in this section we discuss the dependence of the S linewidth on the  $I=1$  irradiation strength  $\omega_1$  at resonance. The asymptotic behavior for large  $\omega_1^2/\omega_Q$  was described in Eqs. (59)–(61) and experimental results were shown in Figs. 18 and 19. The question is whether we can say something about the line shape under these conditions and also about the  $\omega_1$  dependence over the whole  $\omega_1$  range. At resonance, the appropriate Hamiltonian in (63) for double-quantum decoupling with large  $\omega_1^2/\omega_Q$  is given by (54) with  $\theta_D = 90^\circ$ . The trace can be evaluated and yields the same as (66) if  $b_j$  is replaced by

$$\bar{b}_j = \lambda_j b_j, \quad \text{large } \omega_1^2/\omega_Q, \quad (68)$$

where

$$\lambda_j = b_j^2 \omega_Q^2 / 2\omega_1^4. \quad (69)$$

Thus, for large  $\omega_1^2/\omega_Q$  the S- line shape should

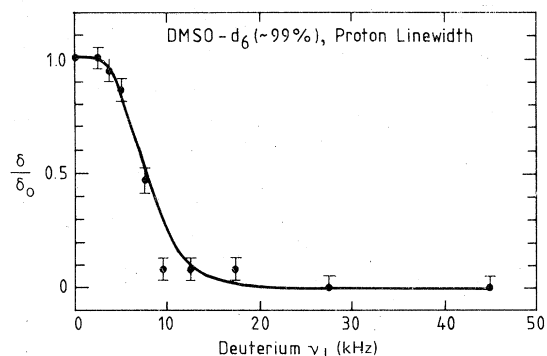


FIG. 20. Comparison of the data in Fig. 18 with the full theoretical  $\omega_1$  dependence of the linewidth calculated from Eq. (71) with  $\omega_1^*/2\pi = 7.4$  kHz.

still remain the same and be scaled by (69). To account for the full (including small  $\omega_1$  and no decoupling)  $\omega_1$  dependence, we assume

$$\bar{b}_j = \lambda_j / (1 + \lambda_j). \quad (70)$$

This reduces to the correct limits for  $\omega_1 \rightarrow 0$  (no decoupling) and  $\omega_1 \rightarrow \infty$  (asymptotic behavior) and is found to be an excellent assumption in exact calculation on a small number of spins. Using (70), the dependence of  $S$  linewidth on  $I$ - $\omega_1$  at resonance can be explicitly calculated; assuming that the linewidths are proportional to the second moments as in Eq. (32) we find

$$\delta/\delta_0 = [1 + (\omega_1/\omega_1^*)^4]^{-1}, \quad (71)$$

where  $\omega_1^*$  can obviously be regarded as a threshold decoupling intensity and is given by

$$\omega_1^{*4} = (1.18)^{2/3} I(I+1) \mu^{1/2} \omega_0^2 \delta_0^2. \quad (72)$$

Equation (71) thus provides an extension of (61) to the full  $\omega_1$  range.

Figure 20 demonstrates that indeed (71) predicts the  $\omega_1$  dependence on resonance of the  $S$  linewidth quite well. The experimental data from Fig. 18 are compared this time with the full expression in (71) yielding a best value for the threshold decoupling intensity of

$$\omega_1^*/2\pi = 7.4 \text{ kHz},$$

which agrees quite well with the value estimated from the lattice constants for DMSO.

## V. COUPLED SPINS AND MULTIPLE-QUANTUM EFFECTS

In this section we mention two rather natural extensions of the double-quantum effects described in this paper, namely, to an  $I$ -spin system which consists itself of coupled spins- $\frac{1}{2}$  [e.g., two strongly coupled protons ( $I$ ) coupled to  $^{13}\text{C}$  ( $S$ )] and second to higher-order multiple-

quantum effects (e.g.,  $I > 1$  or several coupled spins- $\frac{1}{2}$ ). These extensions are obvious not only to the spin-decoupling phenomena, but also to multiple-quantum coherence, i.e., the excitation and detection of specific multiple-quantum transitions for spin  $I > 1$  or for coupled spin- $\frac{1}{2}$  systems. This latter extension to Fourier-transform multiple-quantum spectroscopy will be described in detail elsewhere.

As a simple example of a coupled spin- $\frac{1}{2}$  system we take two equivalent protons ( $I$ ) coupled equally to another spin- $\frac{1}{2}$  ( $S$ ) as described in Fig. 21. This is a system of practical interest, since  $^1\text{H}_2$ - $^{13}\text{C}$  groups occur in the aliphatic chains of liquid crystals, polymers, and biological membranes where NMR studies are of great importance. We wish to know how the two  $I$  spins are decoupled from the  $S$ -spin by irradiating them near resonance. The Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_{II} + \mathcal{H}_{IS}, \quad (73)$$

where in the rotating frame at resonance for  $S$  and off resonance by  $\Delta\omega$  for  $I$ ,

$$\begin{aligned} \mathcal{H}_{II} = & -\Delta\omega(I_{1z} + I_{2z}) + \frac{2}{3}a(3I_{1z}I_{2z} - \vec{I}_1 \cdot \vec{I}_2) \\ & -\omega_1(I_{1x} + I_{2x}), \end{aligned} \quad (74)$$

$$\mathcal{H}_{IS} = b(I_{1z} + I_{2z})S_z. \quad (75)$$

We know that two equivalent coupled protons produce orthogonal singlet and triplet states.<sup>13</sup> We expect that the singlet does not couple to the

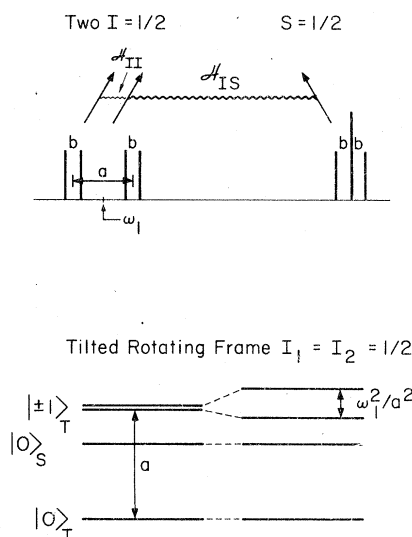


FIG. 21. Spin decoupling case for two equivalent spins  $I = \frac{1}{2}$  coupled strongly (a) to each other and weakly (b) to a spin  $S$ , showing coupled spins, typical spectrum and  $I$  energy levels. The triplet manifold  $|\pm 1\rangle_T$ ,  $|0\rangle_T$  of the  $I$  spins behaves exactly as the spin  $I = 1$  case in Fig. 7 with  $\omega_0$  replaced by  $a$ .

S spin and that the triplet can be treated identically to the spin  $I=1$  problem in the previous sections. We thus define double-quantum fictitious spin- $\frac{1}{2}$  operators  $I_p^{i-j}$  (see Ref. 7) for the  $|\frac{1}{2}, -\frac{1}{2}\rangle$  (denote this state  $|-1\rangle$  by  $i=1$ ) to  $|\frac{1}{2}, \frac{1}{2}\rangle$  (denote this state  $|+1\rangle$  by  $j=4$ ) proton transitions:

$$\begin{aligned} I_x^{1-4} &= I_{1x} I_{2x} - I_{1y} I_{2y}, \\ I_y^{1-4} &= I_{1x} I_{2y} + I_{1y} I_{2x}, \\ I_z^{1-4} &= \frac{1}{2}(I_{1z} + I_{2z}). \end{aligned} \quad (76)$$

These behave exactly as  $-I_{z,3}$ ,  $I_{z,2}$ , and  $I_{z,1}$  of Sec. III. They are a special case of the general fictitious spin- $\frac{1}{2}$  operators  $I_p^{i-j}$  defined by Vega and by Ernst *et al.*<sup>7</sup> in a multilevel system. Levels 2 and 3 refer to the singlet and the remaining triplet state which do not enter the DQ behavior.

Proceeding now by exact analogy to the double-quantum condition of Sec. III, in the case that  $\omega_1 \ll a$ , we transform the Hamiltonian in (73) by the infinitesimal transformation operator analogous to (44) with the angle

$$\psi = \tan^{-1}(2\omega_1/a), \quad (77)$$

yielding to a good approximation the effective double-quantum Hamiltonian

$$\mathcal{H}_{DQ} \approx -2\Delta\omega I_z^{1-4} + (\omega_1^2/a) I_x^{1-4} + 2b I_z^{1-4} S_z. \quad (78)$$

The term proportional to  $(3I_{1z} I_{2z} - \vec{I}_1 \cdot \vec{I}_2)$  commutes with  $\mathcal{H}_{DQ}$  and with  $I_z^{1-4}$  and has thus been dropped since it will not affect the experiment. The problem is now formally identical to the spin-1 case [Eq. (47)] and the decoupling conditions at resonance can be written immediately:

$$\omega_1^2/a \approx b. \quad (79)$$

Thus, the rf intensity does not always need to be larger than the  $I$  spectral width ( $a$ ) as is commonly thought. The two  $I$  spins can be made to flip coherently up and down by the resonant double-quantum process more easily than each one separately. This effect was noticed previously in our liquid-crystal work where moderate  $\omega_1$  fields on protons decoupled them from  $^{13}\text{C}$  spins on aliphatic end chains despite the strong proton-proton couplings.<sup>4,19</sup> All the other analogous properties to spin-1 may be treated in a similar fashion.

As a final simple example consider the case of a spin  $I=\frac{3}{2}$  (relevant to lithium NMR) coupled to spin  $S=\frac{1}{2}$  in high magnetic field. In direct extension of the double-quantum ideas, Fig. 22 shows that here we expect resonant triple- as well as single-quantum transitions.<sup>7</sup> The cross section in the regime  $\omega_1 \ll \omega_Q$  for the triple-quantum transitions should go as  $\omega_1^3/\omega_Q^2$  from

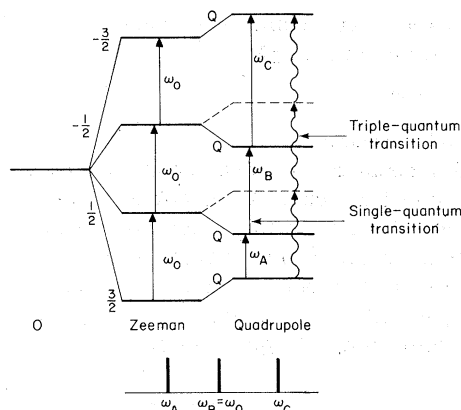


FIG. 22. Schematic description of triple-quantum transition in spin  $I=\frac{3}{2}$  system with  $\omega_1 \ll \omega_Q$ . The splitting is  $\omega_A - \omega_C = 2\omega_Q$ .

third-order perturbation theory<sup>4</sup>; more precisely it is given by  $3\omega_1^3/2\omega_Q^2$  where  $2\omega_Q$  is the full width of the  $I$  spectrum. Thus, as shown in Fig. 23, we expect that when a resonant rf field of intensity  $\omega_1$  is applied to the  $I=\frac{3}{2}$  spins the  $\pm\frac{3}{2}$  transition should flip at a rate of  $3\omega_1^3/2\omega_Q^2$  and the  $\pm\frac{1}{2}$  single-quantum transition at  $2\omega_1$ . Thus the condition for the onset of decoupling in this case and observation of a sharp S signal is

$$\omega_1^3 \approx D\omega_Q^2, \quad (80)$$

where again  $D$  characterizes the  $I$ -S dipolar coup-

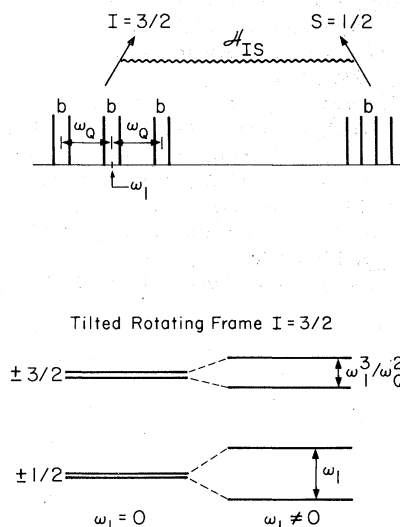


FIG. 23. Spin decoupling case when  $I=\frac{3}{2}$ ,  $S=\frac{1}{2}$ , showing coupled spins, typical spectrum and  $I$  energy levels. Applying a resonant rf field of intensity  $\omega_1$  to the  $I$  spins splits the  $\pm\frac{1}{2}$  levels in the rotating frame by  $2\omega_1$  and the  $\pm\frac{3}{2}$  levels by  $\frac{3}{2}\omega_1^3/\omega_Q^2$  thus causing inversions of these pairs of level at the above frequencies.

ling (a particular coupling  $b$  is shown in Fig. 23). The extension to spin  $\frac{1}{2}N$

$$\omega_1^N \geq D\omega_Q^{N-1} \quad (81)$$

is straightforward.

Similar considerations can be applied to  $N$  equivalent coupled protons. As mentioned previously<sup>4</sup> under conditions where the proton-proton coupling is much stronger than the proton S-spin coupling, the proton system behaves in many respects as an independent set of spins  $N+1$ ,  $N-1$ , ... which could exhibit multiple-quantum effects of the type

discussed above. Note that as  $N$  gets large the criterion (81) approaches the accepted rule that  $\omega_1$  must be of the order of the stronger  $I-I$  coupling.

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