Submitted to Journal of Chemical Physics

UCRL-18605
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A SCHEME FOR SENSITIVE NUCLEAR DOUBLE RESONANCE DETECTION: DEUTERIUM AND C^{13}

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August 1969

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ERRATA

To: All recipients of UCRL-18605

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Subject: UCRL-18605, "A Scheme for Sensitive Nuclear Double Resonance Detection: Deuterium and C^{13}" by M. Schwab and E. L. Hahn, September 1969.

Please make the following corrections to subject report.

1. Page 3 - line 12, "30 Hz" should read "30 MHz"
2. Page 9 - line 17 should read "with other present spin species B, C and A' as described below, and among"
3. Page 10 - line 4 from the bottom, delete symbol "$\mathcal{H}_{DD}^{AB}$"
4. Page 10 - last line, insert "where H_L^B" after "width ~ $\gamma_B H_L^B$ ".
5. Page 13 - Eq (23), The (1/2, - 1/2) matrix element should be "0" instead of "1".
6. Page 20 - line 15 following "Zeeman state" add "which may be used to level cross with a mixed Zeeman and quadrupole C spin system".
7. Page 44. Footnote "10' should be labeled "11" and footnote "11" labeled "10".
8. Page 47. Fig. 6. "B spin spectra is" should read "B spin spectra of".
9. The symbols H_L^A and H_{LA} appear in a number of places in the preprint. They are meant to symbolize the same local field. i.e. $H_L^A \equiv H_{LA}$. This is true for H_L^B and H_{LB} as well i.e. $H_L^B \equiv H_{LB}$.
10. Page 15. Eq. (30) " β_A=" should read "$\dot{\beta}_A$ ="

    Eq. (31) "β_B =" should read "$\dot{\beta}_B$="

A SCHEME FOR SENSITIVE NUCLEAR DOUBLE RESONANCE DETECTION: DEUTERIUM AND C^{13}

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ABSTRACT

An experiment which involves the participation of three nuclear spin species is carried out to accomplish sensitive double-resonance detection of nuclei. An ordered nuclear quadrupole spin system (A) is used to establish and monitor a metastable ordered state of a second abundant spin system (B). A double-resonance coupling is brought about between the B spin system and a third rare or weakly interacting system (C) to accomplish the detection of the C resonance. The usefulness of this scheme lies in the choice of an A system with a short spin-lattice relaxation time (T_{1A}) and a B system with a long spin-lattice relaxation time (T_{1B}). The choice of a long T_{1B} increases the sensitivity of the experiment in that a long time is available during which effective nuclear dipole-dipole cross-relaxation can occur between the B and C systems. With a short T_{1A}, the cycling rate at which information is gathered to detect the C system is enhanced by a factor $\sim T_{1B}/T_{1A}$ over that of the earlier two species double resonance method. For increased sensitivity T_{1B} can be chosen arbitrarily long, while for the purposes of an

increased rate of data acquisition, T_{1A} can be chosen arbitrarily short, thus producing an efficient double-resonance scheme. This scheme is applied to a 12% deuterium enriched sample of paradichlorobenzene. The nuclear quadrupole coupled Cl^{35} reservoir acts as the A system. The zero field nuclear quadrupole resonance system (at 34.78 mHz at 77°K) supplants the usual high field stabilized magnet and power supply required in an NMR double-resonance experiment. The B proton system has a zero field lifetime of 46 seconds, and approximately a one hour lifetime at 135 gauss. The C systems investigated are (1) deuterium and (2) the naturally abundant C^{13} nuclei in paradichlorobenzene. An analysis of double-resonance detection of I = 1 spin systems is given and shows that for a well resolved nuclear quadrupole asymmetry η splitting, a double-resonance cannot be detected because of the non-secular character or quenching of cross-relaxation interaction terms. The analysis is extended to include the unquenching effect of constant magnetic fields and the integer I > 1 quadrupole system is discussed. The observation of the C^{13} resonance is the first reported observation through the nuclear magnetic resonance techniques of the 1.1% naturally abundant C^{13} in a solid.

I. INTRODUCTION

A large collection of spins is usually required in the investigation of the spin interactions of nuclear magnetic dipole moments with applied and local magnetic fields, and of nuclear electric quadrupole moment interactions with local electric field gradients. If a rare isotopic spin system is to be studied, we encounter the problem of low or nearly null signal detection sensitivity. The signals available from direct resonance investigations are proportional to the number of nuclei involved in the resonance, so we can expect a signal reduced from an optiumum (100% abundant spin species) by the natural abundance of the spin. In solids with 100% abundant nuclear species at liquid nitrogen temperatures, 100/1 is a strong NMR signal-to-noise ratio expected at an ~ 30 Hz resonance frequency. However, signal-to-noise ratios of about 1/1 would occur for ~ 1% naturally abundant C^{13}, and 1/100 for ~ 10^{-2}% naturally abundant deuterium under otherwise identical conditions. Standard signal averaging techniques have been applied successfully to liquid and solid state resonance investigations where T_1 is short and where high repetition sweep rates are possible[1], but the time required to detect a resonance point can exceed a few hours or more.

The nuclear magnetic double-resonance technique involving two spin species has served as a successful alternative to direct methods in enabling the observation of rare spin system[2-7]. In this technique we assume the existence of an abundant spin system called the A spin system with a resonance which gives a strong signal. The rare spin system, called the B spin system, is readily observed by exciting B spin quantum transitions

and observing enhanced dipolar cross-relaxation between the A and B spins by its effect on the A spin signal. By using double-resonance techniques it has been possible to observe[7] B system concentrations as low as one part in 10^7, where the time to observe a resonance at one point has been at most in the range of ten to fifteen minutes, beyond which time the yield of data together with increasing instabilities becomes unpractical.

The two species double-resonance spectroscopy is carried out as follows. A measuring sequence begins by allowing the A system to come into equilibrium with the lattice. We assume initially that no radio-frequency fields are present and the A system is ordered by the nuclear magnetic or electric quadrupole interaction in a spin-lattice relaxation time T_1, which must be long to detect rare B spins. The A system is next prepared in an ordered metastable state which can be characterized by a low spin-temperature[8]. This metastable state is usually described in some interaction representation or rotating reference frame by a time independent hamiltonian which, along with the low spin-temperature, implies that the nuclear magnetic moments are preferentially aligned along a rotating radio-frequency field or local dipolar fields. The initial metastable nature of the A system implies the absence of a thermodynamic equilibrium between the A spins and the lattice. This equilibrium, however, is approached through spin-lattice relaxation mechanisms which act in the new frame of reference. The time rate of change of the inverse spin temperature of the A system is given by[9]

$$\frac{d\beta_A}{dt} = -\frac{1}{T_1^*}(\beta_A - \beta_o), \qquad (1)$$

where $\beta_A = 1/kT_{sA}$, $\beta_o = 1/kT_L$, T_{sA} and T_L are respectively the A spin-temperature and the lattice temperature, and $(1/T_1^*)$ is the spin-lattice relaxation rate in the interaction representation. During the lifetime

T_1^* of the A metastable state, the B system is excited by a radio-frequency field applied at or near the B resonance. In the presence of this field the A and B spin systems are resonantly coupled, interact through dipolar interactions, and an additional relaxation mechanism is provided to relax the A spins. Equation (1) is then modified to give

$$\frac{d\beta_A}{dt} = -\frac{1}{T_1^*}(\beta_A - \beta_o) - \frac{1}{\tau_{AB}}(\beta_A - \beta_B), \qquad (2)$$

where τ_{AB}^{-1} is the transfer rate of spin energy or order between the A and B systems, and β_B is the inverse B spin-temperature. With the experimental conditions prevailing that $\beta_A \gg \beta_o$ ($T_{sA} \ll T_L$), and $\beta_B \approx 0$ as a result of saturation of the B spins in their rotating frame or interaction representation, we may write Eq. (2) as

$$\frac{d\beta_A}{dt} = -\left(\frac{1}{T_1^*} + \frac{1}{\tau_{AB}}\right)\beta_A, \qquad (3)$$

and

$$\beta_A = \beta_A(0)\exp\left(-\left(\frac{1}{T_1^*} + \frac{1}{\tau_{AB}}\right)t\right). \qquad (4)$$

The steps in a double resonance spectroscopy experiment are indicated in Fig. 1. The A system is first allowed to come to equilibrium with the lattice under the influence of at most a constant magnetic field. After a time of order $\sim 3T_1$, the A spin temperature is essentially in equilibrium with the lattice, and $\beta_A = \beta_o$. The A spins are then prepared in an ordered metastable state in an interaction representation where the system is described by a time-independent hamiltonian and an initially large value of β_A. As indicated in Fig. 1b and Eq. (1), the inverse spin temperature relaxes with an exponential decay rate given by $(1/T_1^*)$ for the A spins in their transformed frame of reference. During a time of the order of the A relaxation time T_1^* the B spins are excited by a suitable

radio-frequency field, and an additional relaxation term $(1/\tau_{AB})$ is provided, as indicated in Eq. (2). The rate of relaxation corresponding to this term is maximized when the B irradiation frequency is in the neighborhood of the laboratory B resonance, and it is proportional to the number of B spins present[2,7,11]. The behavior of β_A when there is a contribution from the $(1/\tau_{AB})$ term is indicated by the dashed line in Fig. 1b. Following the turnoff of the B radio-frequency field, β_A is measured in terms of the amplitude of the A spin free induction decay[10]. The sequence of events is then repeated continuously while sweeping the B radio-frequency through the B resonance, and the B resonance is displayed by recording the changes in the detected A signal. The minimum rate $1/\tau_{AB}$, or equivalently, the minimum number of B spins, detectable in such an experiment, is inversely proportional to the available A spin signal-to-noise ratio and to T_1^*. The advantage of a long T_1^* is clearly in the length of time available to effect cross-relaxation between the A and B spin systems. But a long T_1^* is usually determined by a long laboratory frame relaxation time T_1. This is a distinct disadvantage, as can be seen in Fig. 1a, for it means that while the sensitivity increases with T_1^*, a corresponding increase in the double resonance cycling equilibration time occurs, thereby reducing the data acquisition rate as well as increasing the stability requirements of the apparatus. While it is desirable to have a long T_1^*, it is desirable to have as short a T_1 as possible.

To circumvent the long T_1 equilibration time referred to above, the introduction of a third spin species is made. Let us consider the three spin systems A, B, and C as depicted in Fig. 2, which we can selectively excite and couple to each other. Suppose that the C spins have such a low abundance that they cannot be observed directly, and it is these spins that we wish to detect. Let the B spins be denoted as an abundant spin system (they now

play the role of the A spins in the previous discussion) which can be established in a metastable state with a long T_1^*, and thus can provide a high double resonance sensitivity for C spin detection. Finally we define a new A spin system as a third spin system with a short T_{1A}, which is to serve as the source of energy and order for the B system. We now specify that a short T_{1A} will allow the A spins to reach equilibrium quickly. The first step is to create a metastable ordered A state, and transfer the order of this state to the B spins which initially are in equilibrium with the lattice, thereby reducing the B spin-temperature. This transfer takes place in a time corresponding to the cross-relaxation time of the coupled A and B systems. A typical time is on the order of one millisecond. Thus, within a time on the order of T_{1A}, we can order the B spins without requiring that one must wait a long B spin-lattice equilibration time T_{1B}. We have thereby reduced by a factor $\sim T_{1B}/T_{1A}$ the time necessary to establish the B spins in an ordered metastable state. For Cl^{35} A spins and proton B spins in paradichlorobenzene at 77°K this is a factor of approximately 100 in zero magnetic field. Following the establishment of the B metastable state by the A spins, a double resonance experiment is performed with the B and C spin systems, taking full advantage of the long B spin-lattice relaxation time. The ordering of the B system, as well as the sampling of the B spin temperature, is performed by radio-frequency pulses applied to the A system. This will be explained in detail below. The B spin temperature is monitored by measuring the amplitude of the free induction decay of the A signal.

This sequence has been successfully applied to the detection of enriched deuterium and naturally abundant carbon 13 in a sample of paradichlorobenzene. The observation of carbon 13 is the first reported for this nucleus in natural abundance in a solid. The usefulness of this new

scheme manifests itself in two ways. For sensitive detection of unknown C spins, the ability to perform the double-resonance experiment with a long B spin-lattice relaxation time of the order of an hour, and a signal-to-noise ratio for the A spins of 50/1, makes it possible to observe the effect of a cross-relaxation rate $(1/\tau_{BC}) \sim (25 \text{ hours})^{-1}$ with a signal-to-noise ratio of 2/1. And associated with the sensitivity there are the advantages of stability and experimental practicality because the measurement of a signal from the A system with a short T_1 allows for an easily observable and repeatable signal, and one to which the apparatus can be readily tuned. If one chooses a zero field quadrupolar system for the A system, as was done in the experimental work reported here, the need for a large magnetic field (~ 10 kilogauss) and costly stabilized magnet does not exist. It is thus possible to achieve a reduction in experimental costs and bulk at the price of somewhat more complicated electronics.

The creation of the ordered proton state in paradichlorobenzene reported in this work is similar to the experiment of Goldman and Landesman[12]. The difference in our approach lies in the use of pulsed spin-locking techniques rather than the continuous wave off-resonance excitation method of the above authors.

II. PARADICHLOROBENZENE EXPERIMENT

Preparation and Monitering of the B System

The three species double-resonance method outlined above can be applied to a variety of systems. As for the particular work reported here, we will apply it in detail to the relevant spin systems in paradicholorobenzene ($C_6H_4Cl_2$). We assume that at all times we can describe each spin system by an appropriate density matrix and spin temperature.[8] At all times we shall keep in mind the basic thermodynamic model shown in Fig. 2.

The A system is comprised of the 75.4% abundant Cl^{35} spins ($I = 3/2$). In zero external magnetic field the A spins are described by a large quadrupole interaction plus small dipolar interactions. The A system hamiltonian is given by

$$\mathcal{H}^A = \mathcal{H}_Q^A + \mathcal{H}_{DD}^{AB} + \mathcal{H}_{DD}^{AC} + \mathcal{H}_{DD}^{AA'} + \mathcal{H}_{DD}^{AA}, \tag{5}$$

where

$$\mathcal{H}_Q^A = \sum_{A\ \text{spins}} \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right] \tag{6}$$

and $\mathcal{H}_{DD}^{AB}$, $\mathcal{H}_{DD}^{AC}$, $\mathcal{H}_{DD}^{AA'}$, and $\mathcal{H}_{DD}^{AA}$ are the dipolar interactions of the A spins with other spin species B, C and A' for the first three terms, and among themselves for the last term. The indicated sum in (6) is to be taken over all Cl^{35} spins in the sample volume. As shown in Fig. 3a the laboratory zero field spectrum consists of two doubly degenerate levels separated by the angular frequency[13]

$$\omega_A = \frac{e^2 q Q}{2\hbar}\left(1 + \frac{\eta^2}{3}\right)^{1/2}. \tag{7}$$

For the Cl^{35} nucleus in paradichlorobenzene at liquid nitrogen temperatures this corresponds to a 34.78 mHz splitting. The measured A spin-lattice

relaxation time at 77°K is $T_{1A} = 0.39$ sec, and is determined by quadrupolar spin-lattice interactions. The remaining dipolar terms in Eq. (5) are expressed in terms of the usual dipolar hamiltonian.[14]

$$\mathcal{H}_{DD}^{IS} = \sum_{I\ \text{spins}} \sum_{S\ \text{spins}} \frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3} (A+B+C+D+E+F), \tag{8}$$

where

$$A = I_z S_z (1 - 3\cos^2\theta), \tag{9}$$

$$B = (I_+ S_- + I_- S_+)(1/4)(1 - 3\cos^2\theta)\, e^{-i\phi}, \tag{10}$$

$$C = (I_z S_+ + S_z I_+)(-3/2)\sin\theta\cos\theta\, e^{+i\phi}, \tag{11}$$

$$D = C^* = (I_z S_- + S_z I_-)(-3/2)\sin\theta\cos\theta\, e^{-i\phi}, \tag{12}$$

$$E = I_+ S_+ (-3/4)\sin^2\theta\, e^{-2i\phi}, \tag{13}$$

$$F = E^* = I_- S_- (-3/4)\sin^2\theta\, e^{+2i\phi}. \tag{14}$$

The spin operator I corresponds to the A (Cl^{35}) spins while the spin operator S corresponds to the B spins (protons) in the term $\mathcal{H}_{DD}^{AB}$, the C spins (carbon 13 or deuterium) in $\mathcal{H}_{DD}^{AC}$, the Cl^{37} spins in $\mathcal{H}_{DD}^{AA'}$, and finally the Cl^{35} spins in $\mathcal{H}_{DD}^{AA}$, the dipole-dipole interaction among A spins. Since the quadrupole interaction is quite large, the term $\mathcal{H}_Q^A$ clearly dominates Eq. (5) and the dipolar terms are small perturbations.

The protons comprise the B spin system, and in zero field are described by the dipole-dipole hamiltonian $\mathcal{H}_{DD}^{BB}$ of form of Eq. (8). The A-B dipolar interaction has been arbitrarily associated with the A spin hamiltonian, and the B-C dipolar interactions will be associated with a C spin hamiltonian. In either case $\mathcal{H}_{DD}^{BB}$ clearly dominates $\mathcal{H}_{DD}^{AB}$ for $\gamma_B \gg \gamma_A, \gamma_C$, and the number density of B spins (N_B) is larger than either the number density of A spins (N_A) or C spins (N_C). In zero field the B spins are characterized by a dipolar spectrum of width $\sim \gamma_B H_L^B$ is the average local field seen by the B spins.

The local fields, due mainly to protons, are of the order of three to four gauss in solids, and the width of the B dipolar spectrum is ~ 12 to 16 kHz as indicated in Fig. 3c. The zero field proton spin-lattice relaxation time in paradichlorobenzene is measured to be $T_{1B} \simeq 46$ seconds.

It is readily seen from the zero field spectra of the A and B spins, as shown in Figs. 3a and 3c, that any direct coupling between the two spin systems in the absence of external fields is small due to the large difference in their characteristic splittings. To bring about this coupling and the establishment of a B system metastable state a "spin-locking" procedure[2] is applied to the A spins during which the A and B spins are strongly coupled by dipolar interactions. The metastable state is attained in zero field, and decays through spin-lattice relaxation mechanisms with a time constant $T^*_{1B} = T_{1B} = 46$ sec. for the protons. This state will be characterized by an initially low spin-temperature which relaxes toward the lattice temperature $T_L = 77°K$.

The spin-locking procedure is described first in terms of a pure magnetic system in an external magnetic field (H_o), as follows. At t = o let the system be in equilibrium with the lattice at the temperature T_L with a magnetization

$$M_o = C\, H_o/T_L, \tag{15}$$

aligned along the z or magnetic field axis, where

$$C = N\gamma^2 \hbar^2 I(I + 1)/3k.$$

A radio-frequency magnetic field is applied along the x-axis at the resonance frequency $\omega_o = \gamma H_o$. The field is applied for a time $t_w = \pi/(2\gamma H_1) << T_2$, where H_1 is the magnitude of the rotating component of the field, and T_2 is the spin-spin relaxation time. At the time t_w the magnetization has been rotated into the x-y plane. In a frame of reference rotating about the z-axis at the angular frequency ω_o the magnetization now lies along the y-axis,

and H_1 lies along the x-axis. The phase of the radio-frequency field is then shifted in a time $\tau << 2\pi/\gamma H_1$ such that H_1 and M_o now lie parallel in this rotating frame. Following this phase shift we have, in the rotating frame, a large magnetization aligned along a small constant field. To obtain the initial spin-temperature in this reference frame we apply Eq. (15) to the rotating frame magnetization after the phase shift has occurred and before any relaxation takes place; C is a constant independent of reference frame and H_o is replaced by H_1 giving

$$M_o = CH_1/T_s(0), \tag{16}$$

where $T_s(0)$ is the initial spin temperature in the rotating frame. Combining the equilibrium value of M_o from Eq. (15) with Eq. (16) we have

$$T_s(0) = T_L\ (H_1/H_o), \tag{17}$$

which for H_1 = 10 gauss, $H_o = 10^4$ gauss, and $T_L = 77°K$, results in an initial rotating frame spin-temperature of $T_s(0)$ = 77 millidegrees. Following the establishment of this rotating frame spin state and temperature, the system undergoes spin-lattice relaxation, expressed by

$$T_s(t) = T_s(0)\ e^{(t/T_1^*)}. \tag{18}$$

Note that if H_1 is turned off suddenly at any point the remaining transverse magnetization (proportional to the inverse spin-temperature) will precess in the laboratory field and decay with characteristic time T_2. By measuring the amplitude of this magnetization we obtain a direct measure of the inverse spin-temperature in the rotating frame at the end of the radio-frequency pulse.

The above description of spin-locking can be carried over to a pure quadrupole (I = 3/2) Cl^{35} A spin system;[15] and it can be shown that the +3/2 and +1/2 levels can be considered for simplicity as decoupled from the -3/2 and -1/2 levels, each pair acting as a pseudospin I = 1/2 spin system

in an interaction representation. Let us return to the hamiltonian of Eq. (5) and add to it a radio-frequency interaction $\mathcal{H}^A_{rf}$ at resonance with the Cl^{35} quadrupole splitting, determined by $\mathcal{H}^A_Q$, so that

$$\mathcal{H}^A_{rf} = -\gamma\hbar 2H_1 I^A_x \cos \omega_A t , \tag{19}$$

and the total A hamiltonian becomes

$$\mathcal{H}_A = \mathcal{H}^A_Q - \gamma\hbar 2H_1 I^A_x \cos \omega_A t + \text{(dipolar terms)}. \tag{20}$$

It is assumed that H_1 is larger than the effective local fields acting on the Cl^{35} nuclei so that we may drop dipolar contributions as a good first approximation. As in the spin-locking description for a pure magnetic system, the hamiltonian of Eq. (20) becomes time independent upon application of a suitable transformation operator, namely

$$U = \exp (i \mathcal{H}^A_Q t/\hbar). \tag{21}$$

$\mathcal{H}_A$ transforms to the interaction representation according to

$$(\mathcal{H}_A)^* = U^{-1} \mathcal{H}_A U - \mathcal{H}^A_Q. \tag{22}$$

With some manipulation the spin operators U, $\mathcal{H}^A_Q$, and I^A_X may be expressed as 4×4 matrices. Upon performing the operation indicated in Eq. (22) and dropping negligible dipolar contributions, the result is[15]

$$(\mathcal{H}_A)^* = (-\hbar\gamma H_1 \sigma) \begin{array}{c} \begin{array}{cccc} [3/2] & [1/2] & [-1/2] & [-3/2] \end{array} \\ \begin{vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix} \end{array} \begin{array}{c} \\ [3/2] \\ [1/2] \\ [-1/2] \\ [-3/2] \end{array}$$

$$+ \text{(time dependent terms)}, \tag{23}$$

where

$$\sigma = \sqrt{3}\ (\alpha^4 + \beta^4) + 2\alpha\,\beta\,(\alpha^2 - \beta^2),$$
$$\alpha = 1/(1 + L^2)^{1/2},\ \beta^2 = 1 - \alpha^2,$$
$$L = \sqrt{3}\,[(1 + \eta^2/3)^{1/2} - 1]/\eta.$$

We retain only the secular (time-independent) terms, and drop non-secular terms oscillating at the frequencies $\pm\omega_A$ and $\pm 2\omega_A$, because these terms average to zero quickly, and also drop the secular dipolar terms because they can be considered as a small perturbation. We are then left with a secular A spin hamiltonian in the interaction representation with Zeeman energy eigenvalues

$$\lambda = \pm\,(\hbar\,\sigma\,\gamma\,H_1). \tag{24}$$

The λ energy splitting as indicated in Fig. 3b characterizes the A spins in the spin-locked state. Since λ is a function of H_1, and H_1 can be varied experimentally, it is then possible to bring about an overlap of the A interaction-representation spectrum (the λ splitting) and the B laboratory dipolar spectrum to obtain resonant cross-relaxation.[16] It is important to note that the effective cross-relaxation occurs only when the A radio-frequency pulse is applied, and that the pulse thereby acts as an on-off coupling switch between the A and B systems. The coupling terms are the secular terms of $U^{-1}\,\mathcal{H}_{DD}^{AB}\,U$ implicit in Eq. (22).

One may obtain a value for the initial spin-temperature of the quadrupole system after spin-locking by noting that the laboratory precessing magnetization following a 90° radio-frequency pulse is described, for $I = 3/2$ and $\eta = 0$, by [13, 17]

$$\langle M_x \rangle = M_o \sin \omega_A t, \tag{25}$$
$$\langle M_y \rangle = \langle M_z \rangle = 0,$$

where

$$M_o = \sqrt{3}\ N_A\ \omega_A\ \hbar^2\ \gamma_A/4kT_L. \tag{26}$$

Under spin-lock conditions for an I = 3/2 and η = 0 quadrupole system in zero field, M_o is aligned along the effective field, $\sqrt{3}\ H_1$, in the interaction representation. The model of a pseudo-spin I = 1/2 conveniently portrays the interaction representation for the quadrupole system. Using Eq. (17) and replacing H_1 by $\sqrt{3}\ H_1$, and H_o by an equivalent field necessary to produce the magnetization of Eq. (26), the initial A spin temperature in the spin-locked state is given by

$$T_s(0) = \frac{\gamma_A H_1}{\omega_A}\ T_L. \tag{27}$$

For $T_L = 77°K$, $H_1 = 10$ gauss and $\omega_A \simeq 35$ mHz, $T_s(0) \simeq 10^{-2}°K$.

The density matrix for the A and B spin systems is approximated by

$$\rho = \exp\ \{-\beta_A\ (\mathcal{H}_A)^*_s - \beta_B\ \mathcal{H}^{BB}_{DD}\}\ /\mathrm{Tr}\ \{1\} \tag{28}$$

where the subscript "s" indicates only the secular terms are present. Cross-relaxation between A and B spins comes about via the secular terms of the transformed A-B dipole interaction

$$(\mathcal{H}^{AB}_{DD})^*_s = (U^{-1}\ \mathcal{H}^{AB}_{DD}\ U)_s\ . \tag{29}$$

By considering the rate of change of $\langle (\mathcal{H}_A)^*_s \rangle$ and $\langle \mathcal{H}^{BB}_{DD} \rangle$, using second order perturbation theory, and the spin-temperature assumption, it has been shown[15,18] that the inverse spin-temperatures β_A and β_B for the A and B systems obey the relations

$$\beta_A = \frac{\epsilon_{AB}}{\tau_{AB}}\ (\beta_A - \beta_B), \tag{30}$$

and

$$\beta_B = \frac{1}{\tau_{AB}}\ (\beta_B - \beta_A), \tag{31}$$

where

$$\epsilon_{AB} = \frac{\mathrm{Tr}\{(\mathcal{H}_{DD}^{BB})^2\}}{\mathrm{Tr}\{(\mathcal{H}_A^*)_s^2\}} = \frac{N_B\ \gamma_B^2\ H_{LB}^2\ I_B\ (I_B + 1)}{N_A\ \gamma_A^2\ 3H_1^2\ I_A\ (I_A + 1)}, \tag{32}$$

$$(\tau_{AB})^{-1} = \frac{\int_0^\infty d\tau \mathrm{Tr}\{(\mathcal{H}_A^*)_s[\mathcal{H}'(0), [\mathcal{H}'(-\tau), (\mathcal{H}_A^*)_s]]\}}{\hbar^2\ \mathrm{Tr}\{(\mathcal{H}_{DD}^{BB})^2\}},$$

and

$$\mathcal{H}'(\tau) = [\exp(i\tau\hbar^{-1}\{(\mathcal{H}_A^*)_s + (\mathcal{H}_{DD}^{BB})\}](\mathcal{H}_{DD}^{AB})_s^*\ [\exp(-i\tau\hbar^{-1}\{(\mathcal{H}_A^*)_s + (\mathcal{H}_{DD}^{BB})\}]. \tag{33}$$

ϵ_{AB} is the ratio of the heat capacities at a common spin-temperature of the Cl^{35} spins in the interaction representation and of the proton laboratory spin system. For an applied field $H_1 \sim 17.5$ gauss, and effective local field $H_{LB} \sim 4$ gauss, Eq. (32) gives $\epsilon_{AB} \sim 1$; and we see from Eqs. (30) and (31) that β_A and β_B change nearly at the same rate. These are the conditions to which the experimental work reported here were subject. We may express τ_{AB} in the approximate form[2,15]

$$\tau_{AB} \approx T_{AB}^2/T_{BB}, \tag{34}$$

where T_{AB}^{-2} and T_{BB}^{-2} are the component contributions to the B spin dipolar second moment caused by A and B neighbors respectively. For Cl^{35} (A) and proton (B) spins in paradichlorobenzene the values of $T_{BB} \sim 10$ us. and $T_{AB} \sim 200$ us. apply. Therefore Eq. (34) yields $\tau_{AB} \sim 2$ m sec., which is approximately the measured time constant for the proton-chlorine cross-relaxation.

Let us assume that the spin-locking pulses applied to the A system have a duration of at least several relaxation times τ_{AB}. Then, by Eq. (30) we see that the A and B spin-temperatures reach a common value $\beta_A \simeq \beta_B$. The final spin-temperature of the coupled A and B spins is

derived by a simple conservation of energy argument. Let t = 0 be defined just following the 90° phase-shift of the A spin-locking pulse, where the initial A spin-temperature is given by Eq. (27) and the B spin-temperature is assumed to have an initial value $T_B(0)$. With $\tau_{AB} << T^*_{1A}$ ($T^*_{1A} \simeq 45$ ms for the spin-locked state in the interaction representation at 77°K in paradicholorobenzene), we may equate the initial and final expectation values of the summed energies of the two spin systems. Using the density matrix of Eq. (28), the identities $\mathrm{Tr}\,\{(\mathcal{H}^*_A)_s\} = \mathrm{Tr}\{\mathcal{H}^{BB}_{DD}\} = 0$, and the high temperature approximation, the energy expectation values for the A and B spins are expressed as

$$\begin{aligned} \langle (\mathcal{H}^*_A)_s \rangle &= \mathrm{Tr}\{\rho(\mathcal{H}^*_A)_s\} \simeq -\beta_A\ \mathrm{Tr}\ \{(\mathcal{H}^*_A)^2_s\}/\mathrm{Tr}\ \{1\}, \\ \langle \mathcal{H}^{BB}_{DD} \rangle &= \mathrm{Tr}\{\rho\ \mathcal{H}^{BB}_{DD}\} \simeq -\beta_B\ \mathrm{Tr}\{(\mathcal{H}^{BB}_{DD})^2\}/\mathrm{Tr}\{1\}. \end{aligned} \tag{35}$$

Equating the initial summed energies of the two spin systems at different spin-temperatures to the final energy at a common spin-temperature results in an expression for the final equilibrium spin-temperature,

$$\beta^{AB}_e = \frac{\beta_A\ (0)}{1 + \epsilon_{AB}} + \frac{\beta_B\ (0)}{1 + \epsilon^{-1}_{AB}}, \tag{36}$$

where ϵ_{AB} is given by Eq. (32). For the Cl^{35} A and proton B systems in paradichlorobenzene described in the experimental work of this paper, $\epsilon_{AB} \sim 1$, and we have

$$\beta^{AB}_e \cong 1/2\ (\beta_A(0) + \beta_B(0)). \tag{37}$$

The initial inverse spin-temperature $\beta_A(0)$ is determined by the assumed spin-lattice equilibrium state of the A spins before application of the radio-frequency pulse as well as the amplitude of the pulse. To obtain $\beta_A(0)$ we rewrite Eq. (27) according to $\beta = 1/kT$, which results in

$$\beta_A(0) \equiv (\omega_A/\gamma H_1)(1/kT_L). \tag{38}$$

The preparation of the B metastable state is shown in Fig. 4. At $t = t_o$ both the A Cl^{35} quadrupole and B proton dipolar spin systems are in equilibrium with the lattice, and a spin-locking pulse at the A quadrupole resonance frequency, affecting only the A spins, is initiated. At $t = t_1$ the phase of the radio-frequency field has been shifted by 90° to bring the H_1 field parallel to the A magnetization. After a short Cl^{35} spin-spin relaxation time the inverse A spin-temperature $\beta_A(0)$ of Eq. (38) is established. At $t = t_2$ the pulse, and therefore the A-B coupling, is abruptly turned off. During the time $(t_2-t_1) \simeq 3\tau_{AB}$ the A and B spin systems indicated in Figs. 3b and 3c have undergone cross-relaxation and have reached a common temperature given by Eq. (36), resulting in a marked lowering of the B spin-temperature. At $t = t_3$ the A spins have once again come into equilibrium with the lattice $((t_3 - t_2) \sim 3T_{1A})$, while β_B has essentially remained constant as a consequence of the long B spin-lattice relaxation time. The spin-locking process is repeated at $t = t_3$ and at $t = t_4$ and, as indicated in Fig. 4, the B spin-temperature is further reduced. By application of a sequence of A spin-locking pulses separated by a few T_{1A} it is then possible to reduce the B spin-temperature from its initial value to $T_B \cong T_A(0)$, where $T_A(0)$ is the initial A spin-temperature of Eq. (27). The protons are then in a metastable zero field dipolar ordered state characterized by an initial low spin-temperature which relaxes to T_L, the lattice-temperature, at a rate $1/T_{1B}$. The time period necessary to develop this initial state is of the order of a few time constants T_{1A} (~ 5 seconds in paradichlorobenzene). An alternative method of producing this initial zero field dipolar spin-temperature is to apply the method of adiabatic demagnetization. The sample would be placed in a field H_o, allowed to come into equilibrium with the lattice (high field proton T_{1B} ~ hours in paradi-

chlorobenzene), and then removed to zero field in a time short compared to T_{1B}. Equating entropy in the initial applied field (H_o) to entropy in the final effective local field (H_{LB}) leads to a final zero field temperature $T_B(0) \approx (H_{LB}/H_o)T_L$. To bring about the same B spin-temperature as in the scheme described above, using values of $H_{LB} \sim 4$ gauss, $T_L = 77°K$ and $T_B(0) \sim 10^{-2}$ °K, a field $H_o \sim 30$ kilogauss would be required. The high field equilibration time and the necessity of a large magnetic field make the adiabatic demagnetization technique unattractive as compared to the novel cooling scheme we have introduced in this paper.

The B spin-temperature in the three spin species double-resonance method can be measured as follows. The inverse A spin-temperature at the termination of a spin-locking pulse is given by Eq. (36). It will vary between the limits $\beta_A(0)$ and $\beta_A(0)/(1 + \epsilon_{AB})$ as the B spin-temperature varies between $\beta_A(0)$ (when the B spins have been precooled by the A spins) and zero (when the B system has been saturated or, approximately, when it is in equilibrium with the lattice). This variation of β_e^{AB} is then a direct measure of β_B through Eq. (36), and is observed by measuring the amplitude of the A free induction decay following the spin-locking pulse: the larger the A signal at the end of the pulse the lower the B spin-temperature at the beginning of the pulse. Therefore at any time in zero field the B spin-temperature can be sampled by applying an A spin-locking pulse and observing the A spin free-induction decay.

Double Resonance Detection of the C System

Following a sequence of A spin-locking pulses the B spin system is left in a low temperature metastable state and can now be coupled to a third (C) system which we wish to observe by means of the usual double resonance techniques. Both B spin-lattice relaxation and cross-relaxation

between the B and C spins will produce an increased B spin temperature which is measured as described above. Sequentially, therefore, (1) the B spins are prepared at a low spin-temperature by a sequence of A pulses; (2) the B spins are brought into dynamic interaction with the C spins; and (3) the B spin-temperature is measured by application of an A spin-locking pulse which senses the extent of the previous B-C cross-relaxation and C spin radio-frequency excitation during the B-C interaction time in terms of the increase in the B spin-temperature.

Once the B metastable state has been established it is possible to apply both constant and radio-frequency magnetic fields, and depending upon the nature of the C spin system to be detected it is of advantage to make use of one of the following four prepared B spin states:

(1) The zero field ordered dipolar state produced as described above.

(2) We may apply a pulsed magnetic field of strength H_o as indicated in Fig. 5b. This results in an ordered B Zeeman state.

(3) By applying a radio-frequency pulse of frequency $\omega = \gamma_B H_o$ beginning at the end of the rise of the pulsed field of (2) and ending at the beginning of the fall of the field as indicated in Fig. 5c, we may spin-lock the proton magnetization along the applied radio-frequency field in the rotating frame. The spin-locking and spin-unlocking occur during the rise and fall of the magnetic field pulse and the dynamics are the same as those occurring in fast passage experiments[19] in which the Zeeman magnetic resonance is swept through the fixed frequency of the radio-frequency transmitter.

(4) Finally, it is possible to produce and recover an adiabatically demagnetized state in the rotating frame by turning off and on the B radio-frequency field as indicated in Fig. 5d.

The characteristic splittings of these four alternative B spin states are summarized in Fig. 6. In Fig. 6a is shown the zero field dipolar spectrum characterized by the local field H_L^B. H_L^B is defined from the expression for $\langle \mathcal{H}_{DD}^{BB} \rangle$ of Eq. (35) by setting $\langle \mathcal{H}_{DD}^{BB} \rangle = \gamma_B \hbar \langle I_Z^B H_L^B \rangle$ where H_L^B is the equivalent of a Zeeman field necessary to provide the B spins an internal Zeeman energy equal to the dipolar energy. Figure 6b shows the Zeeman splitting in field H_o, Fig. 6c shows the Zeeman splitting in the rotating frame along the rotating magnetic field, and Fig. 6d shows the dipolar spectrum in the rotating frame characterized by a modified local field $H_L'^B \leq H_L^B$. In defining $H_L'^B$ one proceeds as in the case for H_L^B except that only the secular terms of $(\mathcal{H}_{DD}^{BB})^*$ in the rotating frame are retained.

As we have noted above, the A and B spin systems come into equilibrium through an effective cross-relaxation mechanism in times of the order of milliseconds. Once the B spin system has been prepared in one of the above four described states it will be brought into contact with the C system. The interaction between the B and C spin systems is similar to that between the A and B systems. A radio-frequency magnetic field of strength H_{1C} is applied to the C spins at their laboratory resonance frequency (Fig. 3e) and the analysis follows by transforming to the C spin interaction representation where a spin-temperature is defined for the C spins, and the C splittings are characterized by $\gamma_C H_{1C}$ (Fig. 3d). The equations governing the B and C spin-temperatures are those of Eqs. (30) to (34) where we replace A by C; $(\mathcal{H}_C^*)$ of Eqs. (32) and (33) is obtained from the C hamiltonian (neglecting the small dipolar terms)

$$\mathcal{H}_C = \mathcal{H}^C \text{ (Zeeman and/or quadrupole)} + \mathcal{H}_{rf}^C$$

by the transformation

$$(\mathcal{H}_C^*) = \exp(-i\mathcal{H}^C t/\hbar)\, \mathcal{H}_C \exp(i\, \mathcal{H}^C t/\hbar) - \mathcal{H}^C.$$

The equilibrium value of the spin-temperature is obtained from Eq. (36) by replacing $\beta_A(0)$ by $\beta_C(0)$ and ϵ_{AB} by ϵ_{CB} giving,

$$\beta_e^{BC} = \frac{\beta_C(0)}{1+\epsilon_{CB}} + \frac{\beta_B(0)}{1+\epsilon_{CB}^{-1}} . \tag{39}$$

From Eq. (32) we obtain $\epsilon_{CB} \approx N_B/N_C$, and note that if the C spins are rare ($N_C << N_B$) then, from Eq. (39), β_e^{BC} will be nearly the same as $\beta_B(0)$. In such a case, to obtain a significant change in the B spin-temperature, it is necessary to maintain by external means a high C spin-temperature, and thus prevent the B and C systems from coming into thermal equilibrium. A number of techniques have been used to accomplish this task: (1) periodically pulsing on and off of the C r.f. field[20]; (2) periodic π-phase shift of the C r.f. field [2]; (3) audio rotary saturation of the C spins in the rotating frame[21]; (4) saturation of the C spins by frequency modulation (a form of rotary saturation) of the C r.f. field.[7] The C resonance is then detected through an increase in the B spin-temperature, which is in turn monitored by measurement of the A free induction decay. Equation (3) is now rewritten for the B spins to express the rate of change of B spin temperature in terms of the B-C cross-relaxation rate $1/\tau_{BC}$ and T_{1B},

$$\left(\frac{d\beta_B}{dt}\right) = -\left(\frac{1}{T_{1B}} + \frac{1}{\tau_{BC}}\right)\beta_B, \tag{40}$$

where it is assumed that the C spins are saturated ($\beta_C = 0$) by external means. It is shown [22] in Reference 2 that τ_{BC} can be written as

$$\tau_{BC} \simeq \frac{N_B}{N_C} \left(\frac{8}{\pi}\right)^{1/2} \frac{T_{BC}^{\;2}}{T_{BB}} \quad , \tag{41}$$

where T_{BC}^{-2} and T_{BB}^{-2} are the contributions to the B spin second moment due to C and B spins respectively. It is evident from Eqs. (40) and (41) that a long T_{1B} makes it possible to observe the effect of a long τ_{BC} and consequently a small N_C.

In summary an ordered proton (B) dipolar state is produced by a sequence of Cl^{35} (A) spin-locking pulses. The B spins are then coupled in one of the four alternative states to a resonantly excited C spin system. The B spins are finally returned to the zero field dipolar state and coupled to the A system. The B spin-temperature is then sampled by recording the amplitude of the A free induction decay following a final A spin-locking pulse as is indicated in Fig. 5.

The sensitivity of the scheme presented here can be expressed in terms of the minimum detectable ratio of C to B spins $(N_C/N_B)_{min}$ as follows. The B spin-temperature evolves according to Eq. (40) with the initial condition $\beta_B = \beta_A(0)$. Allowing B-C cross-relaxation for a time T_{1B}, the fractional change in B spin-temperature, $\Delta\beta_B/\beta_B$, computed without ($\tau_{BC} = \infty$) and with effective B-C cross-relaxation is given by

$$\left.\frac{\Delta\beta_B}{\beta_B}\right)_{t=T_{1B}} = (1-e^{-T_{1B}/\tau_{BC}}) \sim T_{1B}/\tau_{BC} \quad . \tag{42}$$

The change in B spin-temperature is sensed in the measurement of the A spin-temperature as determined by Eq. (36), where β_e^{AB} is the spin-temperature of the A spins in thermodynamic equilibrium with the B spins and is proportional to the amplitude of the observed A signal. The minimum

observable change in the A signal, S_A, is then given by

$$\left(\frac{\Delta S_A}{S_A}\right)_{min} = \frac{1}{(S/N)_A} = \frac{\Delta\beta_e^{AB}}{\beta_e^{AB}} , \tag{43}$$

where $(S/N)_A$ is the observed A signal-to-noise ratio. Noting that in Eq. (36) $\beta_A(0)$ is a constant, we may write $\Delta\beta_e^{AB} = (1+\epsilon_{AB}^{-1})^{-1}\,\Delta\beta_B$ where $\Delta\beta_B$ is the variation of the B spin temperature as found just prior to the application of a an A spin-lock sensing pulse. Combining this with Eqs. (41), (42), and (43) we find

$$\left(\frac{N_C}{N_B}\right)_{min} \simeq \left(\frac{8}{\pi}\right)^{1/2} \frac{(1+\epsilon_{AB}^{-1})}{W_{BC}\,T_{1B}\,(S/N)_A} , \tag{44}$$

where the rate W_{BC} is defined by $W_{BC} = T_{BB}/T_{BC}^2$. Using the experimental values $\epsilon_{AB} \sim 1$, $W_{BC} \sim 10^3$ sec.$^{-1}$, and $(S/N)_A \sim 50$ in Eq. (44), the sensitivity for three spin double-resonance detection in paradichlorobenzene may be expressed as

$$\left(\frac{N_C}{N_B}\right)_{min} \sim \frac{4\times10^{-5}}{T_{1B}(\text{sec})}$$

In zero field $T_{1B} \sim$ 46 sec, in high field $T_{1B} \sim 1$ hr, and in the high field adiabatically demagnetized state in the rotating frame (ADRF) $T_{1B} \sim 12$ sec. These yield the following sensitivities,

$$\left(\frac{N_C}{N_B}\right)_{min} \text{(zero field)} \sim 10^{-6}, \tag{45}$$

$$\left(\frac{N_C}{N_B}\right)_{min} \text{(high field)} \sim 10^{-8}, \tag{46}$$

and

$$\frac{N_C}{N_B}_{min} (ADRF) \sim 3\times10^{-6}. \quad (47)$$

III. EXPERIMENTAL RESULTS

The paradichlorobenzene sample used was a cylinder of approximately 1/2 inch diameter and 3/4 inch length. All measurements reported in this paper were taken at 77°K in a liquid nitrogen bath. The electronic techniques used were relatively standard ones applied in previous double-resonance experiments and the apparatus is indicated in the block diagram of Fig. 7. The A sample coil served as both the transmitter and receiver coil for the A system. A single (B-C) coil mounted concentrically with the A coil was switched by means of a mechanical relay between the B and C radio-frequency transmitter tank circuits. Audio and pulsed d.c. current Helmholtz coils are placed perpendicular to the A and B-C coils as shown.

Detection of Deuterium

The observed deuterium (I=1) zero field quadrupole resonance line for a 12% deuterium enriched sample of paradichlorobenzene is shown in Fig. 8. The $|+> \leftrightarrow |0>$ and $|->\leftrightarrow|0>$ pure quadrupole transitions are at 140.2 kHz and 134.8 kHz respectively with an $\eta e^2qQ/2h = 5.4$ kHz splitting. These results were obtained under zero field conditions, as indicated in Fig. 5a, by sequentially applying A spin-locking and C search radio-frequency pulses, thereby alternating A-B and B-C coupling. The C radio-frequency pulse had a duration of 1.0 sec, an amplitude of 2 gauss, and was π-phase switched every 5 ms. The experiment was performed at 77°K with an overall repetition time of 1.2 seconds.

An obvious feature of the resonances in Fig. 8 is the strong overlap of the η split lines. It is this overlap which makes possible the observation of this spin I = 1 system. A well resolved and larger η splitting would result in the absence of any secular B-C coupling term, and therefore the detection of the integer spin system with I = 1 would not be possible in the transformed representation. This property is discussed in detail in the following section. The contributions to the observed deuterium quadrupole linewidth are magnetic dipolar interactions, crystal strain broadening, and B-C cross-relaxation mechanisms.

The expected sensitivity for deuterium detection in zero field is given by Eq. (45) which clearly states that naturally abundant deuterium should be observable. However, detection of the naturally abundant deuterium resonances in this sample, with the techniques described here, was not possible because of overwhelming direct proton saturation effects caused by radio-frequency fields intended to excite only the deuterium transition. This can be seen in Fig. 9 where an extended plot of the observed (12% enriched) deuterium resonances is drawn. The deuterium resonances are shown as superpositions on the proton absorption edge. The upper dotted line in the figure corresponds to the A signal when the protons are at an infinite temperature while the lower corresponds to the proton temperature at the initial temperature of the A spin system. The signal varies between these two limits. The attainment of a high B spin-temperature can be caused by two effects: (1) effective cross-relaxation with a hot deuterium spin system represented by the deuterium resonance lines; and (2) direct heating of the protons by the radio-frequency field applied to the deuterium spins as indicated by the broad absorption shown in Fig. 9. Zero field dipolar absorption is a complicated problem to analyze when the

applied radio-frequency fields are of the order of or greater than the local fields. We will not treat this problem here.

The resonances shown in Fig. 8 were obtained with a field of $H_{1C} \simeq 2$ gauss. The energy matching condition for effective B-C cross-relaxation, evident from Figs. 3c and 3d, is $\omega_B = \gamma_B H_L^B \simeq \gamma_C H_{1C} = \omega_C$. Given $H_L^B \sim 3$ gauss, this condition is satisfied for a field $H_{1C} \approx 20$ gauss, and consequently $H_{1C} \simeq 2$ gauss cannot result in an optimum cross-relaxation rate. Increasing H_{1C} from 2 gauss toward the formally required value of 20 gauss would result in a faster B-C cross-relaxation rate, thereby allowing a stronger deuterium resonance line and observation of a less enriched sample. However, this gain is more than counterbalanced by the movement of the direct proton absorption edge to higher frequencies, resulting in the suppression of the deuterium resonance line. If H_{1C} is not phase shifted the absorption edge moves to lower frequencies such that it no longer covers the deuterium resonance. It was possible because of the relatively high magnetic heat capacity of the enriched (12%) deuterium system to observe the deuterium line by applying a 20 gauss radio-frequency field with no phase shifting, but for a naturally abundant (.01%) deuterium system of low heat capacity this is not possible. One might also decrease the rate at which the C radio-frequency field is shifted in phase by π radians. This favors less direct proton absorption because of reduction in undesired harmonics, but the decrease in double-resonance sensitivity is much greater because the deuterium system is no longer kept at a high spin-temperature. Consequently two contributions to direct proton absorption, heating in the wings of the line and heating due to the phase shift modulation, prevent the observation

of naturally abundant deuterium.

We have spoken only of saturation of the deuterium resonance by π-phase shifting. Audio saturation cannot be used because the audio radio-frequency fields used to heat the deuterium spins would directly couple into the zero field proton spectrum and heat the protons directly. The frequency modulation technique should be applicable because of the absence of low frequency components of the radio-frequency field which can heat the proton system directly. A number of attempts have been made to observe the deuterium resonance in a naturally abundant sample, and despite the care taken to avoid mixing problems, as described by Slusher[11], and the knowledge of the location of the deuterium resonance, an excessive amount of "mixing" noise was seen which masked any determinable deuterium line.

Detection of Carbon 13

In order to perturb the C^{13} system without directly affecting the proton system a Zeeman field must be applied, as shown in Fig. 5b. To then thermodynamically couple the protons and C^{13} spin systems the protons are spin-locked in a radio-frequency field of strength H_{1B}, and the C^{13} spins are subjected to a radio-frequency field of strength H_{1C}, applied at the C^{13} Zeeman resonance frequency, as shown in Fig. 5c. The cross-relaxation matching condition is then $\omega_B = \gamma_B H_{1B} \cong \gamma_C H_{1C} = \omega_C$. This method requires two radio-frequency fields applied to the sample at the same time. Large radio-frequency fields, $H_{1B} \gtrsim 5$ gauss (to effectively spin-lock the protons) and $H_{1C} \gtrsim 20$ gauss (to satisfy the matching condition above), are required. Although these experimental requirements can be met, it is much easier to apply the adiabatic demagnetization technique shown in Fig. 5d.

In the adiabatic demagnetization technique the separate B and C

radio-frequency pulses are applied to the sample at different times, and by using the switching relay shown in Fig. 7, only a single radio-frequency tank coil is needed. Cross-relaxation occurs between the B (proton) dipolar levels in the B rotating frame and the C^{13} Zeeman levels in the C^{13} rotating frame. The double-resonance matching condition is then $\gamma_B H_L^{'B} \simeq \gamma_C H_{1C}$, where $H_L^{'B} \sim 3$ gauss is a measure of the proton dipolar linewidth in the rotating frame. Radio-frequency fields of 5 to 10 gauss applied to the C resonance are then sufficient to satisfy the cross-relaxation matching condition. The presence at any time of at most one radio-frequency field, the use of a single B-C radio-frequency coil, and the reduction in the required strength of the C radio-frequency field make the method of adiabatic demagnetization in the rotating frame an easily applied one. The sequencing of magnetic field and radio-frequency pulses is shown in Fig. 10. A series of these pulses is shown, and one set of the pulses is expanded. The A spin-locking pulse barely appears as a pip centered between adjacent magnetic field pulses.

The time available to perform double-resonance between B and C spins is of the order of the T_1^* of the adiabatically demagnetized protons which is measured to be 12 sec at 77°K in a field of 130 gauss. The proton - C^{13} double-resonance cross-relaxation time of Eq. (41) is measured to be $\tau_{BC} \approx 0.1$ sec. For naturally abundant C^{13} and protons in paradichlorobenzene $(N_B/N_C) \simeq 60$, $T_{BB} \sim 10^{-5}$ sec, and $T_{BC} \sim 10^{-4}$ sec., which when inserted into Eq. (41) yields $\tau_{BC} \sim 0.16$ sec. The expected sensitivity for C^{13} double-resonance detection is calculated from Eq. (44) to be $(N_C/N_B)_{min} \sim 5\times10^{-6}$, and as the natural abundance of C^{13} yields the ratio $(N_C/N_B) \simeq 1/60$, the C^{13} double-resonance is easily observed. Double-resonance spectra were measured for both audio and π-phase-shift saturation of the C^{13} resonance. A typical audio-saturated line is shown in Fig. 11. The linewidth indicated

in the figure is not the natural linewidth of the C^{13} Zeeman system - rather is is characteristic of the double-resonance process. We choose here not to carry out an analysis to account for the lineshape, which would require consideration of the double-resonance dynamics when the C^{13} system is excited off resonance. The center dip is characteristic of the audio saturation technique and serves to establish the center of the line.

Comments

In the pulsed magnetic field experiments described here, care must be taken in adjusting the beginning and end of the B radio-frequency spin-locking pulse. Starting too early or ending too late may bring the radio-frequency field into such a position in time that the pulse, being of fixed frequency $\nu_B = 2\pi\gamma_B H_o$, will coincide with the magnetic field at a value $H_o/2$ (H_o being the maximum value of the field). Under such conditions the strongly coupled proton spins are subject to transitions in which the spin system absorbs a single photon and undergoes two spin flips, conserving energy, and resulting in the undesired effect of direct heating of the B spin system. This results in a suppression of the double-resonance detection sensitivity.

With regard to the adiabatic demagnetization scheme used to detect C^{13}, one might rightly question the necessity of applying the second of the two B radio-frequency pulses. If the magnetic field is turned off without the application of this pulse, then the rotating frame B order will remain in the B dipolar spectrum as the field is decreased and, upon reaching zero field, will reside in the zero field dipolar spectrum where it is sampled by the application of an A spin-locking pulse. Unfortunately, this process results in the undesired heating of the B spin system through a level crossing with the A spins. This comes about as

follows. The chlorine systems (Cl^{35} and Cl^{37}) both exhibit short spin-lattice relaxation times and by the end of the magnetic field pulse they will be in equilibrium states at the lattice temperature. In the presence of a magnetic field the degeneracy of the zero field $|\pm 1/2>$ chlorine states is lifted; for weak fields the splitting is proportional to $H_o \cos\theta$, θ being the angle between the magnetic field and the quadrupole quantization axis. Before the field is reduced the splitting of these levels is much larger than the B dipolar splitting, while in zero field the Cl dipolar splitting is smaller than the corresponding B dipolar splitting because of the length of the crystal internuclear distances and the relation $\gamma_C << \gamma_B$. It follows then that, as the magnetic field is reduced, the magnetic splitting of the Cl $|\pm 1/2>$ levels must cross the proton dipolar level splittings. When this happens the hot ($T = T_L$) Cl spins will cross-relax with the colder proton spin systems, irreversibly heating the latter. To avoid this situation, the second of the two B radio-frequency pulses is applied. This pulse serves to keep the Cl and proton systems decoupled by successively transferring the rotating frame proton dipolar order to rotating frame Zeeman order, laboratory frame Zeeman order, and finally to laboratory frame dipolar order. No crossing can occur as the magnetic field is lowered because the proton Zeeman splitting ($\sim \gamma_B H_o$) is always larger than the Cl $|\pm 1/2>$ splitting ($\sim \gamma_A H_o \cos\theta$). In zero field, a cross-relaxation between the proton and Cl dipolar spectra exists, but, because of the low specific heat of the Cl dipolar system, this can be neglected over short times. It is estimated that such a cross relaxation between Cl and proton spins combined with the short Cl spin-lattice relaxation time contributes to an effective T_{1B} for the protons equal to approximately one-half the observed zero field value. During the second B radio-frequency pulse

a possible crossing between rotating frame proton Zeeman order and the hot Cl spins is possible for weak radio-frequency fields. For the experimental conditions of our experiments this crossing can be neglected.

IV. INTEGER SPIN QUENCHING OF CROSS-RELAXATION IN THE INTERACTION REPRESENTATION

The quenching of the dipolar fields of a nuclear spin I = 1 quadrupole spin system in the laboratory reference frame has been observed[23,24] and analyzed[25]. This effect concerns the quenching of the magnetic dipole interaction between deuterium spins and neighboring spins in the absence of external magnetic fields. This effect was confirmed in a sample of $Ba(ClO_3)_2 \cdot D_2O$, as observed in a pulsed spin-echo double-resonance experiment[23]. The spin-echo double-resonance experiment performed was one in which the effect of the deuterium-chlorine local dipolar magnetic field interactions, in the periods of absence of applied radio-frequency fields, was observed. A detailed analysis shows[25] that the quenching can be lifted by the application of a constant magnetic field. In such a field, the second moment of the deuterium-chlorine interaction has the following form,

$$M_2(i) = \frac{x_i^2}{1 + x_i^2} \quad M_2(0) ,$$

where $M_2(0)$ is the Van Vleck second moment, and $x_i = \gamma_D H_z / K\eta$, $2\gamma_D H_x / K(3+\eta)$, and $2\gamma_D H_y / K(3-\eta)$ for the cases in which the external field is parallel respectively to the Z, X, and Y crystal-field gradient axes. γ_D is the deuterium gyromagnetic ratio, K is as defined in Eq. (55), η is the asymmetry parameter, and H_x, H_y, and H_z are the respective magnetic fields. In zero magnetic field it is seen that in first order, neglecting the effect of local dipolar fields, except for the case i = z and $\eta = 0$, $M_2(i)$ is quenched. As the field H_i is increased, x_i increases and $M_2(i)$ becomes sizeable or is "unquenched" as it approaches $M_2(0)$. The dipolar fields of the I = 1 spin, which cause cross-relaxation with the surrounding spins, will correspondingly increase as unquenching occurs. To include the local dipolar fields to second order we replace the applied field H_i by $(H_i^2+H_L^2)^{\frac{1}{2}}$, where H_L^2 is on the order of the mean square local field.[25]

The quenching in the laboratory frame has thus been observed and explained for the pulsed spin-echo double resonance. The question next arises as to how the quenching will manifest itself in the more sensitive double-resonance experiments involving spin-locking or adiabatic demagnetization, where an integer spin system is to relax by dipolar interaction with a second spin system while subject to a resonant radio-frequency field. Such experiments have been described in the second section of this paper, and we wish now to demonstrate that integer spin quenching is important not only in the absence of radio-frequency fields, as in the spin-echo experiment, but must also be taken into account in the presence of such fields. The quenching and magnetic field unquenching in the absence of a resonant radio-frequency field was demonstrated in the calculation of $M_2(i)$. In the presence of the resonant radio-frequency field we will demonstrate the quenching and unquenching effect by direct calculation of the appropriate cross-relaxation terms.

We now examine the possible cross-relaxation of an $I = 1$ quadrupole spin system (C) with a dipolar $I = 1/2$ spin system (B) in zero field. Although the analysis to follow specifically concerns $I = 1$, the physical results can be extended to quadrupolar systems of integer spin $I > 1$. The C spin system is assumed subjected to a resonant radio-frequency field, and the analysis of B-C cross-relaxation is facilitated by transforming the problem to the C interaction representation where the C hamiltonian is time independent. As the analysis is made for zero external field, the B spin system is described by dipolar interactions. In the paradichlorobenzene experiment described in this paper the B system is a dipolar $I = 1/2$ proton spin system in the laboratory reference frame. The relevant zero field hamiltonian for the combined B and C spin systems is given by

$$\mathcal{H} = \mathcal{H}_Q^C + \mathcal{H}_{DD}^{BC} + \mathcal{H}^B, \tag{48}$$

where

$$\mathcal{H}_Q^C = \sum_{C \text{ spins}} \frac{e^2qQ}{4I(2I-1)} \left[3I_Z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right],$$

and $\mathcal{H}_{DD}^{BC}$ is the dipolar interaction between B and C spins. The B system hamiltonian, $\mathcal{H}^B$, is a laboratory dipolar hamiltonian in accordance with the zero field, I = 1/2, proton spin system. The dipolar interaction $\mathcal{H}_{DD}^{CC}$ between C spins has not been included as it represents only a small perturbation on the C spins. The dipolar interaction is written in the usual fashion as a set of bilinear operators coupled with angular factors.

In order to effect a cross-relaxation between the B and C spins a radio-frequency magnetic field is applied near one of the non-degenerate ($\eta \neq 0$) C transitions affecting only the C spins. The total hamiltonian is now

$$\mathcal{H} = \mathcal{H}_Q^C + \mathcal{H}^B + \mathcal{H}_{DD}^{BC} + \mathcal{H}_{rf}^C, \tag{49}$$

where $\mathcal{H}_{rf}^C = -2\gamma_C \hbar H_1 I_X^C \cos \omega t$, and $2H_1$ is the amplitude of the field applied. We assume $\mathcal{H}_{DD}^{CC}$ is small as compared to $\mathcal{H}_{rf}^C$, and $\hbar\gamma_c H_1$ does not correspond to any transition in the energy spectrum of $\mathcal{H}_Q^C$.

Transforming to the C interaction representation through the operator $U = \exp(i\mathcal{H}_Q^C t/\hbar)$, the combined B-C density matrix then obeys the equation

$$\dot{\rho}^* = \frac{i}{\hbar}[\rho^*, \mathcal{H}^*], \tag{50}$$

where

$$\mathcal{H}^* = (U^{-1}\,\mathcal{H}U) - \mathcal{H}^C_Q = \mathcal{H}^B + U^{-1}\,\mathcal{H}^C_{rf}\,U + U^{-1}\,\mathcal{H}^{BC}_{DD}U. \tag{51}$$

The general requirements for a double-resonance cross-relaxation process are as follows. In the hamiltonian of Eq. (51) there must exist time-independent, or secular, B and C system hamiltonians for which B and C spin temperatures can be separately defined. In Eq. (51) $\mathcal{H}^B$ serves as the secular B spin hamiltonian for which a B spin-temperature is defined. The effective C system Zeeman interaction defined by $(\mathcal{H}^C_Z)^* = U^{-1}\,\mathcal{H}^C_{rf}\,U$ is the equivalent term for the C spin system in the C interaction representation. In general $(\mathcal{H}^C_Z)^*$ contains both secular and non-secular terms. The non-secular terms average to zero quickly and their frequencies do not correspond to any frequencies within the spectrum of the secular terms; we shall drop all non-secular terms of $(\mathcal{H}^C_Z)^*$, and denote this secularization by $(\mathcal{H}^C_Z)'$. $(\mathcal{H}^C_Z)'$ is formed by constructing the operator $U = \exp(i\mathcal{H}^C_Q\,t/\hbar)$ in the eigenstate representation of $\mathcal{H}^C_Q$. Then $U^{-1}\,\mathcal{H}^C_{rf}\,U$ is formed in the same representation, and finally the result is expressed in the I^C_z representation. Omitting the algebra, the transformed operator I^C_x as well as I^C_y and I^C_z are expressed in the I^C_z representation as follows:

$$U^{-1}\,I^C_x\,U = \frac{1}{\sqrt{2}}\begin{vmatrix} 0 & \phi & 0 \\ \phi^* & 0 & \phi^* \\ 0 & \phi & 0 \end{vmatrix}, \tag{52}$$

$$U^{-1}\,I^C_y\,U = \frac{-i}{\sqrt{2}}\begin{vmatrix} 0 & \theta & 0 \\ -\theta^* & 0 & \theta^* \\ 0 & -\theta & 0 \end{vmatrix}, \tag{53}$$

and

$$U^{-1} I_z^C U = \frac{1}{2} \begin{vmatrix} (\mu^* + \mu) & 0 & (\mu^* - \mu) \\ 0 & 0 & 0 \\ (\mu - \mu^*) & 0 & (-\mu^* - \mu) \end{vmatrix} , \qquad (54)$$

where

$$\phi = \exp(iK(3 + \eta)t) = \exp(i\omega_+ t) ,$$

$$\theta = \exp(iK(3 - \eta)t) = \exp(i\omega_- t) ,$$

$$\mu = \exp(i2\eta Kt) = \exp(i\omega_\eta t) , \qquad (55)$$

and

$$K = \frac{e^2 qQ}{4\hbar} .$$

We see, therefore, from Eqs. (52) and (55) that, if the applied angular frequency satisfies $\omega = \omega_+$, we obtain a secular contribution to $(\mathcal{H}_z^C)^* = -2\gamma_C \hbar H_1 U^{-1} I_x U \cos \omega t$, so that

$$(\mathcal{H}_Z^C)' = -\gamma_C \quad H_1 I_x^C . \qquad (56)$$

If H_1 were applied along the y or z axis, then from inspection of the appropriate transformed component of the angular momentum, I_y or I_z, it would be necessary to set $\omega = \omega_-$ or $\omega = \omega_\eta$ respectively in order to obtain secular terms.

For double-resonance to take place, not only must mutual spin flips in the B and C spin systems conserve energy, but there must also exist a cross-relaxation term, $U^{-1} H_{DD}^{BC} U$ in Eq. (51), which does not commute with either the B or C hamiltonian.

The form of $\mathcal{H}_{DD}^{BC}$ is as in Eqs. (8) through (14) where the S operator is identified with the B spins and the I operator with the C spins. The relevant transformations for the C spin operators of $\mathcal{H}_{DD}^{BC}$ are given in (52), (53) and (54). Without writing down the terms of $U^{-1}\mathcal{H}_{DD}^{BC}U$ we note that there is no explicit time dependence in $\mathcal{H}_{DD}^{BC}$, and that (52), (53), and (54) are all time dependent; thus <u>all</u> terms of $U^{-1}\mathcal{H}_{DD}^{BC}U$ are non-secular and hence the effects of the cross-relaxation term average to zero for η sufficiently large. Implicit in the above analysis is the assumption that the splitting of the degenerate C transitions due to η asymmetry is larger, by at least a factor of two or three, than the linewidths of the B and C transitions. We have demonstrated secular B and C hamiltonians coupled by only non-secular terms, implying that no cross-relaxations will occur. By this analysis, then, the I = 1 deuterium spins in the presence of a strong η asymmetry cannot be observed by their interaction frame cross-relaxation with a laboratory dipolar spin system. However, when the condition that the η splitting is larger than the B and C linewidth is not met, as is the case in the deuterium spectrum of paradichlorobenzene, then the degeneracy in the overlapping lines lifts the quenching, and a cross-relaxation is possible, thereby allowing the I = 1 zero field quadrupole resonance to be observed. This can be formally seen in writing down the zero field second order contribution due to local fields on the Van Vleck second moment. We have from our previous discussion as applied to zero applied field

$$M_2 = \frac{x^2}{1+x^2} \quad M_2\,(0)\ ,$$

where $x = \gamma_D H_L / K\eta$, and there is then a significant contribution in

zero field to M_2, and thus the cross relaxation rate, when the η splitting is on the order of the local field splittings or $x \approx 1$.

The presence of the η asymmetry is responsible for the quenching as well as for the splitting of the degenerate ($\eta = 0$) quadrupolar transitions. This splitting comes about because of the presence of a $\Delta m = \pm 2$ matrix element of the quadrupole hamiltonian, proportional to η, between the degenerate $m_I = +1$ and -1 levels. To extend our argument to $I > 1$ integer quadrupole systems we note that quenching of the cross-relaxation term is tied to the splitting of a previously degenerate level. In analogy with the $I = 1$ case, we do not expect quenching of the cross-relaxation term when there is two-fold degeneracy in one of the energy levels which defines the transition we are attempting to observe. The degeneracy allows a secular contributions to local fields and thus to the cross-relaxation term. We note in proof the results of Jones and Hartmann[26] for the K^{40} ($I = 4$) double resonance detection in $KClO_3$. For the unenriched sample they state that the only transitions observable are those which terminate in the upper energy level ($m_I = \pm 4$), which, because of the $\Delta m = \pm 2$ selection rule associated with the η term in the hamiltonian, remains essentially degenerate. All other transitions terminate in non-degenerate levels and could only be observed in the enriched K^{40} (2.8%) sample.

In a similar manner to that in which the laboratory frame quenching is lifted, the interaction representation quenching is lifted in first order by the application of a constant laboratory magnetic field, and in higher order by the local dipolar fields. The unquenching is due to the magnetic field mixing of states and is formally seen in the appearance of secular components in the cross-relaxation term $U^{-1} \mathcal{H}_{DD}^{BC} U$ of Eq. (51).

The simplest case to treat is that in which the applied magnetic field is parallel to the deuterium z principle quadrupole field gradient axis, and we shall neglect the higher order dipolar field effect, which is equivalent to the assumption of isolated single spin states. In this case, the deuterium (C) hamiltonian is written

$$\mathcal{H}^C = \sum_{C\ \text{spins}} \left[\hbar\gamma_C H_Z I_Z + \frac{e^2qQ}{4} \left(3I_Z^2 - 2 + \frac{\eta}{2}\left(I_+^2 + I_-^2\right)\right)\right]. \tag{57}$$

The isolated spin eigenstates and eigenenergies are as follows:

$$\begin{aligned} |\alpha\rangle &= a_\alpha|+\rangle + b_\alpha|-\rangle, \\ |\beta\rangle &= a_\beta|+\rangle + b_\beta|-\rangle, \\ |\gamma\rangle &= |0\rangle, \end{aligned} \tag{58}$$

and

$$\begin{aligned} E_\alpha &= K(1+\Delta), \\ E_\beta &= K(1-\Delta), \\ E_\gamma &= -2K, \end{aligned} \tag{59}$$

where

$$a_\alpha = -b_\beta = \frac{1}{\sqrt{2}} \left(1 + z^2 + z\,(1 + z^2)^{1/2}\right)^{-1/2}, \tag{60}$$

$$a_\beta = b_\alpha = \frac{1}{\sqrt{2}} \left(1 + z^2 - z\,(1 + z^2)^{1/2}\right)^{-1/2},$$

$$\Delta = \eta\,(1 + z^2)^{1/2},$$

$$z = \gamma_c H_z / \eta K,$$

and K is defined as in Eq. (55) . In the eigenstate representation of Eq. (58) one may easily express the operator $U_z = \exp(i\mathcal{H}^C\, t/\hbar)$ and form the matrix representations of the operators I_x, I_y, and I_z. Upon carrying this out, we find that only the terms proportional to I_z^C in $\mathcal{H}_{DD}^{BC}$ contribute secular terms to $U_z^{-1}\, \mathcal{H}_{DD}^{BC}\, U_z$. These correspond to the terms A, C, and D of the dipolar hamiltonian as given in Eq. (9), (11), and (12).

The transformed I_z^C term is given by

$$U_z^{-1}\, I_z^C\, U_z = \frac{z}{(1+z^2)^{1/2}} \begin{array}{c} \begin{array}{ccc} [\alpha] & [\beta] & [\gamma] \end{array} \\ \left|\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{array}\right| \end{array} \begin{array}{c} \\ [\alpha] \\ [\beta] \\ [\gamma] \end{array}, \tag{61}$$

where the matrix is expressed in the eigenstate representation of Eq. (58). The transformed hamiltonian of Eq. (51) can then be written

$$\mathcal{H}^* = \mathcal{H}^B + \frac{z}{(1 + z^2)^{1/2}} \left[\mathcal{H}_{DD}^{BC}\right] + \hbar\gamma_C H_1 \left[1_{\alpha\gamma}\right] . \tag{62}$$

where we have assumed that the C radio-frequency field is applied in the

x-direction at the angular frequency $\omega = (E_\alpha - E_\gamma)/\hbar$. The term $[\mathcal{H}_{DD}^{BC}]$ symbolically represents the I_z^C terms of dipolar strength, and is bilinear in B and C spin operators, but not of the same form as any of the terms of Eqs. (9) through (14). The final term, $[I_{\alpha\gamma}]$, is a matrix with unit entries connecting the $|\alpha\rangle$ and $|\gamma\rangle$ states. The quenching and unquenching is clearly seen in the $z/(1 + z^2)^{1/2}$ term which governs the magnitude of the effective cross-relaxation term. These results have been derived for the case in which the applied magnetic field is parallel to the deuterium z principle quadrupole field gradient axis. For the field parallel to the x or y axis, as well as for a mixed case, a similar quenching results but because of the complexity of the analysis, we choose not to perform the calculations here. As the rate of B-C double resonance is proportional to the square of the cross-relaxation term (see Eqs. (32) and (33)), we find the cross-relaxation rate, or equivalently the sensitivity of the interaction frame double-resonance, is proportional to $z^2/(1 + z^2)$, as is the case for the laboratory frame spin-echo experiment. To second order in local field strength z is given by

$$z = \frac{\gamma_c \, (H_z^2 + H_L^2)^{1/2}}{\eta \, K} \quad ,$$

and in zero applied field the local field, H_L, can lift the quenching in the case of small η, or equivalently when the dipolar energy spread is on the order of the η splitting.

V. CONCLUSIONS

A method for a sensitive nuclear double-resonance detection has been presented, in which two abundant spin reservoirs are used - the B spins, with long T_1, to sense the resonance of a third (C) rare spin system, and the A spins with short T_1, to establish and monitor an ordered metastable B spin state. We have made use of an ordered proton spin system to observe the zero field nuclear quadrupole resonance of 12% enriched deuterium, and naturally abundant C^{13} in the solid paradichlorobenzene. An analytical discussion has been given of zero field integer spin double-resonance detection showing in detail that, for an $I = 1$ spin, a double resonance cannot be detected when the splitting due to η asymmetry in the quadrupole interaction is well resolved. The argument is extended to integer $I > 1$ quadrupole spin systems and to the case of small magnetic fields where the cross-relaxation term is unquenched by the applied fields. An ordered metastable B spin system which can be easily produced and monitored is useful, not only for sensitive C spin detection, but to sense any weak perturbations which affect the long lived B spin state: Such a system would be sensitive for example to slow diffusion of any internal impurities or constituent atoms,[27] external electric fields, and relaxation caused by optically produced excitations.

VI. ACKNOWLEDGMENTS

We wish to thank Dr. J. Koo for many invigorating discussions. We are indebted to the National Science Foundation and the U. S. Atomic Energy Commission through the Inorganic Materials Division of the University of California Lawrence Radiation Laboratory for their financial support.

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Figure Captions

Fig. 1. (a) Two spin species double resonance cycle showing sequentially the equilibration time, the time to establish the A spin system in a spin locked state at low spin temperature, and finally the period during which the A spins relax through spin-lattice and double-resonance mechanisms. (b) Time dependence of the inverse A spin-temperature $\beta_A = 1/kT_{sA} = \beta_A(o) \exp(-t(1/T_1^* + 1/\tau_{AB}))$ with (dotted line) and without (solid line) A-B cross-relaxation. The observed A signal is proportional to β_A and is observed after the A and B spins have cross-relaxed for a time T_1^*.

Fig. 2. Thermodynamic model for the three spin species double-resonance experiment. The blocks represent thermal reservoirs with well defined temperatures for the A, B, and C spin systems and the lattice. The circles indicate thermal switches connecting the A and B, and B and C spin systems, which are normally open and are closed by application of resonant A and C radio-frequency fields respectively. The coupling time constants between the reservoirs are indicated and satisfy the relations $\tau_{AB} \ll \tau_{BC} \ll T_{1A} \ll T_{1B}$.

Fig. 3. Energy level diagrams for the three spin species double-resonance experiment as applied to paradichlorobenzene. (a) Laboratory A spin quadrupole splitting of Cl^{35} ($\omega_A \sim 35$ mHz). (b) Interaction representation Cl^{35} splitting due to presence of resonant radio-frequency field applied to A resonance. ($2\lambda = \hbar \sigma \gamma H_1 \sim 12$ k Hz). (c) B spin Laboratory dipolar spectrum of protons ($\gamma_B H_L^B \sim 12$ k Hz). (d) Rotating frame Zeeman (C^{13}) or interaction representation (deuterium) splitting of C spin system due to presence of resonant radio-frequency field applied to appropriate C resonance

($\gamma_C H_{1C} \sim 12$ k H $_Z$). (e) Laboratory splitting of C resonance excited: $\omega_C = \gamma_C H_o \sim 150$ kHz for C^{13} and $\omega_C \sim 140$ kHz for deuterium.

Fig. 4. Preparation of low spin temperature B metastable state by a series of A spin-locking pulses. (a) Evolution of spin-temperature of A (Cl^{35}) system in interaction representation following spin-locking and B (proton) spin-temperature in the laboratory reference frame. (b) Sequence of A radio-frequency pulses. At $t = t_1$, and corresponding times for pulses 2 and 3, an initial and fixed low A spin temperature is established by the spin-locking technique. During the period t_1 to t_2 a common spin-temperature is attained by the coupled A and B spins. At $t = t_2$ the pulse is turned off and a free induction signal, proportional to the inverse final spin temperature, is observed. The process is repeated at t_3 and t_4, resulting in a progressive lowering of the B spin temperature and increase of the free induction signal.

Fig. 5. Four alternative external conditions under which double-resonance coupling can be effected between the B and C spin system. The B state which participates in the cross-relaxation in each case is (a) the zero field dipolar state, (b) the Zeeman state in applied field H_o, (c) the spin-locked state in the rotating frame, and (d) the adiabatically demagnetized dipolar state in the rotating frame. The C search radio-frequency field is applied as indicated for a time on the order of the spin-lattice relaxation time for each B state. The B radio-frequency fields are applied at the resonance frequency in the field H_o.

Fig. 6. B spin spectra is the four alternative B states of Fig. 5. (a) and (d) are the dipolar spectra of width ~ 12 k Hz in zero field and in the adiabatically demagnetized state in high field respectively. (b) and (c) are Zeeman spectra in the laboratory H_o field and in the spin-lock field H_1 respectively. $H_1 \gtrsim 5$ gauss, $H_o \gtrsim 100$ gauss.

Fig. 7. Block diagram of apparatus. The sample is contained in the coil marked "A", which serves as both the A transmitter and receiver coil. Both B and C transmitters use the relay switched "B-C" coil in their tank circuits. The "A" and "B-C" coils are coencentric and in a liquid nitrogen bath. Audio and d.c. Helmholtz coils are coencentrically placed and perpendicular to the radio-frequency coils.

Fig. 8. Zero field deuterium quadrupole double resonance spectra in paradichlorobenzene. The $|+\rangle \leftrightarrow |0\rangle$ and $|-\rangle \leftrightarrow |0\rangle$ pure quadrupole transitions are at $\omega_+ \cong 140.2$ kHz and $\omega_- \cong 134.8$ kHz respectively.

Fig. 9. Extended plot of observed zero field deuterium double-resonance in paradichlorobenzene. The limits of variation of the B spin temperature as measured by the A signal are indicated by S_∞ and S_m. S_∞ corresponds to $\beta_B = 0$ or, equivalently, a saturated B spin system, while S_m indicates a maximum A signal corresponding to the condition $\beta_B = \beta_A(0)$.

Fig. 10. The radio-frequency and magnetic field pulses used in the observation of the C^{13} resonance in the three spin-species experiment. A sequence of pulses is shown and one set is enlarged in the lower half of the figure. The A radio frequency pulses barely appear as pips centered between the trapazoidal H_o pulses.

Fig. 11. A typical C^{13} double-resonance spectrum in paradichlorobenzene by the three spin-species experiment. Experimental parameters are indicated in the figure. The apparent doublet is due to the audio technique used to saturate the C^{13} resonance and is not characteristic of the C^{13} spectrum.

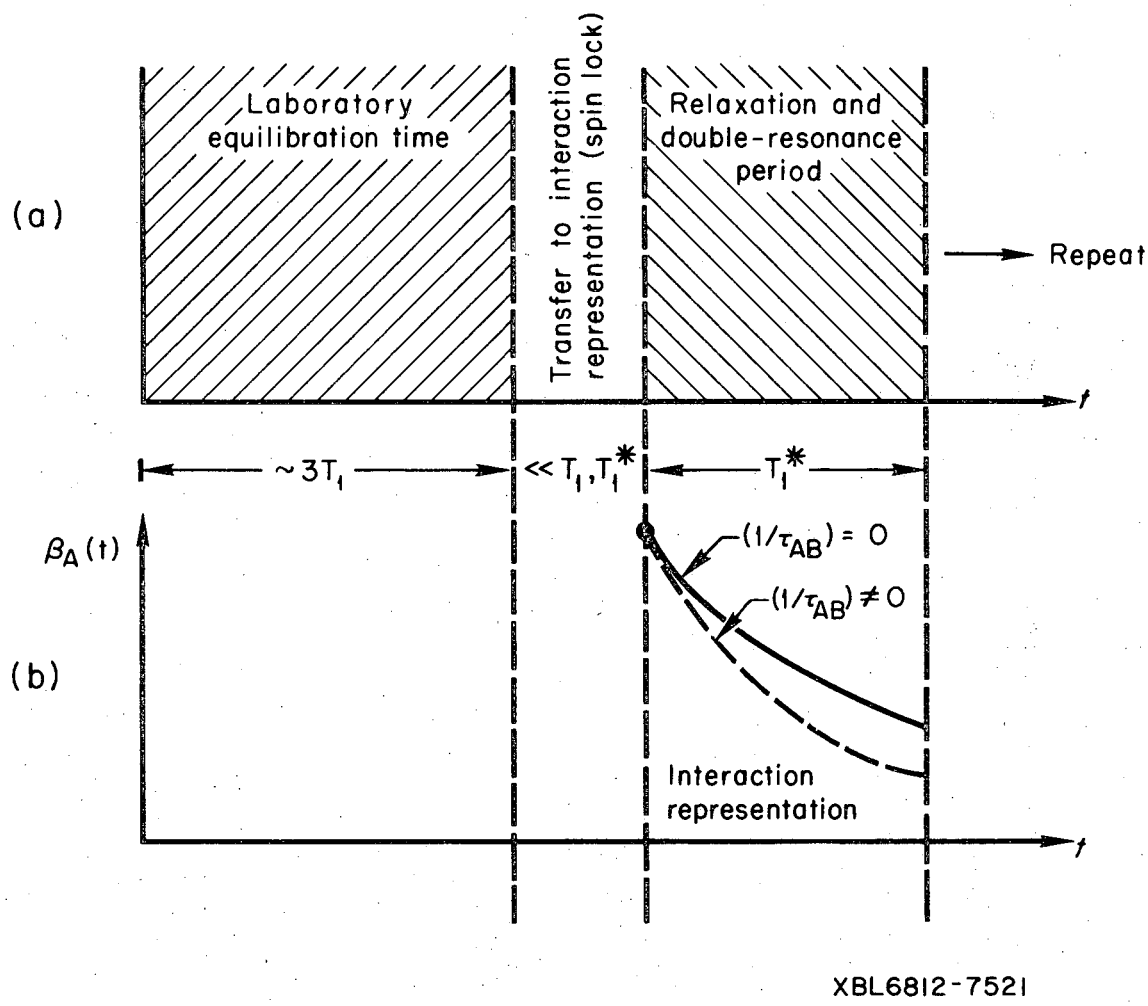
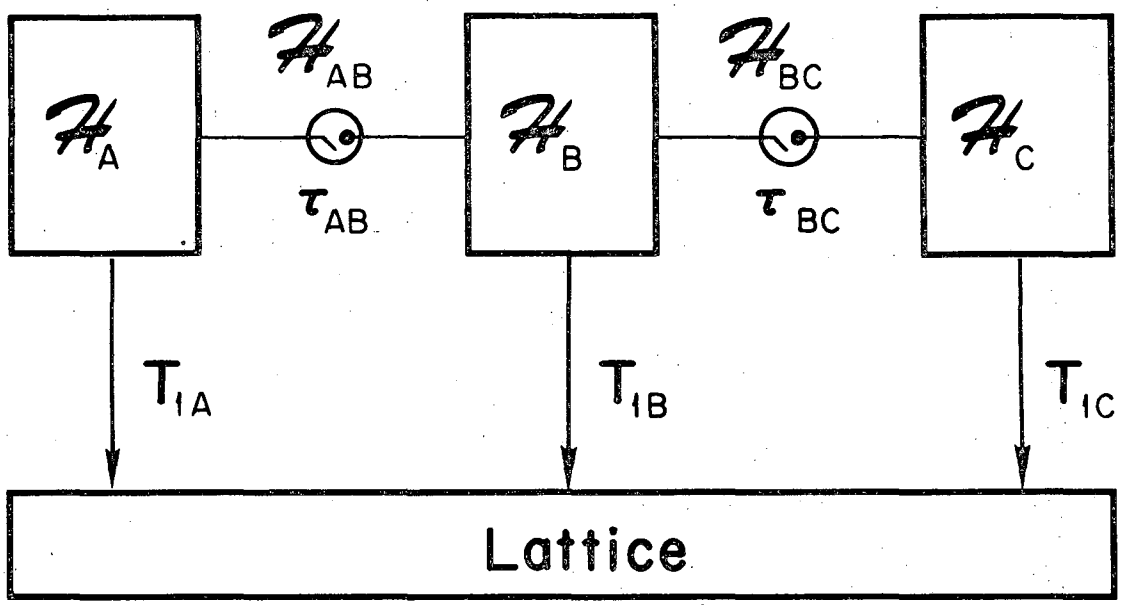
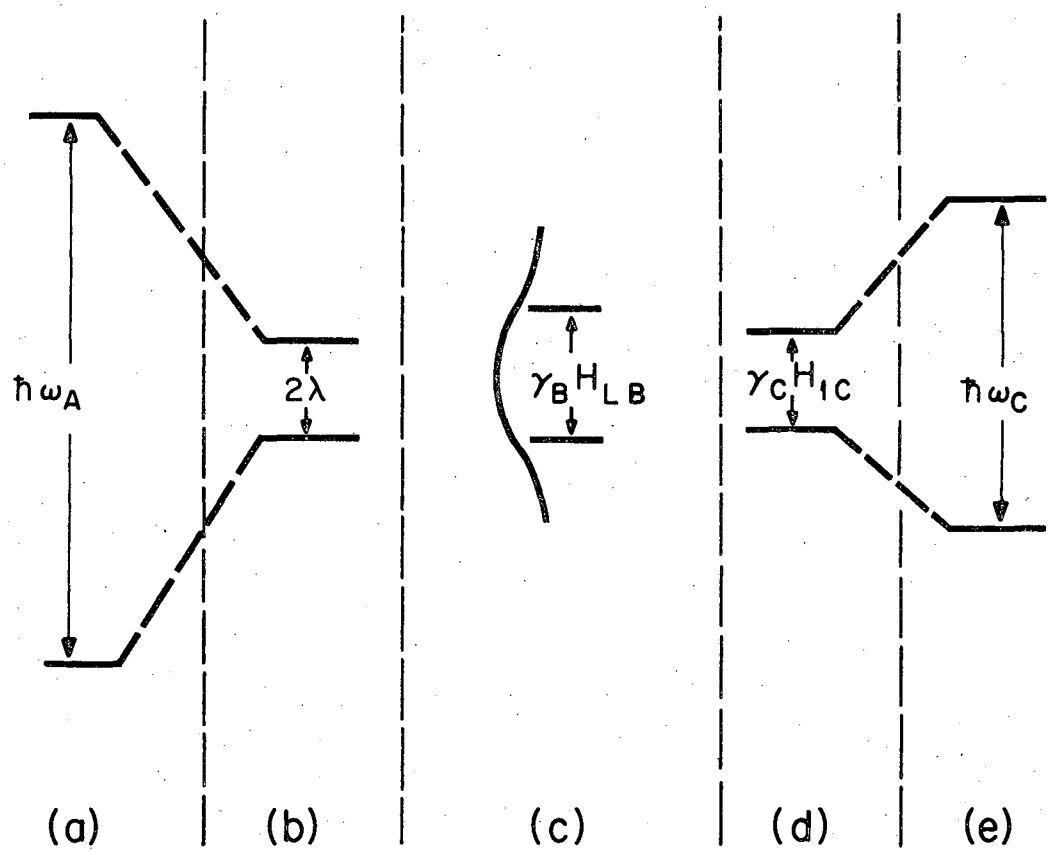

(a)
Laboratory equilibration time
Transfer to interaction representation (spin lock)
Relaxation and double-resonance period
Repeat
t
~3T1
<< T1,T1*
T1*
(b)
βA(t)
(1/τAB) = 0
(1/τAB) ≠ 0
Interaction representation
t
XBL6812-7521

Figure 1



XBL6812-7520

Figure 2



XBL6812-7519

Figure 3

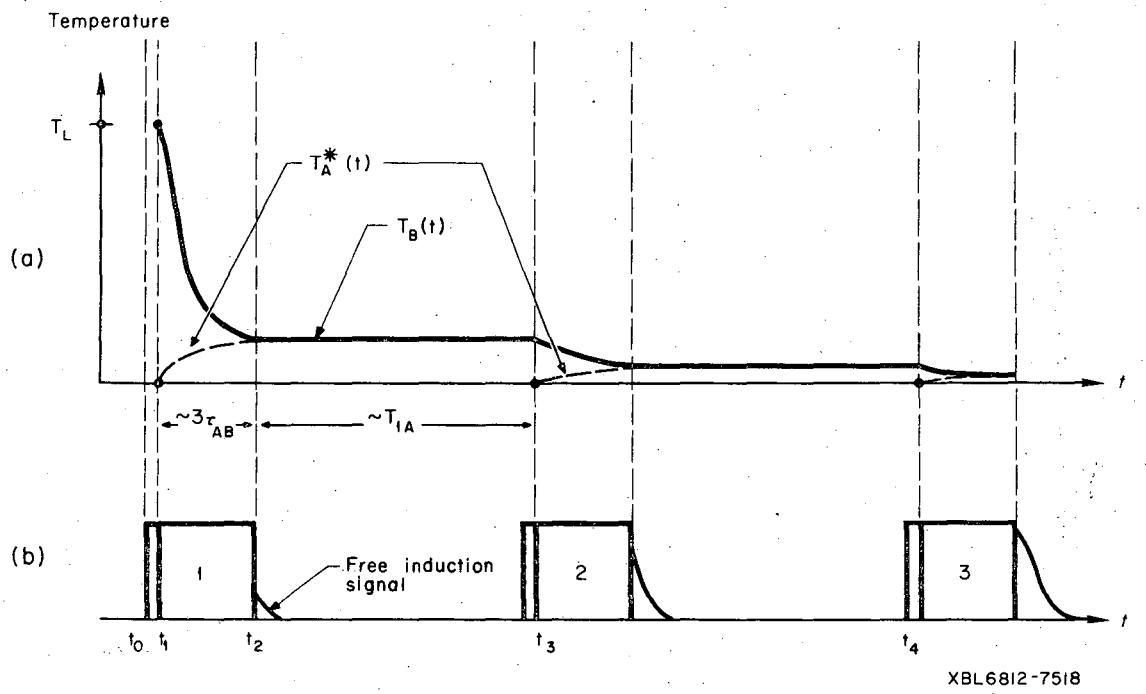

Temperature
T_L
$T_A^*(t)$
$T_B(t)$
(a)
$\sim 3\tau_{AB}$
$\sim T_{1A}$
t
(b)
1
Free induction signal
2
3
t_0
t_1
t_2
t_3
t_4
t
XBL6812-7518

Figure 4

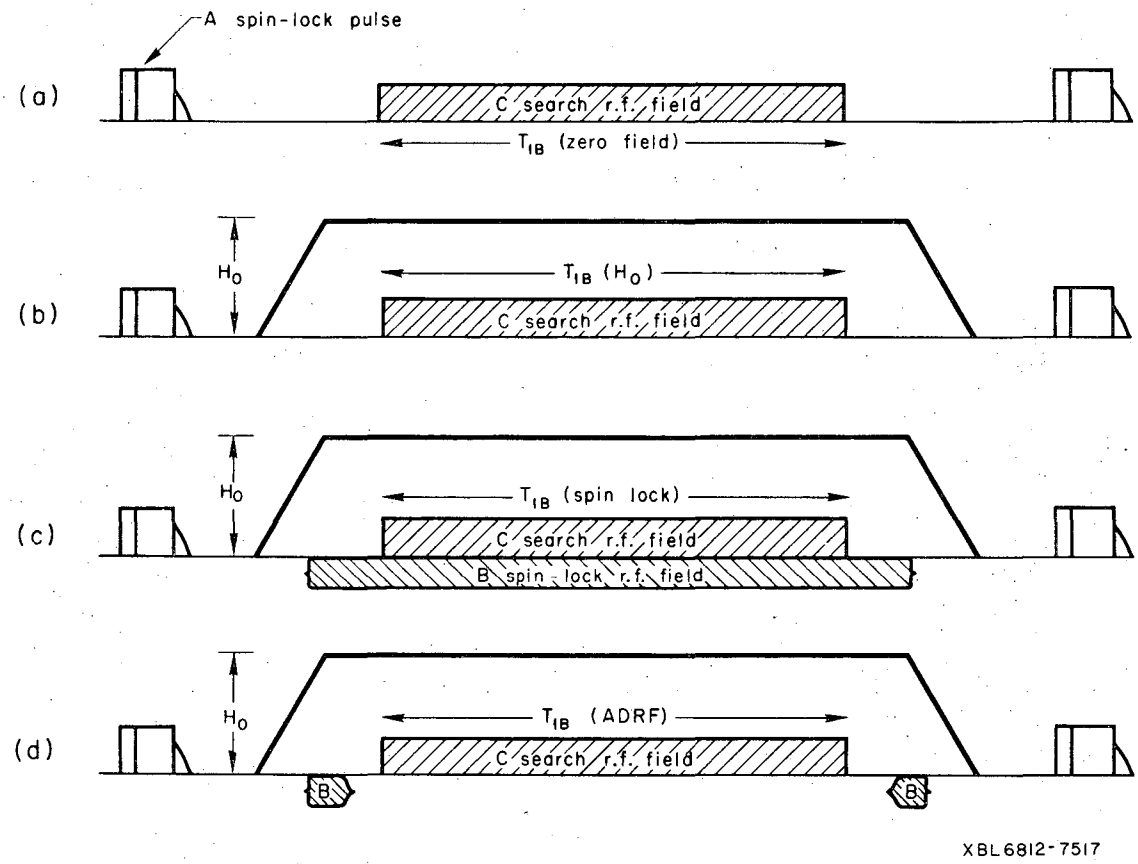

A spin-lock pulse
(a)
C search r.f. field
T_{1B} (zero field)
(b)
H_0
T_{1B} (H_0)
C search r.f. field
(c)
H_0
T_{1B} (spin lock)
C search r.f. field
B spin lock r.f. field
(d)
H_0
T_{1B} (ADRF)
C search r.f. field
B
B
XBL6812-7517

Figure 5

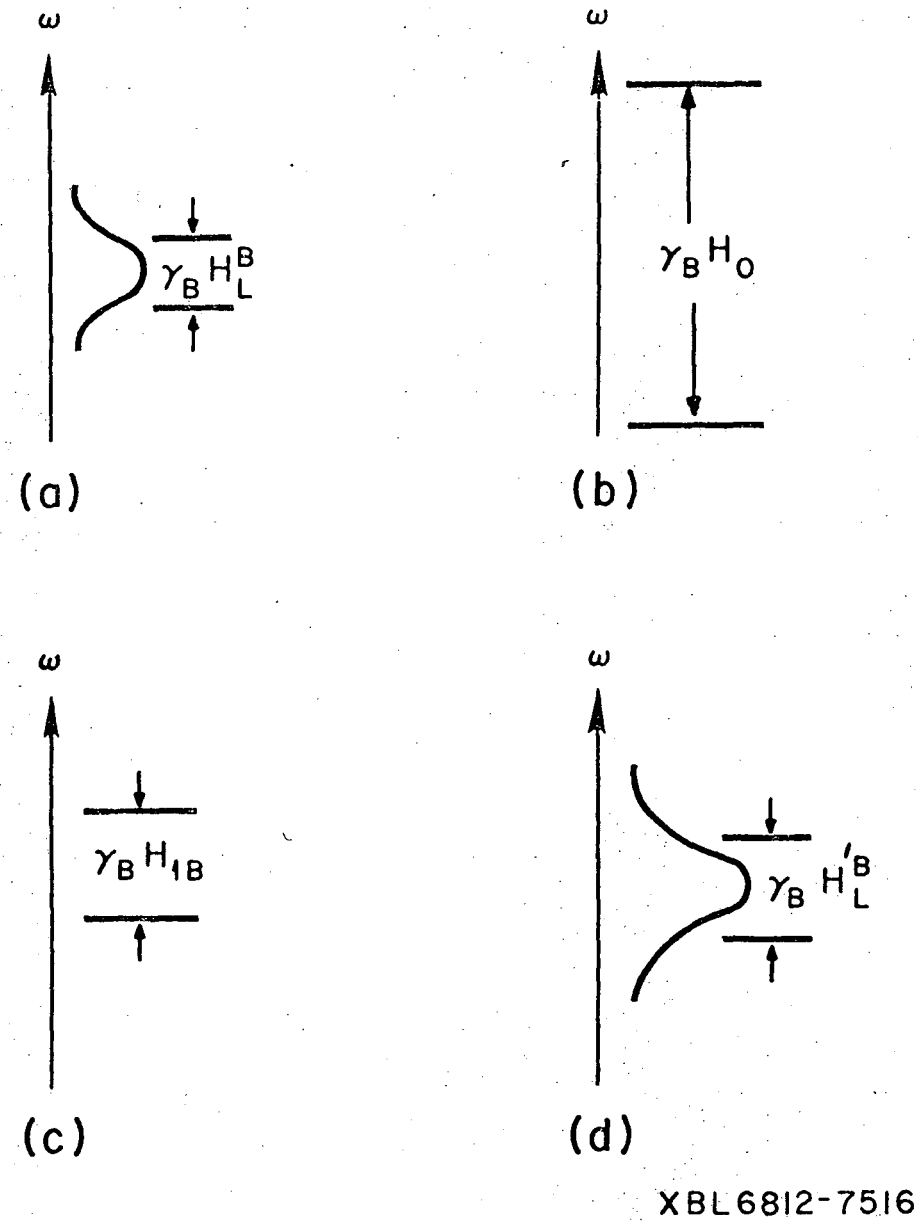

ω
$\gamma_B H_L^B$
(a)
ω
$\gamma_B H_0$
(b)
ω
$\gamma_B H_{1B}$
(c)
ω
$\gamma_B H_L'^B$
(d)
XBL6812-7516

Figure 6

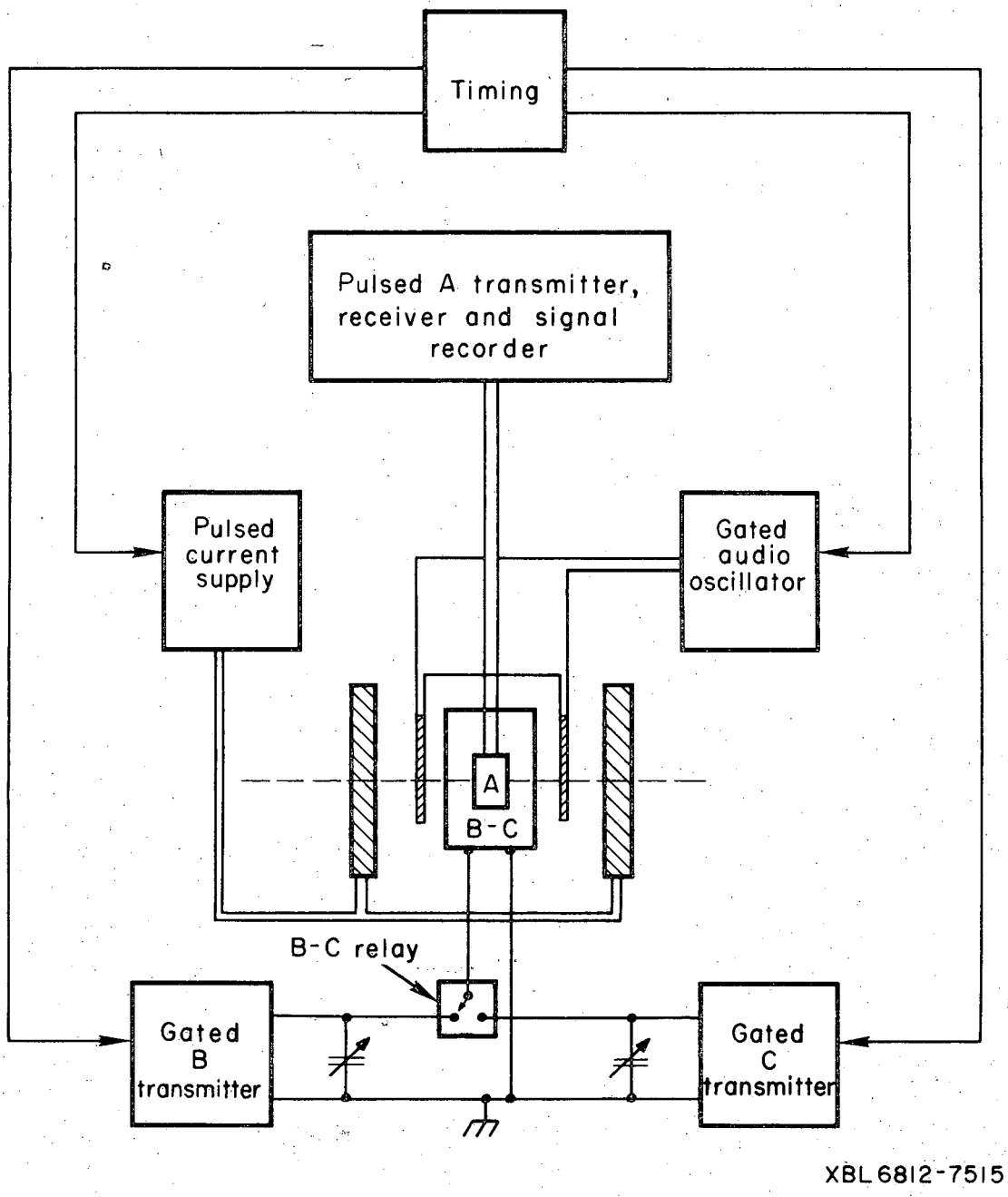
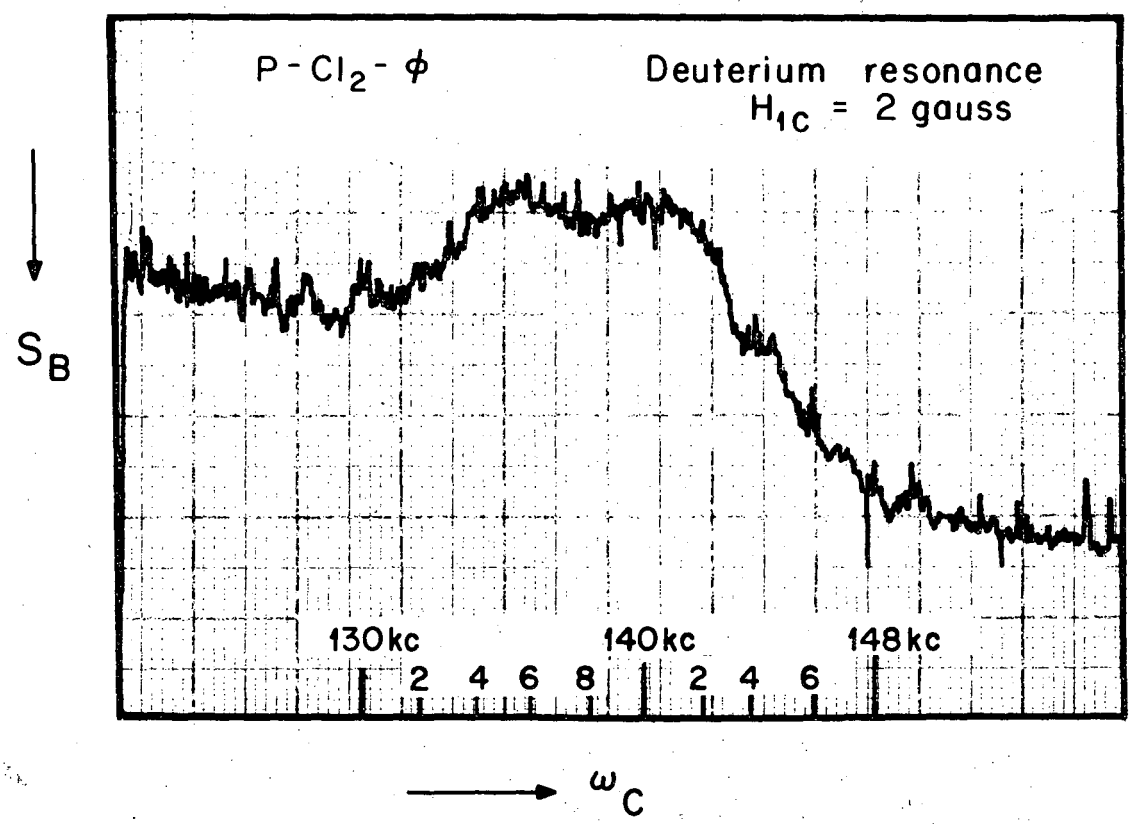

Timing
Pulsed A transmitter, receiver and signal recorder
Pulsed current supply
Gated audio oscillator
A
B-C
B-C relay
Gated B transmitter
Gated C transmitter
XBL 6812-7515

Figure 7



XBL686-990

Figure 8

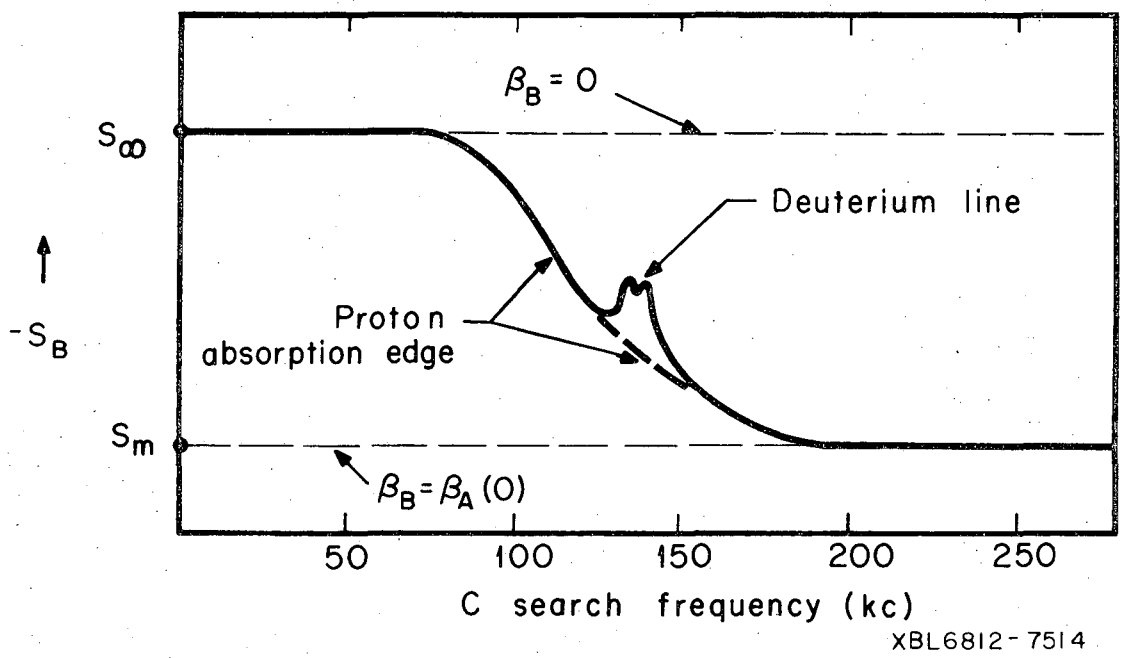
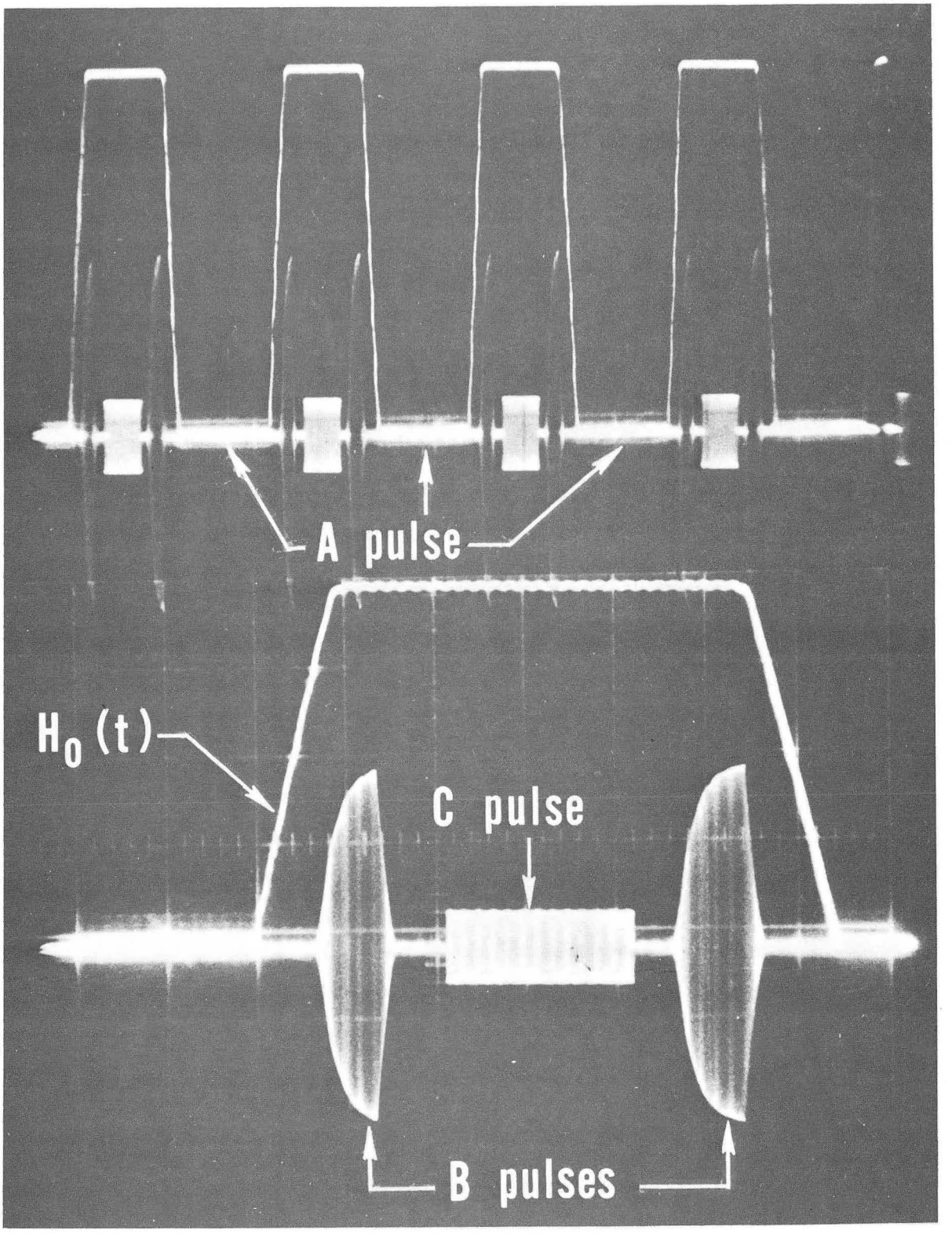
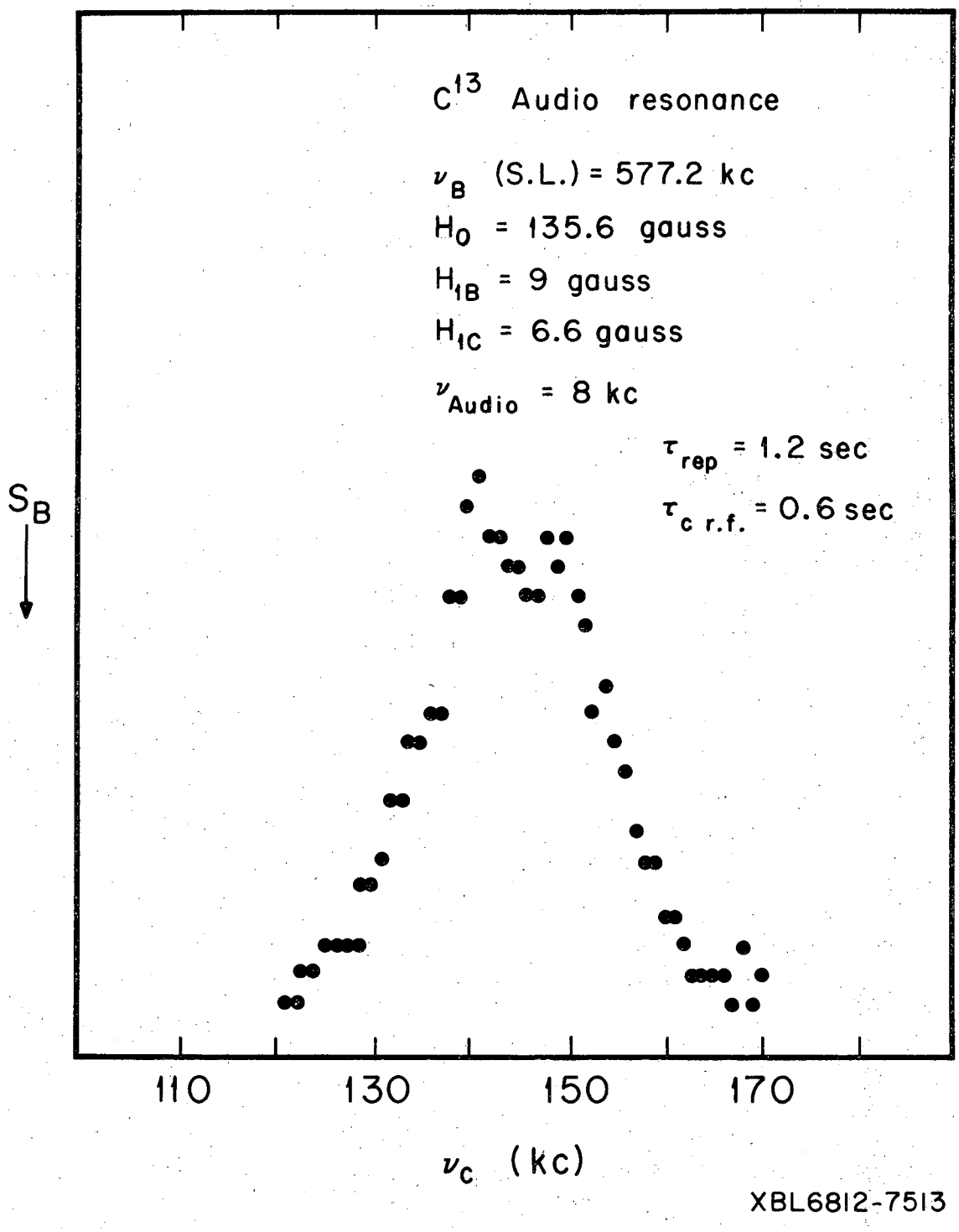

$\beta_B = 0$
S_∞
Deuterium line
$-S_B$
Proton
absorption edge
S_m
$\beta_B = \beta_A(0)$
50
100
150
200
250
C search frequency (kc)
XBL6812-7514

Figure 9



XBB 686-3516-A

Fig. 10



XBL6812-7513

Figure 11

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