Double-quantum cross-polarization NMR in solids*

S. Vega, T. W. Shattuck, and A. Pines

Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
and Department of Isotope Research, The Weizmann Institute of Science, Rehovot, Israel
(Received 10 December 1979)

Double-quantum NMR is a useful way to obtain spectra of quadrupolar nuclei ($^2$D, $^{14}$N, ...) in solids. This allows measurements of the chemical shifts for these nuclear spins. The theory of Hartmann-Hahn cross polarization between $I = 1/2$ and such $S = 1$ spins is discussed. Particular attention is drawn to the cross polarization of the double-quantum transition. The thermodynamics and the dynamics of the process are evoked in detail using a fictitious spin-1/2 formalism. The spin $S = 1$ Hamiltonian can always be factored into two commuting parts (independent thermodynamic reservoirs), one of which behaves as a fictitious spin 1/2 which is cross polarized with the $I = 1/2$ spins. Modified Hartmann-Hahn conditions emerge from the theory, and the dependence of cross-polarization times $T_2$ on rf intensity and frequency for spin locking and adiabatic demagnetization in the rotating-frame experiments are calculated. Measurements on the $^1$H-$^2$D double resonance in dilute solid benzene--d$_4$ are reported, verifying the predictions and indicating that cross polarization provides a sensitive means of detecting the $^2$D double-quantum transition. Values are reported for the thermodynamic parameters and cross-polarization times as a consequence. Three possible versions of double-resonance detection of double-quantum spectra are possible—direct detection of the cross-polarized double-quantum decay, indirect detection of the frequency spectrum following Hartmann and Hahn, and indirect detection of the free-induction decay following Mansfield and Grannell.

I. INTRODUCTION

Recently it was demonstrated that it is possible to obtain chemical shift spectra of deuterium nuclei in solids from novel NMR techniques.$^1$ In these experiments the coherence of the "forbidden" ($\Delta M = 2$) double-quantum transitions of these spins ($I = 1$) was excited and its time-dependent behavior was monitored.$^1$ The spectral lines of the double-quantum transitions, which are obtained by Fourier transformation of the measured time dependence of the double-quantum coherence, are not shifted by the quadrupole interaction. This is unlike the spectral lines of the allowed ($\Delta M = 1$) transitions, which are split (and in powders therefore broadened) due to this interaction. The small deuterium shifts, due to the chemical shielding in single crystals and powder samples, were obtained for the first time and compared with proton chemical shift data.$^1$ This technique makes it attractive to replace hydrogen atoms in solids partially by deuterium and to perform high-resolution NMR spectroscopy on the double-quantum transitions of the deuterium spins.$^2$ The spectral line-widths, due to dipole-dipole interactions between deuterium nuclei, can be made very narrow by sufficient dilution of the deuterium spins together with proton spin decoupling.

This rather simple approach forms a complementary method to the multiple-pulse techniques for the observation of high-resolution proton NMR in solids.$^1$ However, because of the very low abundance of the deuterium atoms in the solid, the measured signal intensities are very small and we would like to be able to apply cross-polarization techniques for signal enhancement.$^{11-15}$ In these experiments nuclear polarization is transferred between the abundant spin system and the rare nuclei in the sample. The polarization of the transitions of the rare spins can result in an enhancement of their NMR signal intensities. Alternatively, the free-induction decay of the $S$ spins is monitored by observing the $I$ spins using cross polarization. These methods are well understood and widely used for abundant spins (protons) and rare spins (like $^{13}$C, $^{15}$N, and $^{29}$Si) where both spin systems have a spin value $I = \frac{1}{2}$. In our case it would be most attractive to cross polarize or detect the double-quantum coherence of the deuterium spins with $S = 1$ directly from the abundant protons. This would provide high-sensitivity double-quantum spectra directly. In this paper we discuss such NMR cross-polarization experiments between abundant nuclei with spin $I = \frac{1}{2}$ and rare nuclei with $S = 1$. We show experimentally and theoretically that it is indeed possible to polarize the double-quantum transition of deuterium from protons in a solid.

In Sec. II we review briefly the spin thermodynamics of cross-polarization experiments for two spin $I = \frac{1}{2}$ systems (e.g., $^{13}$C--H), in order to form a basis for the new material in this paper. In Sec. III the theory of spin thermodynamics is extended to a spin $S = 1$, $I = \frac{1}{2}$ system. The fictitious spin-$\frac{1}{2}$ operators$^1$ used to describe single- and double-quantum coherences in the $S$-spin system...
compacty, are introduced and used for the description of the thermodynamics of this spin system. The Hartmann-Hahn conditions for different cross-polarization experiments are derived. In Sec. IV the spin dynamics of the cross-polarization process is discussed. The theory of spin dynamics for spin \( S = \frac{1}{2}, \> I = \frac{1}{2} \) systems is extended to systems with \( I = \frac{1}{2} \) and \( S = 1 \). The relaxation phenomena during cross polarization of the single- and double-quantum transitions of the \( S \)-spin systems are described. In Sec. V experimental results are presented. These results are compared with the theoretical derivations in Secs. III and IV. The modified Hartmann-Hahn conditions for the single- and double-quantum double-resonance experiments are verified. The cross-polarization time in deuterated benzene in the solid state is measured and the ratio of the heat capacities of the \( I \) spins and the \( S \) spins in the solid is obtained from the experiments and compared with the theoretical value.

II. SPIN THERMODYNAMICS WITH \( I = \frac{1}{2} \) AND \( S = \frac{1}{2} \)

In this section we review briefly the spin thermodynamics of the cross-polarization process between high-abundance spins \( I = \frac{1}{2} \) and low-abundance spins \( S = \frac{1}{2} \) in the solid. The presentation of the theory of cross polarization in this section serves as a reminder of notation and equations required for the remainder of this paper. The Hamiltonian in the laboratory frame of the spin system under consideration, in an external magnetic field \( \mathbf{H}_0 \) and with applied \( rf \) irradiation fields at the Larmor frequencies, can be represented by

\[
H = -\omega_0 I_x - \omega_0 S_x - 2\omega_1 I_x \cos \omega_0 t - 2\omega_1 S_x \cos \omega_0 t + H_{1f} + H_{1s},
\]

with

\[
S_p = \sum_{S_p} S_{pS}, \quad I_p = \sum_{I_p} I_{pI}, \quad \rho = x, y, z.
\]

\( \omega_0 = \gamma_0 H_0 \) and \( \omega_0 = \gamma_2 H_0 \) are the Larmor frequencies of the \( I \) and \( S \) spins, respectively. \( \gamma_1 \) and \( \gamma_2 \) are the magnetogyric ratios of the \( I \) and \( S \) spins and \( 2\omega_1 \) is the \( I \) spin and \( 2\omega_1 \) is the \( S \) spin frequencies in frequency units.

\[
H_{1s} = \sum_{Is} b_{Is} I_1 \alpha S_{1Is},
\]

\[
b_{Is} = -2\gamma_1 \gamma_2 H_{1s} \cos \theta_{1s}
\]

and

\[
H_{1f} = \sum_{If} a_{If} (I_1 I_f - 3I_1 I_f),
\]

\[
a_{If} = \gamma_2^2 \hbar^2 \alpha_{If} P_2(\cos \theta_{1f})
\]

are the secular parts of the magnetic dipole-dipole interactions with respect to the Zeeman interaction between the high-abundant \( I \) spins and the secular part of the dipole-dipole interaction between the \( I \) spins and the low-abundant \( S \) spins, respectively. The interaction between the \( I \) spins and the \( S \) spins is ignored because of their low abundance. The total spin system can be described by the spin density matrix \( \rho \) and in thermal equilibrium

\[
\rho_{st} = Z^{-1} \exp[-\beta \left( -\omega_0 I_x - \omega_0 S_y \right)],
\]

where we use the high-temperature approximation

\[
Z = \text{Tr}\left\{ \exp[-\beta \left( -\omega_0 I_x - \omega_0 S_y \right) \right]\} = \text{Tr}(1),
\]

and where \( \beta \) is \( 1/kT \), with \( T \) the laboratory temperature.

In the rotating frame defined by the transformation operator

\[
U_0 = \exp[-i\omega_0 I_x + \omega_0 S_y],
\]

the density matrix becomes

\[
\rho^* = U_0^* \rho U_0
\]

and the Hamiltonian

\[
H^* = -\omega_1 I_x - \omega_1 S_y + H_{1f} + H_{1s} = H_I^* + H_S^* + H_{1s}
\]

with

\[
H_I^* = -\omega_1 I_x + H_{1f},
\]

\[
H_S^* = -\omega_1 S_y.
\]

The * signs for the notation of operators in the rotating frame are dropped from now on, because all following equations and discussions apply to this frame.

With the spin temperature hypothesis the general form of the density matrix in the rotating frame is

\[
\rho = Z^{-1} (1 - \beta_I H_I - \beta_S H_S),
\]

where \( \beta_I \) and \( \beta_S \) are the spin temperature coefficients of the \( I \)-spin system and the \( S \)-spin system, respectively. According to Hartmann and Hahn, for an initial condition \( \beta_I \neq \beta_S \) the two spin temperature coefficients will evolve to a common value \( \beta \) due to the influence of \( H_{1s} \) on \( H_I \) and \( H_S \). The rate of equilibration is strongly dependent on the rf irradiation field intensities. With the proper experimental conditions, this cross-polarization process can be used to enhance the NMR signals of the \( S \) spins. The intensities of these signals are
proportional to $\beta_s$ and we therefore wish to increase this coefficient as much as possible by cooling the S-spin system.

A schematic representation of the cross-polarization process is given in Fig. 1. The enhancement of the S-spectral line intensities is performed by cooling the I spins first $\beta_I \gg \beta_S$, and then cross-polarizing the two spin systems in order to increase $\beta_S$. Two types of experiments for the preparation of the I spin and the cross-polarization process are discussed here. In the first experiment the I spins are cooled by spin locking (SL) and during the cross-polarization period the Hartmann-Hahn condition

$$\omega_{I} = \omega_{S}$$  \hspace{1cm} (2.10)

is fulfilled. The cooling of the I spins in the second experiment is performed by adiabatic demagnetization in the rotating frame (ADRF). In this case the cross-polarization process occurs with no applied rf irradiation field on the I spins. A schematic representation of these two experiments is given in Fig. 2. In both cases after the preparation of the I spins we have (using $\| \|$ to denote magnitude)

$$\| \beta_I H_I \| \gg \| \beta_S H_S \|$$

and the density matrix can be written as

$$\rho_{\text{initial}} = Z^{-1}(1 - \beta_I H_I),$$  \hspace{1cm} (2.11)

where we neglected the $H_S$ term. After cross-polarization the density matrix becomes

$$\rho_{\text{final}} = Z^{-1}[1 - \beta_I(H_I + H_S)].$$  \hspace{1cm} (2.12)

During the evolution period of $\rho_I$ energy is conserved and the initial energy $E_{\text{initial}}$ of the total spin system is equal to the final energy $E_{\text{final}}$:

$$E_{\text{initial}} = E_{\text{final}},$$  \hspace{1cm} (2.13)

with

$$E_{\text{initial}} = \text{Tr}(\rho_{\text{initial}} H),$$

$$E_{\text{final}} = \text{Tr}(\rho_{\text{final}} H)$$

$$= -Z^{-1}\beta_I [\text{Tr}(H_I^2) + \text{Tr}(H_S^2)].$$  \hspace{1cm} (2.14)

In order to obtain explicit expressions for $\beta_I$ from Eq. (2.13) we must distinguish between the SL experiment and the ADRF experiment. We therefore evaluate $\beta_I$ and the enhancement of the S-spin intensities for the two techniques separately.

FIG. 1. Schematic representation of the cross-polarization process between two spin systems with spin values $I = S = \frac{1}{2}$. The spin systems have Hamiltonians $H_I + H_{II}$ and $H_S$, respectively. The two systems are connected by the magnetic dipolar interaction $H_D$. This interaction causes an energy flow from the S spins to the I spins, if the applied rf irradiation field intensities $\omega_{I}$ and $\omega_{S}$ have the right values ($H_D = -\omega_{I}I_z = -\omega_{S}S_z$). In a spin-lock experiment these intensities must be taken according to the Hartmann-Hahn condition in Eq. (2.10) $\omega_{I} = \omega_{S}$. 

FIG. 2. Representation of four cross-polarization experiments on a spin system, consisting of high-abundant I spins and rare S spins. The two experiments at the top of the figure are spin-lock experiments. Here the I spins are prepared by a 90° pulse followed by a 90° phase shift of the rf irradiation field. After this preparation the cross-polarization process takes place during the application of an additional rf field on the S spins. The intensity of this rf field must be chosen according to the Hartmann-Hahn condition. At the end of the cross polarization we can detect the increase of the S signal intensity directly (left) or monitor the polarization of the S spins indirectly by the detection of the decrease of the I signal intensity (right). At the bottom of the figure two ADRF experiments are represented. In these cases after the preparation of the I spins as in the spin-lock case, the rf irradiation field is decreased to zero. The cross polarization occurs again by the application of an rf field on the S spins. The direct detection of the S signal after the cross-polarization period is the same as for the spin-lock case. For the indirect detection we must apply an additional 45° pulse on the I spins in order to recover the I signal.
A. Spin locking experiment

In the spin-lock experiment the I spins are cooled by a 90° rf pulse followed by an immediate 90° phase change of the irradiation field in order to lock the I spins to this field. After this preparation we apply simultaneously an rf irradiation field on the I spins and the S spins according to the Hartmann-Hahn condition (2.10). The Hamiltonian in Eq. (2.7) with \( ||\omega_I I_x|| \gg ||H_{II}|| \) becomes

\[
H = H_I + H_S = -\omega_I I_x - \omega_S S_x ,
\]

where we neglect \( H_{II} \) and \( H_{IS} \) and

\[
\rho_{\text{initial}} = e^{-i(\pi / 2)S} \rho_{\text{eq}} e^{i(\pi / 2)I},
\]

where \( S = Z^{-1}(1 - \beta_Z \omega_0 I_x - \beta_Z \omega_0 S_x) \).

For convenience we transform the spin system by the unitary operator

\[
U_{\text{SL}} = \exp[-i \frac{\pi}{2}(I_x + S_x)],
\]

in order to obtain the Hamiltonian in terms of operators in the \( z \) direction

\[
H^T = U_{\text{SL}}^{-1} H U_{\text{SL}} = H_I^T + H_S^T = -\omega_I I_x - \omega_S S_x .
\]

The initial density matrix is now written according to Eqs. (2.11) and (2.16) as

\[
\rho_{\text{initial}}^T = U_{\text{SL}}^{-1} \rho_{\text{initial}} U_{\text{SL}} = Z^{-1}(1 - \beta_T H_I^T),
\]

with

\[
\beta_T = \beta_Z \omega_0 / \omega_I ,
\]

which gives indeed \( \beta_T \gg \beta_Z \). After this preparation the \( I \) - and \( S \)-spin systems will evolve to a state given by

\[
\rho_{\text{final}}^T = Z^{-1}(1 - \beta_T (H_I^T + H_S^T)) .
\]

With Eqs. (2.13) and (2.14) it is now possible to calculate \( \beta_T \) with

\[
\begin{align*}
E_{\text{initial}} &= Z^{-1} \beta_T \omega_0^2 \text{Tr}(I^T_2) = \beta_T C_I , \\
E_{\text{final}} &= Z^{-1} \beta_T \{ \text{Tr}(I^T_2) + \text{Tr}(S^T_2) \} \\
&= \beta_T (C_I + C_S) ,
\end{align*}
\]

and

\[
\beta_T = \frac{\beta_T C_I}{C_I + C_S} = \beta_T (1 + \frac{C_S}{C_I} )^{-1} .
\]

The heat capacities \( C_I \) and \( C_S \) of the I and S spins, respectively, introduced in Eq. (2.21) are defined as

\[
\begin{align*}
C_I &= \frac{\delta E / \delta \beta_I}{\beta_I} = -Z^{-1} \text{Tr}(H_I^T)^2 = Z^{-1} \omega_0^2 I_x \text{Tr}(I^T_2) , \\
C_S &= \frac{\delta E / \delta \beta_S}{\beta_S} = -Z^{-1} \text{Tr}(H_S^T)^2 = Z^{-1} \omega_0^2 S_x \text{Tr}(S^T_2) ,
\end{align*}
\]

and with

\[
Z^{-1} = (2I + 1)^N (2S + 1)^N
\]

and

\[
\begin{align*}
\text{Tr}(I^T_2) &= \text{Tr}[\sum_i I^T_{2i}] \\
&= \frac{1}{2} (2S + 1)^N (2I + 1)^N r_{II} , \\
\text{Tr}(S^T_2) &= \text{Tr}[\sum_i S^T_{2i}] \\
&= \frac{1}{2} (2I + 1)^N (2S + 1)^N r_{II} ,
\end{align*}
\]

they become

\[
C_I = \frac{1}{2} \frac{N_I}{2I + 1} \omega_I = \frac{1}{4} N_I \omega_I^2 ,
\]

and

\[
C_S = \frac{1}{2} \frac{N_S}{2S + 1} \omega_S = \frac{1}{4} N_S \omega_S^2 .
\]

Realizing that \( N_S \ll N_I \) and \( \omega_{1S} \approx \omega_{1I} \), the ratio \( \epsilon \) between the heat capacities is very small

\[
\epsilon = \frac{C_S}{C_I} = \frac{N_S}{N_I} \frac{\omega_I^2}{\omega_S^2} ,
\]

and to a good approximation we can write

\[
\beta_T = \beta_T (1 + \epsilon)^{-1} \approx \beta_T (1 - \epsilon) = \beta_T (\omega_0 / \omega_I) (1 - \epsilon) .
\]

B. ADRF experiment

The cooling of the I spins in the case of an adiabatic demagnetization in a rotating frame (ADRF) experiment is performed by first spin locking these spins to an rf field and then reducing this field to zero adiabatically. The spins are then locked to their local fields due to their neighboring I spins. The initial condition of the spin system is here given by

\[
\rho_{\text{initial}} = Z^{-1}(1 - \beta_T H_{II}) ,
\]

with

\[
\beta_T = \beta_Z \omega_0 / \omega_I ,
\]

where \( \omega_J \) represents the local field intensity defined by

\[
\omega_J = \frac{\text{Tr}(H_{II}^T)}{\text{Tr}(I^T_2)} .
\]

After the preparation of the I spins an rf field is applied to the S spins and the cross-polarization process will start. During the cross polarization we have

\[
H = H_I + H_S = H_{II} - \omega_1 S_x
\]

and in order to represent \( H \) in terms of \( S \) we again perform a transformation of the spin sys-
tem, but now defined by the operator
\[ U_{\text{ADRF}} = \exp(-i\frac{\pi}{2}S_y) \]  

(2.36)
The Hamiltonian becomes
\[ H_T = U_{\text{ADRF}}^* H U_{\text{ADRF}} = H_T^I - \omega_1 S_z \]  

(2.37)
and the final density matrix
\[ \rho_{\text{final}} = U_{\text{ADRF}}^* \rho_{\text{initial}} U_{\text{ADRF}} \]
\[ = Z^{-1}\left[1 - \beta_0 (H_{T} - \omega_1 S_z)\right] \].  

(2.38)
Energy conservation leads to a similar result as in Eq. (2.22) for \( \beta_f \)
\[ \beta_f = \beta_0 C_f / C_s, \]
with \( C_s \) as in Eq. (2.24) and
\[ C_f = Z^{-1} \text{Tr}(H_{Tf}^I). \]  

(2.40)
Here again because of \( C_f \gg C_s \) we have
\[ \beta_f = \beta_0 (1 - \epsilon). \]

C. Signal intensities
The results for \( \beta_f \) from the SL and the ADRF experiments can now be used to evaluate the increase in intensity of the \( S \)-spin signals after cross polarization. This signal intensity \( M_2 \) must be compared with the \( S \)-signal intensity \( M_2^S \) after a single 90° pulse on the \( S \) spins. The signal intensity \( M_2 \) is proportional to \( \beta_f \) and can be represented by
\[ M_2 = \text{Tr}(\rho_{\text{final}} S_2) = Z^{-1} \omega_1 \beta_f \text{Tr}(S_2^I) = \frac{1}{2} \beta_f N_0 \omega_0 \epsilon. \]  

(2.41)
The signal intensity \( M_2^S \) is easily calculated and equals
\[ M_2^S = \text{Tr}(\rho_{eq} S_2) = Z^{-1} \omega_0 \omega_1 \beta_f \text{Tr}(S_2^I) = \frac{1}{2} \beta_f N_0 \omega_0 \omega_1 \]

(2.42)
and the ratio between these two signals becomes
\[ \frac{M_2}{M_2^S} = \frac{\omega_1 \beta_f}{\omega_0 \beta_f}. \]  

(2.43)
For the SL case and using Eq. (2.31) this ratio becomes
\[ \frac{M_2}{M_2^S} = \frac{\omega_1 \beta_f}{\omega_0 \beta_f} (1 - \epsilon) = \frac{\gamma I}{\gamma_S} (1 - \epsilon), \]

(2.44)
where we used the Hartmann-Hahn condition in Eq. (2.10). For the ADRF case we obtain the same result if we assume that
\[ \omega_I = \omega_1 S. \]  

(2.45)
From (2.44) we see that for an SL or an ADRF experiment the enhancement of the \( S \)-signal intensity is \( \gamma_I/\gamma_S \), which equals 4.2 for \( I = \frac{1}{2} \) and \( S = 1 \) spins.

In addition to the direct detection of the NMR signals of the \( S \) spins it is also possible to monitor the cross-polarization process by an indirect detection method. In that case we monitor the decrease in the signal intensities of the \( I \) spins due to cross polarization. This can be done as a function of time by repolarizing after evolution of the \( S \) spins to monitor the high-resolution \( S \) free-induction decrease (see Fig. 15 of Ref. 13). In the SL experiment this signal intensity just after spin locking equals
\[ \frac{M_I^T - M_I}{M_I^T} = \frac{\beta_I - \beta_f}{\beta_f} = \epsilon. \]  

(2.48)
This is modified to \( \epsilon[2 - S(t)] \), where \( S(t) \) is the \( S \) free-induction decay, for the experiment of Ref. 12.

The small change in \( M_I \) due to the cross-polarization process gives a measure for the ratio of the heat capacities of the \( S \) spins and the \( I \) spins. For ADRF a similar result is obtained for the relative ratio in Eq. (2.48).

III. SPIN THERMODYNAMICS WITH \( I = \frac{1}{2}, S = 1 \)

A. Introduction
We describe here the thermodynamics of cross polarization for the case of abundant spins \( I = \frac{1}{2} \) and rare spins \( S = 1 \). Because the \( S \)-spin system is a three-nuclear-spin-energy-level system, the theory of cross polarization for this system is somewhat richer than the \( I = \frac{1}{2}, S = \frac{1}{2} \) case. However, we realize that under appropriate conditions in an NMR experiment the cross-polarization process occurs only between the \( I \) spins and one of the transitions of the \( S \) spins. Both the two allowed transitions \( (\Delta M = 1) \) and the forbidden double-quantum transition \( (\Delta M = 2) \) can cross polarize separately with the \( I \) spins, depending on the experimental conditions. The cross-polarizing transition of the \( S \) spins can be treated as a fictitious spin-\( \frac{1}{2} \) transition and the part of the \( S \)-spin system corresponding to this transition, together with the \( I \) spins, forms a spin system similar to the one discussed in Sec. II. Therefore we can use the
formalism of Sec. II to describe the cross-polarization process for the \( I = \frac{1}{2}, S = 1 \) case, and this simplifies the theoretical derivations of the spin thermodynamics.

In this section we discuss the spin thermodynamics of cross polarization for each individual transition of the \( S \) spins separately. For each case the corresponding Hartmann-Hahn condition is derived, spin temperatures are calculated, and the signal intensities from direct and indirect detection measurements are obtained. To simplify the actual calculations we first introduce the fictitious spin-\( \frac{1}{2} \) operator formalism for the \( S \)-spin system. Then the general theory of cross polarization is given and finally explicit expressions are derived.

B. Spin system with \( S = 1 \)

Fictitious spin-\( \frac{1}{2} \) operator formalism

It was shown that for the description of NMR experiments on multilevel spin systems, it is convenient to express the Hamiltonian and the spin density matrix in terms of fictitious spin-\( \frac{1}{2} \) operators.\(^1,11,18\) For spins \( S = 1 \) the matrix elements of these operators are defined in the basis set

\[
|1\rangle = |+1\rangle, \quad |2\rangle = |0\rangle, \quad |3\rangle = |-1\rangle,
\]

(3.1)

where \( |+1\rangle, |0\rangle, \) and \( |-1\rangle \) are the eigenstates of \( S_z \) of the \( S \) spins. The operators are defined by their nonzero matrix elements using the notation

\[
\begin{align*}
\langle i | S^+ | j \rangle &= \langle j | S^- | i \rangle = \frac{1}{2}, \\
\langle i | S^z | j \rangle &= \langle j | S^z | i \rangle = \frac{1}{2} i,
\end{align*}
\]

(3.2)

and we see immediately that the operators \( S^\pm_2 \) and \( S^\pm_3 \) with \( p = x, y, z \) form the single-quantum operators, while \( S^\pm_3 \) are the double-quantum operators. With these definitions we obtain

\[
\begin{align*}
S_x &= \sqrt{2}(S^+_x + S^-_x), \\
S_y &= \sqrt{2}(S^+_y + S^-_y), \\
S_z &= 2S^+_z = 2(S^+_x + S^+_y),
\end{align*}
\]

(3.3)

and with \([S^+_l, S^-_r] = iS^0_l \) where \( p, q, r = x, y, z \) or cyclic permutations we have

\[
U^+_p(-\theta)S^+_pU^-_p(\theta) = S^+_p \cos \theta + S^0_p \sin \theta,
\]

where

\[
U^+_p(\theta) = \exp(\pm iS^0_p \theta).
\]

Additional commutation relations between the \( S^\pm_l \) operators are given elsewhere.\(^11,15\)

Hamiltonian

The Hamiltonian of the \( S \) spins in a solid in an external magnetic field \( H_Z = \omega_0 S_l / \gamma_0 \) and with an rf irradiation field at frequency \( \omega \) and intensity \( \omega_{1s} \), becomes in the rotating frame

\[
H = -\Delta \omega S_z + \frac{3}{2} \omega_0 [S^2_x - S(S + 1)] - \omega_{1s} S_z,
\]

(3.4)

with the quadrupole frequency

\[
\omega_q = \frac{1}{4} e^2 q Q \left( \frac{1}{3} (3 \cos \theta - 1) + \eta \sin^2 \theta \cos 2\phi \right)
\]

and the off-resonance frequency

\[
\Delta \omega = \omega_0 - \omega.
\]

In terms of the fictitious spin-\( \frac{1}{2} \) operators, \( H \) becomes

\[
\begin{align*}
H &= -2\Delta \omega S^2 - \frac{3}{2} \omega_0 [S^2_x - S(S + 1)] \\
&= -\sqrt{2} \omega_{1s} (S^+_x + S^-_x + S^0_x)
\end{align*}
\]

(3.5)

and the general form of the density matrix is

\[
\rho = a_0 I + \sum_{S \sigma} \sum_{p=x,y,z} a^\sigma_{p} S^\sigma_{p} S^\sigma_{p},
\]

(3.6)

with

\[
a^\sigma_{p} = \text{Tr}(\rho S^\sigma_{p}^\dagger).
\]

A schematic representation of \( \rho \) is given in Fig. 4. In this representation we assign to each transition a coordinate system with axes \( x^\tau \), \( y^\tau \), and \( z^\tau \) and we define \( \rho \) by one vector in each of these systems. The three vectors are not totally independent because the \( S^\tau \) operators are not indepen-
The behavior in time of $\rho$ can be represented by the motion of these vectors due to the effective field each of them feels.

Irradiation near allowed transition ($\Delta \omega = \omega_Q$)

For an rf irradiation field at a frequency close to one of the satellites of the spectrum $\Delta \omega = \omega_Q + \delta \omega$ the Hamiltonian becomes

$$H_s = -2(\omega_Q + \delta \omega)(S_x^2 + S_z^2) + \frac{1}{2}(\omega_Q + 2\delta \omega)(S_x^2 - S_z^2) + \sqrt{2}\omega_{1S}(S_x^2 + S_z^2)$$

and with Eq. (3.7) and $\omega_{1S}, \delta \omega \ll \omega_Q$

$$H_s \approx -\delta \omega S_x^2 - \sqrt{2}\omega_{1S}(S_x^2 + S_z^2) - (\frac{4}{3}\omega_Q + \delta \omega)(S_x^2 + S_z^2).$$

In order to change the irradiation term in $H_s$ to a Zeeman-like term, we transform $H_s$ with the unitary operator

$$U_y^{1+}(\frac{1}{2}\pi) = \exp(i\frac{1}{2}\pi S_y^2)$$

and get

$$H_s^R = U_y^{1+}(-\frac{1}{2}\pi)H_s U_y^{1-}(\frac{1}{2}\pi)$$

$$= -3\omega S_x^2 + \sqrt{2}\omega_{1S}(S_x^2 + S_z^2) - (\frac{4}{3}\omega + \delta \omega)(S_x^2 + S_z^2).$$

(3.9)

This Hamiltonian can be written in terms of two commuting parts:

$$H_s^R = H_{s1}^R + H_{s2}^R,$$

with

$$H_{s1}^R = \sqrt{2}\omega_{1S}(S_x^2 - \delta \omega S_z^2),$$

$$H_{s2}^R = -\omega S_x^2 + \delta \omega(S_x^2 + S_z^2),$$

and

$$[H_{s1}^R, H_{s2}^R] = 0.$$  

(3.12)

The commutation relation can be verified using the general rule

$$[S_{x}^{r-j}, S_{x}^{r-k} + S_{r}^{s-k}] = 0, \quad r = x, y, z.$$  

(3.13)

From this form of $H_s^R$ we see that the Hamiltonian looks like a spin-$\frac{1}{2}$ Hamiltonian $H_{s1}^R$ and a remainder $H_{s2}^R$ which is orthogonal to it thermodynamically. In this particular case the 1-2 transition forms the fictitious spin-$\frac{1}{2}$ system. The Hamiltonian $H_{s1}^R$ in this coordinate system consists of an rf irradiation term with an effective field strength $\sqrt{2}\omega_{1S}$ and an off-resonance term with off-resonance frequency $\delta \omega$. In this case the $S_{x}^{r-j}$ vector of $\rho$ behaves like a fictitious spin-$\frac{1}{2}$ magnetization vector under off resonance $\delta \omega$ and irradiation strength $\sqrt{2}\omega_{1S}$ in the 1-2 coordinate system.

Irradiation near other allowed transition ($\Delta \omega = -\omega_Q$)

In the case $\Delta \omega = -\omega_Q$ the Hamiltonian of Eq. (3.5) is of the form

$$H_s = -\delta \omega S_x^2 - \sqrt{2}\omega_{1S}(S_x^2 + S_z^2) + \frac{1}{2}(\omega_Q + \delta \omega)(S_x^2 + S_z^2)$$

(3.14)

and with an additional transformation it becomes

$$H_s^R = U_y^{1+}(-\frac{1}{2}\pi)U_y^{1-}(\frac{1}{2}\pi)$$

$$= -\delta \omega S_x^2 + \sqrt{2}\omega_{1S}(S_x^2 + S_z^2) + \frac{1}{2}(\omega_Q + \delta \omega)(S_x^2 + S_z^2),$$

with

$$U_y^{1+}(\frac{1}{2}\pi) = \exp(i\frac{1}{2}\pi S_y^2),$$

which again can be written as

$$H_s^R = H_{s1}^R + H_{s2}^R,$$

(3.15)
but now
\[
\begin{align*}
H_{S1}^T &= -5\omega_6 S_{x1}^{-3} + \sqrt{2} \omega_1 S_{x1}^{+3}, \\
H_{S2}^T &= \left( \frac{4}{3} \omega_2 + 5 \omega \right) (S_{x2}^{+2} + S_{x2}^{-3}).
\end{align*}
\] (3.16)

From these equations we see that the 2-3 transition forms the fictitious spin-$\frac{1}{2}$ transition and this is exactly the irradiated transition according to the definitions in Eq. (3.1).

**Irradiation near center ($\Delta \omega \sim 0$)**

Weak rf irradiation $\omega_{1S} \ll \omega_6$ near the center of the spectrum of the $S$ spins can introduce double-quantum coherence between the levels $|1\rangle$ and $|3\rangle$. In this case we would like to be able to write the Hamiltonian also in the form of Eqs. (3.10) and (3.14). In order to obtain this form it is necessary to transform $H_\phi$ with the unitary operator
\[
U_\phi^{\dagger} = \exp(i \frac{\phi}{2} \pi S_{y1}^{-3}),
\] (3.17)

which results in
\[
\begin{align*}
H_{S1}^T &= U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} (\theta) \\
&= -25 \omega S_{x1}^{-3} - \omega_6 S_{x1}^{+3} - 2 \omega_1 S_{x1}^{+3} \\
&= -25 \omega S_{x1}^{-3} + \omega_6 S_{x1}^{+3} - 2 \omega_1 S_{x1}^{+3} + \frac{5}{3} \omega_6 (S_{x1}^{+2} + S_{x1}^{-3}).
\end{align*}
\] (3.18)

The actual evaluation of this transformation and a discussion about the fact that the (1-3) transition after this transformation still corresponds to the double-quantum transition, is given elsewhere. An additional transformation of $H_\phi$ with the unitary operator
\[
U_\theta^{\dagger} = \exp(-i \theta \pi S_{y1}^{-3}),
\] (3.19)

will result in
\[
\begin{align*}
H_\phi^T &= U_\theta^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} U_\phi^{\dagger} (\theta) \\
&= -25 \omega \cos \theta S_{x1}^{-3} - 25 \omega \sin \theta S_{x1}^{+3} - (\omega_6^2 + 4 \omega_1^2)^{1/2} S_{x1}^{+3}. \quad (3.20)
\end{align*}
\]

With the assumptions $\omega_1, \omega_6 \ll \omega_6$, and $\theta \ll 1$ this tilted Hamiltonian becomes
\[
\begin{align*}
H_\phi^T &\approx -25 \omega S_{x1}^{-3} - \frac{1}{2} \left( (\omega_6^2 + 4 \omega_1^2)^{1/2} - \omega_6 \right) S_{x1}^{+3} + \frac{5}{3} \omega_6 (S_{x1}^{+2} - S_{x1}^{-3}) \\
&\approx -25 \omega S_{x1}^{-3} - (\omega_6^2 / \omega_6) S_{x1}^{+3} + \frac{5}{3} \omega_6 (S_{x1}^{+2} + S_{x1}^{-3}).
\end{align*}
\] (3.21)

This equation can be written again as
\[
H_\phi^T = H_{S1} + H_{S2},
\] (3.22)

with
\[
H_{S1} = -25 \omega S_{x1}^{-3} - (\omega_6^2 / \omega_6) S_{x1}^{+3},
\] (3.23)

\[
H_{S2} = \frac{5}{3} \omega_6 (S_{x1}^{+2} - S_{x1}^{-3}).
\]

Now the (1-3) double-quantum transition forms the fictitious spin-$\frac{1}{2}$ system.

In all three cases we succeeded in representing the Hamiltonian in terms of two commuting parts, one part representing a fictitious spin-$\frac{1}{2}$ Hamiltonian. We can now apply the theory of Sec. II to describe the cross-polarization process between the $I$ spins and the fictitious spin-$\frac{1}{2}$ transition of $S$. In the following subsection we give a general description of the cross-polarization of all three cases and for each case we derive explicit equations for the various interesting parameters separately.
motion and therefore behave independently from the thermodynamic point of view. Cross polarization occurs only between the I spins and the part of the S spins corresponding to \( H_{S1} \). If the spin system is prepared in a state with \( \beta_I \neq \beta_{S1} \), the density matrix will evolve, during proper applied irradiation fields, towards

\[
\rho_{\text{final}} = Z^{-1} \left[ 1 - \beta_I (H_{S1} + H_I) - \beta_S (H_{S1} + H_S) \right],
\]

(3.26) where the final temperature coefficient is calculated in the same way as in Sec. II:

\[
\beta_J = \frac{\beta_{S1} C_{S1} + \beta_I C_I}{C_{S1} + C_I}.
\]

(3.27)

The heat capacity \( C_J \) of the I spins is defined in Eq. (2.28) and the heat capacity \( C_{S1} \) of the \( H_{S1} \) part of the S spins equals

\[
C_{S1} = \frac{\partial}{\partial H_{S1}} \left[ \text{Tr}(\rho^n H_{S1}) \right].
\]

(3.28)

In a cross-polarization experiment the value of \( \beta_I \) in the initial density matrix is prepared in the same way as described in Sec. II. Again two techniques are considered, spin locking (SL) and adiabatic demagnetization in the rotating frame (ADR). In the thermal mixing period the rf irradiation fields on the I and the S spins must be chosen properly in order to minimize the cross-polarization time. The efficiency of cross polarization as a function of the irradiation field intensities is discussed now for the different transitions of \( S \). In the SL case for each transition the Hartmann-Hahn condition is derived and the \( \beta_I \) and \( \beta_S \) values are evaluated. Direct and indirect detection methods are discussed as well.

D. Single-quantum (\( \Delta M = 1 \)) polarization

Spin temperature and the Hartmann-Hahn condition

Enhancement of one of the NMR spectral lines of rare S spins in a solid can be achieved by cross-polarization between the corresponding allowed single-quantum transition of the S spins and the abundant I spins. With the general description of cross polarization in the spin system with \( I = \frac{1}{2} \) and \( S = 1 \) given in the former paragraph, we can derive easily explicit expressions for the spin temperature coefficients in our case.

We consider an SL experiment on the (1-2) transition of \( S \) and derive the modified Hartmann-Hahn condition. The total Hamiltonian of our spin system, during the thermal mixing time is given in Eq. (3.24)

\[
H_T = H_{T1}^I + H_{T1}^S + H_{T2}^S + H_{T2}^I,
\]

with \( H_{T1}^I \) given in Eq. (2.17) and \( H_{T1}^S \) and \( H_{T2}^S \) in Eq. (3.11). The dipole-dipole interaction \( H_{T2}^S \) is obtained by tilting \( H_{IS} \) (Eq. 2.2) with the unitary operator

\[
U_{SL}^{-1} = \exp \left[ i \frac{1}{2} \pi (S^z_1 + I_j) \right]
\]

(3.29) and results in

\[
H_{IS} = (U_{SL}^{-1}) H_{IS} U_{SL}^{-1} = \left( t_{S1}^{-1} \right) H_{IS} U_{SL}^{-1} \]

\[
= \left( t_{S1}^{-1} \right) \left( 2 \sum b_{is} I_{is} (S^z_{is} - S^z_{is} + S^z_{is} + S^z_{is}) \right) U_{SL}^{-1}
\]

\[
= 2 \sum b_{is} I_{is} (S^z_{is} - S^z_{is} + S^z_{is} + S^z_{is}) \]

(3.30)

We used Eqs. (3.3), (3.7), and (3.9) for the derivation of Eq. (3.30). \( U_{SL}^{-1} \) is the operator which tilts simultaneously, \( H_I \) and \( H_S \) to \( H_{T1}^I \) and \( H_{T2}^S \), respectively. In Fig. 5 we show a schematic representation of the single-quantum cross-polarization process. From Eq. (3.30) we see that \( H_{T2}^S \) can be divided into two commuting parts

\[
[H_{T1}^S, H_{T2}^S] = 0,
\]

(3.31) and for \( \delta \omega = 0 \)

\[
[H_{T1}^S, H_{T2}^S] = 0,
\]

\[
[H_{T1}^S, H_{T2}^S] = 0
\]

(3.32)

From these commutation relations it is clear, that for experiments on the (1-2) transition, only the term \( H_{T1}^S \) in the dipole-dipole interaction is active during the cross-polarization process.

To evaluate the spin temperature coefficients of our spin system after an SL experiment, we per-
form a similar calculation as in Sec. II. After the preparation of the I spins, the density matrix 
\( \rho_{\text{initial}} \) is given again by Eq. (2.18), and thermal mixing will occur when the Hartmann-Hahn condition is fulfilled. In our case cross-polarization takes place between the terms of \( \rho^T \) with

\[
H_{S1}^T = -\delta \omega_S T^2 + \sqrt{2} \omega_{S} S^T \quad \text{and} \quad H_{I}^T = -\omega_{I} I^T,
\]

(3.33)

and the corresponding Hartmann-Hahn condition becomes for \( \delta \omega = 0 \) (see Fig. 6)

\[
\sqrt{2} \omega_{S} = \omega_{I}
\]

(3.34)

and in general

\[
\delta \omega^2 + 2 \omega_S^2 = \omega_I^2.
\]

(3.35)

With the expression for \( \beta_I \) in Eq. (3.27) together with the initial value of \( \beta_I \) for the SL case (Eq. 2.19) we obtain

\[
\beta_I = \beta_I(1 + C_{S1}/C_I)^{-1} \approx \beta_I(\omega_q/\omega_I)(1 - \epsilon_S),
\]

(3.36)

where the heat capacity \( C_I \) is given in Eq. (2.28) and the heat capacity \( C_{S1} \) equals

\[
C_{S1} = \frac{1}{N_I} N_S (\delta \omega^2 + 2 \omega_S^2).
\]

(3.37)

The ratio between \( C_{S1} \) and \( C_I \) is

\[
\frac{C_{S1}}{C_I} = \frac{2}{{\frac{3}{N_I}}} \frac{\omega^2 + 2 \omega_S^2}{\omega_I^2}.
\]

(3.38)

Insertion of \( \beta_I \) in the final expression for the density matrix yields

\[
\rho_{\text{final}}^T = Z^{-1}[1 - \beta_L(\omega_q/\omega_I)(1 - \epsilon_S)(\delta \omega^2 + 2 \omega_S^2 - \omega_{I} I^T) + \beta_S(\frac{3}{4} \omega_q - \delta \omega)(S^T - S^T S)]
\]

(3.39)

which does not affect \( H_I \). By replacing \( \omega_I \) by \( \omega_I \) with \( \omega_I \) [Eq. (2.34)] and taking \( C_I \) from (2.40) in (3.27) we obtain the expression for \( \beta_I \) after the ADRF experiment.

For the ADRF experiments the I spins system is not irradiated during the thermal mixing and in order to obtain \( \beta_I \) from Eq. (3.27) we have to use \( H_I = H_{II} \) (Eq. 2.34). The tilted frame in the ADRF case is obtained by the transformation operator

\[
U_{\text{ADRF}}^{1/2} = \exp(i\frac{\pi}{2} S^T S)
\]

(3.40)

FIG. 6. Energy-level diagram of a spin \( S=1 \) system and a spin \( I=\frac{1}{2} \) in the rotating frame. In addition to the external magnetic field and the internal quadrupolar interaction \( H_0 = \frac{3}{2} \omega_0 B_z^2 - S(S+1) \), rf irradiation fields are applied with \( H_{II} = -\omega_I S_1 - \Delta \omega S_y \) and \( H_{IR} = -\omega_I I_z \). For \( \Delta \omega = \omega_0 \) the Hamiltonian, which corresponds to an irradiation field at the frequency of one of the allowed transitions of the S-spin system, the energy levels of the S spins are the eigenstates of the Hamiltonian \( H_0 + H_{II} \) with \( \Delta \omega = 0 \) and \( \Delta \omega = \omega_0 \). The energy levels of the I-spin system correspond also to the diagonalized Hamiltonian \( H_{IR} \). In a spin-lock cross-polarization experiment the I spins is maximum, when the \( \Delta \omega \) energy difference \( \sqrt{2} \omega_{I2} \) is equal to the \( \Delta \omega \) energy difference \( \Delta \omega^2 \). This is just the Hartmann-Hahn condition in Eq. (3.34).

\[
M^T_{S_I} = \sqrt{2} \text{Tr}(\rho_{\text{final}} S^T_{S_I} S^T_{S_I}) = \sqrt{2} \text{Tr}(\rho_{\text{final}} S^T_{S_I} S^T_{S_I})
\]

\[
= -Z^{-1} \beta_L \frac{\omega_{I2}}{\omega_I} (1 - \epsilon_S) \sqrt{2} \omega_{I1} S_1 \text{Tr}(S^T_{S_I} S^T_{S_I})
\]

\[
= -\frac{\sqrt{2}}{6} N_S \omega_{I2} \beta_L \frac{\omega_{I2}}{\omega_I} (1 - \epsilon_S),
\]

(3.41)

The NMR signal intensity of the \( S \) spins after an SL experiment on the (1-2) transition in the \( x \) direction is

\[
M^T_{S_I} = \sqrt{2} \text{Tr}(\rho_{\text{final}} S^T_{S_I} S^T_{S_I})
\]

which is derived from the definitions of the \( S^T_{S} \) operators in Eq. (3.3). In a similar way we can show that the other contributions to the \( S \) spin signal intensities are all zero.
\[ M_{S^2}^z = \sqrt{2} \text{Tr}(\rho_{\text{final}} S_{y}^z) \]
\[ = \sqrt{2} \text{Tr}(\rho_{\text{init}} S_{y}^z) = 0, \]
\[ M_{S^2}^x = \sqrt{2} \text{Tr}(\rho_{\text{final}} S_{x}^z) \]
\[ = \text{Tr}[\rho_{\text{final}} (S_{x}^z + S_{y}^z)] = 0, \quad (3.42) \]
\[ M_{S^2}^y = \frac{1}{2} \sqrt{2} N g \beta_L \omega_{S} \rho_{\text{init}}. \quad (3.43) \]

The 90° pulse was taken in the y direction.

\[ \rho_{\text{init}} = e^{-i(\epsilon/2)S_z} \rho_{\text{init}} e^{i(\epsilon/2)S_z} \]
\[ = Z[1 - \beta_L \omega_{S} S_z - \beta_L \omega_{I} I_z] \]
\[ = Z[1 - \sqrt{2} \beta_L \omega_{S} (S_z^2 + S_y^2) - \beta_L \omega_{I} I_z] \quad (3.44) \]

with \( \rho_{\text{init}} \) from Eq. (2.4).

Comparison between Eqs. (3.41) and (3.43) gives an enhancement factor
\[ \frac{|M_{S^2}^z|}{|M_{S^2}^z|} = \frac{\omega_{I} \sqrt{2} \omega_{S}}{\omega_{S} \omega_{I}} (1 - \epsilon_S) \]
\[ = \frac{1}{2} \sqrt{2} \omega_{S} \omega_{I} (1 - \epsilon_S). \quad (3.45) \]

With the Hartmann-Hahn condition and \( \delta \omega = 0 \), the enhancement of the signal intensity \( M_{S^2}^z \) is again equal to the ratio of the magnetogyric ratios of the \( I \) and \( S \) spins. This is not surprising, because the cross polarization occurs between the \( I = \frac{1}{2} \) spins and the single-quantum fictitious spin-\( \frac{1}{2} \) (1-2) transition of the \( S \) spins. Exactly the same results are obtained for the (2-3) transition. For an ADRF experiment on the single-quantum transitions of the \( S \) spins we obtain the same expression for \( M_{S^2}^z \) as in Eq. (3.41), except that we replace \( \omega_{I} \) by \( \omega_{r} \).

The destruction of the \( I \)-spin signal intensity after an SL experiment on the (1-2) transition of the \( S \) spins can also be obtained easily. Similar to the derivation in Sec. II we get as in Eq. (2.48)
\[ \frac{M_{I}^z - M_{I}^z}{M_{I}^z} = \frac{\epsilon_S}{2} \frac{N_S}{N_I} \frac{2 \omega_{I}^2 + 5 \omega^2}{\omega_{I}^2}. \quad (3.46) \]

The same relative destruction is obtained for an SL experiment on the (2-3) transition of the \( S \) spins.

For an ADRF experiment the destruction of the \( I \)-spin signal is the same again as for the SL case, except that an efficiency factor \( \eta \) must be added to Eq. (3.46). This factor is dependent on the experimental method for the recovery of an \( I \) signal from the cooled dipole-dipole interaction reservoir of the \( I \) spins. In this article we consider the application of a 45° pulse on the \( I \) spins in order to monitor the spin temperature coefficient \( \beta_I \) of \( \rho_{\text{final}} \).

We now turn to the interesting case where the double-quantum transition of the \( S \) spins is polarized. The cross polarization between the \( I \) spins and this double-quantum transition can be used to create enhanced double-quantum coherence. Because the double-quantum coherence is independent of the quadrupolar interaction, its time behavior after cross polarization is strongly dependent on chemical shifts. Measurements of this time dependence form an alternative method for the detection of high-resolution spectra in solids.
E. Double-quantum (ΔM = 2) polarization

Spin temperature and the Hartmann-Hahn condition

Cross polarization between the I spins and the double-quantum transition of the S spins can also be described with the general theory for cross polarization in the \( I = \frac{1}{2}, S = 1 \) system given before. The Hamiltonian for this case is given again in Eq. (3.24) with \( H_T^I \) for the SL experiment given in (2.17). The terms \( H_{S1} \) and \( H_{S2} \) in the Hamiltonian are given in Eq. (3.23). A representation of this cross-polarization experiment is given in Fig. 8. In this case the dipole-dipole interaction term \( H_{T^I} \) is obtained by the transformation operator

\[
U_{T^I}^{S^1} = \exp \left[ i \frac{1}{2} \mathbf{r} \left( \mathbf{S}^{3^1} \right) \right] \exp \left[ i \theta \mathbf{S}^{2^I} \right],
\]

\[
H_{T^I}^S = (U_{T^I}^{S^1})^{-1} H_I U_{T^I}^{S^1},
\]

\[= \sum b_{s+1} \cos \frac{1}{2} \theta S_{x+1} \mathbf{S}^I \]

\[+ \sum b_{s-1} \sin \frac{1}{2} \theta S_{x-1} \mathbf{S}^I, \tag{3.48}\]

where \( \theta \) is given in Eq. (3.19). For a weak irradiation field with \( \omega I_{S} \ll \omega Q \) we have \( \theta \ll 1 \) and \( H_{T^I}^S \) becomes

\[
H_{T^I}^S \approx 2 \sum b_{s \pm} \omega_{S} S_{x \pm} \mathbf{I}_{x}. \tag{3.49}\]

The final temperature coefficient \( \beta_T^I \) after the thermal mixing of

\[
H_{T^I}^{S^1} = -2\delta \omega S_{x+1}^{3^1} = -\left( \frac{\omega I_{S}}{\omega Q} \right) S_{x}^{3^1},
\]

with

\[
H_{I} = -\omega I_{I} \mathbf{I}_{x},
\]

can be calculated in the same way as we did before

\[
\beta_T^I = \beta(T + 1 + C_{SI}/C_I) \approx \beta_T^I (1 - \epsilon_D). \tag{3.50}\]

The heat capacity of the double-quantum transition is

\[
C_{SI} = \frac{3}{\theta^{2}} N_{S} \left( \omega I_{S}^{3^1} / \omega_{Q}^{2} + 4 \delta \omega_{I} \right),
\]

and the ratio \( \epsilon_D \) between \( C_{SI} \) and the heat capacity of the I spins equals

\[
\epsilon_D = \frac{C_{SI}}{C_I} = \frac{2 N_S \omega I_S^{3^1} / \omega_{Q}^{2} + 4 \delta \omega_{I}}{\omega_{I}^{2}}. \tag{3.52}\]

The Hartmann-Hahn condition for this case becomes with \( \delta \omega = 0 \) (see Fig. 9)

\[
\omega I_{S}^{3^1} / \omega_{Q} = \omega_{I} \tag{3.53},
\]

and in general

\[
\omega I_{S}^{3^1} / \omega_{Q}^{2} + 4 \delta \omega_{I}^{2} = \omega_{I}^{2}. \tag{3.54}\]

The density matrix after the SL cross-polarization experiment is

\[
\rho_{T^I}^{S^1} = Z^{-1} \left[ 1 - \beta_T (\omega I_{S}^{3^1} / \omega_{Q}) (1 - \epsilon_D) \right] - 2 \delta \omega S_{x \pm}^{3^1} - \left( \omega I_{S}^{3^1} \right) S_{x \pm}^{3^1} - \omega I_{I} \mathbf{I}_{x} \right] - \frac{2}{3} \beta_T \omega_{Q} (S_{x \pm}^{3^1} - S_{x \pm}^{3^1}), \tag{3.55}\]

For the description of ADRF experiments on the double-quantum transition we can use exactly the same arguments as were represented for the single-quantum case.

### Detection of the double-quantum coherence

The double-quantum coherence, created at the end of a cross-polarization experiment, cannot be measured directly. In order to transform this double-quantum coherence to single-quantum coherence, it is necessary to apply an additional 90° pulse on the S spins. To transfer the total double-quantum coherence to single-quantum coherence, this 90° pulse must be 45° out of phase with the \( x \) direction.

For the SL case on the (1-3) transition the double-quantum coherence is

\[
\rho_{T^I}^{S^1} = Z^{-1} \beta_T \frac{\omega I_{S}^{3^1} / \omega_{Q}}{(1 - \epsilon_D) \omega_{Q} \omega I_{S}^{3^1}}. \tag{3.56}\]

In Appendix A the effect of this pulse on \( \rho_{T^I}^{S^1} \) is calculated for the ideal case that the irradiation intensity is much stronger than the quadrupole interaction. In the rotating frame the result is
DOUBLE-QUANTUM CROSS POLARIZATION

\[ |1\rangle \langle 3| \text{ } \omega_0^2 \omega_Q \text{ } \omega_{1T} \]

\[ |2\rangle \text{ } \omega_Q \text{ } \omega_{1S} = 0 \text{ } \omega_{1S} \neq 0 \]

**S SPINS** **I SPINS**

FIG. 9. Energy-level diagram of a spin \( S = 1 \) system and a spin \( I = \frac{1}{2} \) system in the rotating frame. In addition to the external magnetic field and the internal quadrupolar interaction \( \{ H_Q = \frac{1}{2} \omega_0 [S_x^2 - S(S+1)] \} \) rf irradiation fields are applied with \( H_{rf} = -\omega_{1S} S_x \) and \( H'_{rf} = -\omega_{1I} I_x \). For \( \omega_{1S} \) much smaller than the quadrupolar frequency \( \omega_Q \), \( H_{rf} \) results in an effective irradiation of the double-quantum transition of \( S \). The energy levels of the \( S \) spin system are the eigenstates of the Hamiltonian \( H_Q + H_{rf} \) with \( \omega_{1S} = 0 \) and \( \omega_{1S} \neq 0 \). The energy levels of the \( I \) spin system are the eigenstates of the Hamiltonian \( H'_{rf} \). In a spin-lock cross-polarization experiment the rate of the energy flow between the \( I \) spins and the \( S \) spins is maximum when the \( S \)-energy difference \( \omega_{1S}^2/\omega_Q \) is equal to the \( I \)-energy difference \( \omega_{1I} \). This is just the Hartmann-Hahn condition in Eq. (3.55).

\[ \rho_{DO} = \frac{1}{2} Z^2 \beta_L \omega_{QI} \omega_{1I} (1 - \epsilon_D) \frac{\omega_Q^2}{\omega_Q} (S_x^2 - S_y^2) + S_x^2 - S_z^2). \] (3.57)

These single-quantum terms of the density matrix can be measured and give a signal intensity of

\[ M_S = Z^2 \beta_L \omega_{QI} \omega_{1I} (1 - \epsilon_D) \frac{\omega_Q^2}{\omega_Q}. \] (3.58)

This signal must be compared with the intensity of the signal after a single strong 90° pulse on the \( S \) spins

\[ M_S' = \text{Tr} \rho_{0} S_+ S_- Z^2 \beta_L \omega_{QS}. \] (3.59)

The ratio between the signals in Eqs. (3.58) and (3.59) becomes

\[ \frac{|M_S|}{|M_S'|} = \frac{\omega_{QI} \omega_{1I} \omega_{1S}}{\omega_{QS} \omega_{1I} \omega_Q} (1 - \epsilon_D) \gamma_I \frac{\omega_Q^2}{\omega_Q} (1 - \epsilon_D). \] (3.60)

From these results it is clear that the double-quantum coherence can be monitored with higher sensitivity than normal single-quantum coherences.

To follow the cross-polarization process with the double-quantum transition, we can detect again the destruction of the \( I \) spin signal intensity after the thermal mixing period. The results for the relative destruction of the \( I \) signals are exactly the same as for the single-quantum cross-polarization case. Changing the effective irradiation field intensity of the single-quantum case to the intensity for the double-quantum case and putting \( \epsilon_D \) instead of \( \epsilon_Q \) in Eq. (3.46) we obtain

\[ \frac{M_S^2 - M_S}{M_S'} = \frac{2 N_S}{3 N_I} \frac{\omega_Q^4 + 4 \omega_{1S}^2}{\omega_{1I}^2}. \] (3.61)

Again, this can be used to monitor the \( S \) high-resolution double-quantum free-induction decay \( [S_D(t)] \) by the method of Ref. 12. In this case \( (M_S^2 - M_S)/M_S' = \epsilon_D^2 [2 - S_D(t)] \) for one contact.

In this section we showed that it is possible to obtain enhanced NMR signals from single- and double-quantum transitions by cross-polarization experiments. Direct and indirect detection methods can be used to follow the cross-polarization processes. Several experimental results of deuterium-proton cross polarization in a powder sample of benzene-\( \alpha \) will be demonstrated later. However, before we compare these experimental results with theory, we shall discuss some of the dynamical properties of cross polarization.

### IV. DYNAMICS OF CROSS POLARIZATION

#### A. Introduction

The most important parameter concerning the dynamics of cross polarization is the rate of spin thermal mixing \( T_{1S} \) between the \( I \) and \( S \) spins. If we know the dependence of \( T_{1S} \) on the experimental parameters \( \omega_{1S}, \omega_{1I}, \) and \( \Delta \omega \), then we can design and perform efficient cross polarization and signal enhancement experiments. In order for the spin system to reach thermal equilibrium, the length of the mixing time of a contact must be of the order of \( T_{1S} \). For mixing times shorter than \( T_{1S} \), the spin system does not reach equilibrium and the spin temperatures \( \beta_I \) and \( \beta_S \) of the \( I \) and \( S \) spins in a crystal do not become equal. In this case the values of \( \beta_I \) and \( \beta_S \) can be calculated from the rate equation, which describes the spin energy flow between the \( I \) and \( S \)-spin systems.

In this section we calculate \( T_{1S} \) as a function of the experimental and lattice parameters for a spin system with spins \( I = \frac{1}{2} \) and \( S = 1 \). McArthur et al. and Demco et al. derived expressions for \( T_{1S} \) for the \( I = S = \frac{1}{2} \) case, and we extend their theory to obtain \( T_{1S} \) for the \( I = \frac{1}{2}, S = 1 \) case. To form a theoretical basis for our extension, we first give a brief review of the \( I = S = \frac{1}{2} \) case. To form the equations for the \( I = S = \frac{1}{2} \) case are used in order to obtain explicit expressions for \( T_{1S} \) for the spin system with \( I = \frac{1}{2} \) and \( S = 1 \).

**B. Cross relaxation between \( I = \frac{1}{2} \) and \( S = \frac{1}{2} \) spins**

During a cross-polarization experiment on abundant \( I \) spins and rare \( S \) spins in a solid, energy
flows from a "cold" \( I \)-spin system to a "hot" \( S \)-
spin system. The rate of the energy transport is
dependent on the experimental parameters and the
dipolar interactions between the spins. The \( I \)
dipolar interaction \( H_{IS} \) between the \( I \) and \( S \) spins
forms the main mechanism for this energy
transfer. Due to the mutual spin flips among
the \( I \) spins, this interaction \( H_{IS} \) is fluctuated.
These fluctuations cause spin flips among the \( I \)
and the \( S \) spins. The efficiency of the energy flow,
created by this mechanism, is strongly dependent
on the external applied \( rf \) fields. In the rotating
frame, the \( I \) and \( S \) spins must be prepared in such
a state that these mutual flips conserve energy.
For example in the case of a spin-lock experiment
this is accomplished by the Hartmann-Hahn condi-
tion.

It is clear from these arguments that the rate of
cross relaxation \( T_{1IS} \) is dependent on the strength
of the \( H_{IS} \) interaction and on the correlation func-
tion of the fluctuations of \( H_{IS} \), caused by the dipole-
dipole interaction \( H_{II} \) between the \( I \) spins. The
expression for \( T_{1IS} \) in terms of these interactions
was given by McArthur et al.\textsuperscript{14} For a spin system
with \( I = \frac{1}{2} \) and \( S = \frac{3}{2} \) they obtained for the cross-rela-
xation rate

\[
T_{1IS} = \frac{1}{\text{Tr}(H_{IS})} e^{-\Delta / T_{1IS}}
\]

From this equation we see that the rate of cross
polarization is equal to the time integral of the
auto correlation function of that part of \( H_{IS} \) which
does not commute with \( H_{SI} \). This part of \( H_{IS} \)
causes the fluctuations in the \( S \)-spin system
and therefore governs the value \( T_{1IS} \). Equation (4.1)
was derived with the assumption that at any time
during cross polarization, the \( I \) and \( S \) spins have
a well defined spin temperature. The spin Ham-
iltonian \( H = H_{I} + H_{S} H_{IS} \) for the \( I = S = \frac{1}{2} \) case is given
in Sec. II and its terms must be inserted in Eq.
(4.1). Because the explicit forms of these terms
are dependent on the type of cross-polarization
experiment, we calculate the cross-relaxation
rates \( T_{1IS} \) for SL and ADRF measurements separa-
tely.

**SL experiments**

In a spin-lock experiment the spin Hamiltonian
in the rotating frame of the spin system with \( I = S
= \frac{1}{2} \) is given in Eq. (2.7). Because the traces in
Eq. (4.1) are independent of the representation of
\( H \), the terms of the tilted Hamiltonian \( H^T \) [Eq.
(2.17)] can also be inserted into the expression for
\( T_{1IS} \). The terms of the tilted Hamiltonian are

\[
H_{IS}^T = \omega_{IS} S_x - \Delta \alpha S_y ,
\]

\[
H_{IS}^T = 2 \sum_1^N b_I I_x S_x ,
\]

\[
H_{II}^T = \sum_1^N a_{II} (I_x I_y - 3 I_z I_z) .
\]

In Eq. (4.2b) an off-resonance term is added in
order to compare its effect on \( T_{1IS} \) in the \( I = \frac{1}{2} \),
\( S = \frac{1}{2} \) case with the effect of off-resonance terms in
cases with \( I = \frac{1}{2} \), \( S = 1 \). The summation in Eq.
(4.2c) is reduced to the \( I \) spins only, because the
\( S \) spins are very low in abundance and they can be
considered as single isolated spins.

If the irradiation field intensity \( \omega_{I} \) is much
larger than the strength of the \( H_{II}^T \) dipolar inter-
action in the \( H^T \) Hamiltonian, this dipolar inter-
action must be truncated. Only the part of \( H_{II}^T \)
which commutes with \( -\omega_{IS} I_x \) (the secular part) re-
 mains and it equals

\[
H_{II}^{(o)} = - \frac{\Delta}{2} \sum_1^N a_{II} (I_x I_y - 3 I_z I_z) .
\]

Before insertion of Eqs. (4.2) into (4.1) we per-
form an additional tilt on the Hamiltonian \( H^T \) in
order to simplify the actual calculations:

\[
H^T(\theta) = U(-\theta) H^T U(\theta) ,
\]

with

\[
U(\theta) = \exp(-i \theta S_z)
\]

and

\[
\tan \theta = \Delta / \omega_{IS} .
\]

This tilt results in the following:

\[
H_{IS}^T = \omega_{IS} S_x ,
\]

\[
H_{IS}^{T(0)} = \omega_{IS} S_x ,
\]

\[
H_{II}^{T(0)} = \omega_{IS} S_x ,
\]

and

\[
\omega^2 = \Delta \omega^2 + \omega_{IS}^2 .
\]

With these equations a straightforward calculation
of \( T_{1IS} \) in (4.1) yields

\[
T_{1IS}^T = \frac{1}{2} \cos^2 \theta M_{IS}^2 J_4 (\omega_{IS} - \omega_{I}) ,
\]

where the second moment \( M_{IS}^2 \) equals

\[
M_{IS}^2 = \frac{\text{Tr}(H_{IS}^T S_x^2)}{\text{Tr}(S_x^2)} \]

and the spectral density \( J_4 (\omega) \) is defined by

\[
J_4 = \int_0^\infty dt \cos \omega t C_4 (t) ,
\]

with the autocorrelation function
\[ C_s(t) = \left[ \text{Tr} \left( \sum_i b_i l_{si} \right)^2 \right]^T \left[ \text{Tr} \left( \sum_i b_i l_{si} e^{-iH_{II}T} \left( \sum_i b_i l_{si} \right) e^{iH_{II}T} \right) \right]. \]  

\[ M_s^2 \] is the second moment of the \( S \)-spin spectral line, broadened by the dipolar interaction between the \( S \) and \( I \) spins. The auto correlation function \( C_s(\tau) \) represents the fluctuations of the dipolar interaction caused by the effective part of the \( H_{II} \) interaction. The spectral density \( J_s(\omega) \) gives the density of these fluctuations at frequency \( \omega \). Because the spectral density is maximum at \( \omega = 0 \), the \( T_{II}^s \) is high when the experimental parameters \( \omega_{1S} \), \( \Delta \omega \), and \( \omega_{1I} \) are chosen according to the Hartmann-Hahn condition

\[ \omega_e = \omega_{1I}. \]

From Eq. (4.6) we see that \( T_{II}^s \) can be calculated, if we know the experimental parameters \( \omega_{1S} \), \( \Delta \omega \), and \( \omega_{1I} \), and if we evaluate \( M_s^2 \) from the positions of the \( I \) and \( S \) nuclei in the sample. The functional forms of the spectral densities for SL and ADRF experiments were derived before and their values together with the other parameters govern the actual values of \( T_{II}^s \).

**ADRF experiments**

The cross-relaxation rate \( T_{II}^s \) for the ADRF experiments must be calculated again from Eq. (4.1). In this case, however, the terms of the tilted Hamiltonian \( H'' \) are given in Eq. (2.37). With the addition of an off-resonance term in \( H'' \) and with the introduction of the til, defined in Eq. (4.4), the Hamiltonian is again given by the expressions in Eq. (4.2) except that \( \omega_{1I} = 0 \). In this case \( H_{II}^T \) should not be truncated. Insertion of Eq. (4.2) in (4.1) gives for the ADRF case

\[ T_{II}^s = \cos^2 \theta M_s^2 J_s(\omega_e), \]  

where the spectral density is now given by

\[ J_s(\omega) = \int_0^\infty dt \cos \omega t C_s(\tau), \]  

with the auto correlation function

\[ C_s(\tau) = \left[ \text{Tr} \left( \sum_i b_i l_{si} \right)^2 \right]^T \left[ \text{Tr} \left( \sum_i b_i l_{si} e^{-iH_{II}T} \left( \sum_i b_i l_{si} \right) e^{iH_{II}T} \right) \right]. \]

Differences between the \( T_{II}^s \) values for the SL and ADRF cases are discussed at length elsewhere.\(^{15}\)

The behavior of the \( I \) and \( S \) spins during cross polarization can be described by the rate equation for the energy flow between the two spin systems in terms of their spin temperatures

\[
\frac{\partial}{\partial t} \beta_s = -\frac{\beta_s - \beta_I}{T_{IS}},
\]

\[
\frac{\partial}{\partial t} \beta_I = -\frac{\epsilon(\beta_I - \beta_S)}{T_{IS}}.
\]  

\( \epsilon \) is the ratio between the heat capacities of the \( S \) and \( I \) spins [Eq. (2.30)]. In these rate equations we neglected all spin-lattice relaxation terms. The solutions of these coupled equations give the time behavior of \( \beta_I \) and \( \beta_S \) during the thermal mixing of a CP experiment. These results can then be used to calculate the enhancements of the S-spin signal intensities and the decrease in intensity of the I-spin signals [Eqs. (2.42) and (2.48)].

After this brief description of \( T_{II}^s \) for \( I = S = \frac{1}{2} \), we will now discuss the case of \( I = \frac{1}{2} \) and \( S = 1 \). The dynamics of the cross polarization of the single- and double-quantum transitions of the S spins are discussed separately.

**C. Single-quantum cross relaxation between \( I = \frac{1}{2} \) and \( S = 1 \) spins**

We discuss here the dynamics of cross polarization between \( I = \frac{1}{2} \) spins and the (1-2) single-quantum (\( \Delta M = 1 \)) transition of the \( S = 1 \) spins. With the concepts of fictitious spin-\( \frac{3}{2} \) transitions for spins with \( S = 1 \), described in Sec. III B, it is easy to calculate the cross-relaxation rate of this process. As was shown in Sec. III the single-quantum transition of \( S \) can be treated as a fictitious single spin-\( \frac{3}{2} \) transition. The Hamiltonian \( H_{I1} \) [Eq. (3.11)], corresponding to this transition, can be considered independently from the remainder of the spin system, if we assume that \( \omega_{1I} \ll \omega_0 \). The dipolar interaction \( H_{II} \) can also be divided into two commutating terms, \( H_{I1} \) [Eq. (3.30)] representing the interaction between the \( I \) spins and the single-quantum transition and \( H_{I1S} \) the interaction with the rest of the \( S \) system. Thus the expression for \( T_{II}^s \) in Eq. (4.1) can be used for the single-
quantum transition, if we consider only those terms in the Hamiltonian which correspond to this transition. The effective Hamiltonian for this case is given in Eqs. (3.11) and (3.30) and in the tilted frame of Eq. (3.29) we get

\[ H^T = H^T_1 + H^T_{Iz} + H^T_{II}, \]

with

\[ H^T_{Iz} = \sqrt{2} \omega I_s S'_z - 2 \delta S'_z, \]

\[ H^T_{II} = 2 \sum_i b_i I_s S'_z, \tag{4.14} \]

and \( H^T_1 \) and \( H^T_{Iz} \) as defined in Eq. (4.2). For convenience we perform an additional tilt on \( H^T \) with

\[ H^{TT} = U(-\theta I^z) H^T U(\theta I^z), \]

\[ U = \exp(i \theta S'_y - \omega_t), \]

\[ \tan \theta = 2 \delta \sqrt{\omega / \omega_t}, \tag{4.15} \]

which results in

\[ H^{TT}_{Iz} = \omega_e I_s S'_z, \]

\[ H^{TT}_{II} = 2 \cos \theta^2 \sum_i b_i I_s S'_z - 2 \sin \theta^2 \sin \delta \sum_i b_i I_s S'_z, \]

\[ H^{TT}_1 = H^T_1, \quad H^{TT}_{II} = H^{TT}_{II}, \tag{4.16} \]

and

\[ (\omega_e - \omega_t)^2 = 2 \omega^2 + 5 \omega_t. \]

For the SL and ADRF experiments we can use Eqs. (4.16) and insert them in Eq. (4.2). The results for \( T_{1s}^{-1} \) have the same form as in Eqs. (4.6) and (4.10). For the SL case we obtain

\[ T_{1s}^{-1} = N(\omega_e - \omega_t) J_s \left( \omega_e - \omega_t \right). \]

The spectral densities \( J_s \) and \( J_r \) are given in Eqs. (4.8) and (4.11) and are exactly the same as for the \( I = S = 1/2 \) case. The second moment in Eqs. (4.17) and (4.18) is

\[ M_{2Q}^{\text{adf}} = \frac{\text{Tr} [H^T_{II} S'_z^2] \text{Tr}(S'_z^2)}{\text{Tr}(S'_z^2)}. \tag{4.19} \]

\( M_{2Q}^{\text{adf}} \) is the second moment of the (1-2) transition of the \( S \) spins due to the interaction between the \( S \) and \( I \) spins. The results of Eqs. (4.17) and (4.18) are the same as for the \( I = S = 1/2 \) case. This is not surprising, because the irradiated (1-2) transition behaves exactly as a spin-1/2 transition as long as the applied rf irradiation field is not strong enough to excite the (2-3) transition also. It is clear that the same results for \( T_{1s}^{-1} \) obtained for cross-polarization experiments on the (2-3) transition of the \( S \) spins.

D. Double-quantum cross relaxation between \( I = 1/2 \) and \( S = 1 \) spins

Cross polarization between the \( i = 1/2 \) spins and the double-quantum transition of the \( S = 1 \) spins can be treated in exactly the same way as in the single-quantum case. We use again the fictitious \( S' = 1 \) character of the double-quantum transition and insert the terms of its fictitious \( S' = 1 \) Hamiltonian in the Eq. (4.1) for \( T_{1s}^{-1} \).

It was shown in Sec. III E that for weak irradiation fields \( \omega_t \gg \omega_q \) near the Larmor frequency of the \( S \) spins, the tilted Hamiltonian corresponding to the double-quantum transition is given by

\[ H^T = H^T_1 + H^T_{Iz} + H^T_{II}, \]

\[ H^T_{Iz} = (\omega'_t / \omega_q) S'_z^2 - 2 \delta S'_z, \]

\[ H^T_{II} = 2 \sum_i b_i I_s S'_z, \tag{4.20} \]

and \( H^T_1 \) and \( H^T_{Iz} \) are defined in Eq. (4.2). For small \( \omega'_t \) values the \( S' \)-spin Hamiltonian \( H'_t \) is again divided into two commuting parts \( H_{Iz} \) and \( H_{II} \) and the dipolar interaction \( H_{II} \) equals \( H^T_{II} \). As we did in the single-quantum case we apply an additional tilt on \( H^T \) and obtain

\[ H^{TT} = U(-\theta I^z) H^T U(\theta I^z), \]

where

\[ U(\theta) = \exp(i \theta S'_y), \]

\[ \tan \theta = 2 \delta \omega / \omega_t. \tag{4.21} \]

We find

\[ H^{TT}_{Iz} = -\omega_e I_s S'_z, \]

\[ H^{TT}_{II} = 4 \cos \theta^2 \sum_i b_i I_s S'_z - 4 \sin \theta^2 \sin \delta \sum_i b_i I_s S'_z, \tag{4.22} \]

where

\[ (\omega_e - \omega_t)^2 = \omega'_t / \omega_t^2 + 4 \delta \omega. \]

Insertion of (4.22) into (4.1) results for the SL case in

\[ T_{1s}^{-1} = \frac{1}{2} \cos \theta^2 \delta M_{2Q}^{\text{adf}}(\omega_e - \omega_t), \tag{4.23} \]

and for the ADRF case

\[ T_{1s}^{-1} = \frac{1}{2} \cos \theta^2 \delta M_{2Q}^{\text{adf}}(\omega_e - \omega_t). \tag{4.24} \]

The spectral density functions \( J_s \) and \( J_r \) are again the same as in Eqs. (4.8) and (4.11). \( M_{2Q}^{\text{adf}} \) is given by

\[ M_{2Q}^{\text{adf}} = \frac{\text{Tr} [H^T_{II} S'_z^2] \text{Tr}(S'_z^2)}{\text{Tr}(S'_z^2)}. \]
and is equal to the second moment of the Fourier-transform double-quantum spectrum of the \( S \) spins, broadened by the heteronuclear dipolar interaction \( H_{IS} \).

The ratio between the cross-relaxation rates of the single-quantum and the double-quantum transition equals

\[
\frac{(T^{-1})_{SQ}}{(T^{-1})_{SQ}} = \frac{\cos^2 \theta - 3 M^2_{SQ}}{\cos^2 \theta - 2 M^2_{SQ}} .
\]

(4.25)

The ratio between the second moments can easily be calculated

\[
M^2_{SQ} = \frac{\text{Tr}(4 \sum_i S^*_i S_i^*)}{\text{Tr}(2 \sum_i S^*_i S_i^*)} = 4 .
\]

(4.26)

From this ratio it follows that the width of the double-quantum spectral lines, broadened by \( H_{IS} \), are twice as large as the width of the single-quantum lines.

To examine the theory of this section and Sec. III we performed some proton-deuterium cross-polarization experiments on solid benzene-\( d_4 \). The experimental results are shown in Sec. V and are compared with the results of this section and Sec. III. The Hartmann-Hahn condition is checked by single- and double-quantum cross-polarization experiments as a function of rf irradiation field strengths and off-resonance frequencies. The efficiency of cross polarization is studied for SL and ADRF measurements, and the cross-relaxation time \( T_{IS} \) is evaluated.

V. EXPERIMENTS

A. Introduction

The experiments were performed on a powder sample of monodeutero-benzene. The spin-lattice relaxation time of this material is relatively short (~0.5 sec) and it is convenient to use this sample for the accumulation of free-induction-decay signals after cross-polarization experiments. The deuterium quadrupole interaction frequency of benzene-\( d_4 \) equals 2\( \nu_Q = 70.4 \) kHz and the maxima in its powder spectrum are at \( \nu_Q = \pm 35.2 \) kHz. In this paper, it is sufficient to consider only the two peaks at \( \pm 35.2 \) kHz for the interpretation of our experimental results, and to ignore the rest of the powder spectrum. If, however, the deuterium enhanced proton-NMR-signal intensities were used to obtain information on the chemical shifts of the deuterium atom, the whole spectrum should be taken into account.

All measurements were done on a home built spectrometer with a static magnetic field of 25 kG. The sample was kept at a constant temperature of \(-35^\circ C\) by a temperature-regulated nitrogen gas stream.

Cross polarization in solid benzene-\( d_4 \) occurs between the protons (\( I = \frac{1}{2} \)) and the deuterons (\( S = 1 \)). The efficiency of the cross-polarization experiments as a function of rf irradiation field intensities and of off-resonance frequencies was measured through the detection of the relative destruction of the proton-signal intensities after the thermal mixing. This indirect detection method is very sensitive and makes it possible to check the Hartmann-Hahn conditions experimentally. Direct detection of the deuterium signals is used to examine the signal enhancements which are caused by cross polarization, and to measure the cross-relaxation rate \( T_{IS} \).

B. Indirect detection

In this subsection we show some experimental results of the destruction of the proton line intensity as a function of the rf irradiation field intensities \( \nu_1 = \omega_{1,R}/2\pi \) and \( \nu_2 = \omega_{2,R}/2\pi \), and the off-resonance frequencies \( \Delta\nu = 5\omega/2\pi \).

The dependence on rf intensities

The relative destruction of the proton-spectrum intensity after a cross-polarization experiment can be calculated from the maximum possible destruction, given in Eqs. (3.46) and (3.61), and the cross-relaxation time \( T_{IS} \). A spin-lock experiment on the (1-2) single-quantum (SQ) transition of the deuterium atom, the relative destruction as function of the experimental mixing time \( t \) can be represented by

\[
d_{SQ}(\nu_{SL}, \Delta\nu) = \frac{M^2_{SQ} - M^2_I (1 - e^{-t/T_{IS}})}{M^2_I} = \epsilon_5 (1 - e^{-t/T_{IS}}),
\]

(5.1)

where \( T_{IS} \) is given in Eq. (4.17). For \( t \) values much smaller than \( T_{IS} \), we can take \( \exp(-t/T_{IS}) \approxeq 1 - t/T_{IS} \) and we get [with \( \theta^{*^{-2}} \) from Eq. (4.15)]

\[
d_{SQ}(\nu_{SL}, \Delta\nu, t) = \epsilon_5 t T_{IS}
\]

\[
\approx \frac{2}{3} \frac{2\Delta^2}{N_I} \frac{\nu_2^2}{\nu_1^2} \frac{\Delta\nu^2}{2\nu_1^2} \frac{1}{3} \cos^2 \theta - 2 M^2_{SQ} J_0 (v_1^{-2} - v_1) \]

\[
= \frac{2}{3} \frac{2\Delta^2}{N_I} \frac{\nu_2^2}{\nu_1^2} \frac{1}{3} \cos^2 \theta - 2 M^2_{SQ} J_0 (v_1^{-3} - v_1) .
\]

(5.2)

For a spin-lock experiment on the double-quantum transition we get in the same way [with \( T_{IS}^3 \) from Eq. (4.23) and \( \theta^{*^{-3}} \) from Eq. (4.21)]

\[
d_{SQ}(\nu_{SL}, \Delta\nu) = \frac{1}{3} \frac{2\Delta^2}{N_I} \frac{\nu_2^2}{\nu_1^2} \frac{1}{3} \cos^2 \theta - 2 M^2_{SQ} J_0 (v_1^{-3} - v_1) .
\]

(5.3)

With \( \Delta\nu = 0 \) and the Hartmann-Hahn conditions...
\[ \sqrt{2} \nu_d = \nu_s, \text{ for the single-quantum and } \nu_{dQ}^2/\nu_s = \nu_{l1} \]

for the double-quantum case, the ratio between \( d_{dQ} \) and \( d_{dQ} \) equals

\[ \frac{d_{dQ}}{d_{dQ}} = \frac{M_{dQ}^2}{M_{dQ}^2} = 4. \]

This shows that the destruction of the \( J \) (proton) spins for the double-quantum case is larger than for the single-quantum case. Furthermore, the maximum destruction is obtained when the Hartmann-Hahn condition is fulfilled and \( J(0) = 1 \). Comparison between the widths of \( d_{dQ} \) and \( d_{dQ} \) as functions of \( \nu_{l1} \) predicts that \( d_{dQ} \) is broader than \( d_{dQ} \). This can be understood best if we take for

\[ J(\nu)^{15} \text{ a Gaussian function } e^{-\nu^2/2}. \]

The destruction spectra \( d_{dQ} \) and \( d_{dQ} \) for the ADRF experiments can also be derived from Eq. (5.2) with \( T_{1S} \) from Eqs. (4.18) and (4.24). The results for \( t \ll T_{1S} \) are

\[ d_{dQ}(\nu_{l1}, \nu_s) = \frac{2 \nu_{l1}^2}{3 \nu_s} + 2N_s \nu_{l1}^2 \]

\[ \frac{d_{dQ}(\nu_{l1}, \nu_s)}{d_{dQ}} = \frac{2 \nu_{l1}^2}{3 \nu_s} + 2N_s \nu_{l1}^2 \]

and

\[ \frac{d_{dQ}(\nu_{l1}, \nu_s)}{d_{dQ}} = \frac{2 \nu_{l1}^2}{3 \nu_s} + 2N_s \nu_{l1}^2 \]

Here it is difficult to predict for what value of \( \nu_{l1} \) the maximum destruction is obtained. If we take for the spectral density function \( J(\nu)^{15} \) an exponential function \( e^{-\nu/\nu_s} \), it is clear that the width of \( d_{dQ} \) as a function of \( \nu_{l1} \) is larger than the width of \( d_{dQ} \) and that the maximum in \( d_{dQ} \) is larger than the maximum in \( d_{dQ} \).

In Fig. 10 we show the relative destruction as a function of \( \nu_{l1} \) of the proton line intensity after a spin-lock experiment on the single- and double-quantum transitions of deuterium in benzene-\( d_1 \). The mixing time in these experiments was \( t = 15 \) msec, which is much smaller than the \( T_{1S} \) value for this compound. The applied proton rf irradiation intensity was equal to \( \nu_{l1} = 10 \) kHz. Maximum destruction for the single-quantum case is obtained when \( \nu_{l1} \) is equal to 7 kHz. This should be equal to \( 2^{1/2} \nu_{l1} = 7.1 \) kHz, according to the Hartmann-Hahn condition [Eq. (3.34)]. Thus agreement is good.

In the double-quantum case the maximum destruction occurs at \( \nu_{l1} = 19 \) kHz and this must be compared with \( (\nu_{l1}/\nu_{l1})^{1/2} = 19.2 \) kHz [Eq. (3.53)]. Again, these experimental results are in excellent agreement with the theory. The results of Fig. 10 show that the maximum single-quantum destruction is smaller than for the double-quantum destruction and that the destruction spectrum for the double-quantum case is wider than for the single-quantum case. This is in agreement with the discussions given above.

The proton destruction spectra for ADRF experiments on the single- and the double-quantum deuterium transitions are shown in Fig. 11. In these experiments we took for the mixing time \( t = 50 \) msec. This value is of the order of \( T_{1S} \) and therefore we measure a larger destruction than in Fig. 10. In the ADRF case we see again that the \( d_{dQ}(\nu_{l1}) \) spectrum is narrower than \( d_{dQ}(\nu_{l1}) \).

In Fig. 12 SL experiments on the double-quantum transition are demonstrated for two different values of the proton rf irradiation strength. The agreement of these results with the double-quantum theoretical Hartmann-Hahn condition, indicated by arrows, is excellent.

**The dependence on off-resonance frequencies**

We now present experimental results for the proton destruction spectra as a function of the off-resonance frequency values \( \Delta \nu \). In Fig. 13 \( d_{dQ}(\Delta \nu) \) is measured for different values of \( \nu_{l1} \) and \( \nu_{l1} \) in a spin-lock experiment. The results for the maxima in the destruction are in full agree-
FIG. 11. The relative destructions of the proton signal intensity \( (1 - M_z/M_0^0) \) (100\%) of solid benzene-\( d_1 \) after ADRF cross-polarization experiments (Fig. 2) between the protons and the deuterium nuclei in this sample. The destruction is measured as function of the rf irradiation field strength \( v_{1S} \) on the \( S \) spins. The mixing time of these experiments was \( t = 50 \) msec. The upper graph is obtained by the irradiation of the allowed transition of the deuterium nuclei at \( v_0 = 35.2 \) kHz. The lower graph is obtained by irradiation at the deuterium Larmor frequency. A discussion of these results is given in the main text.

ment with the Hartmann-Hahn condition of Eq. (3.54). The numerical calculations are given in the figure caption.

The destruction spectrum \( d_{p0}(\Delta \nu) \) for an SL and an ADRF experiment are again shown in Figs. 14 and 15. However, in these figures \( d_{p0}(\Delta \nu) \) is measured for positive and negative values of \( \Delta \nu \). The experimental results show a marked asymmetry in \( d_{p0}(\Delta \nu) \) for opposite signs of \( \Delta \nu \). The experimental parameters for the spin-lock case in Fig. 14 are \( v_{1S} = 8 \) kHz and \( v_1 = 11 \) kHz and the maximum destruction is obtained at \( \Delta \nu = 5 \) kHz. This value for \( \Delta \nu \) gives together with \( v_{1S} \) the effective frequency (in kHz)

\[
v_{1S}^2 = \frac{4\Delta \nu^2 + v_{1S}^2}{v_0^2} = 11,
\]

FIG. 13. Relative destructions of the proton signal intensity \( (1 - M_z/M_0^0) \) (100\%) of solid benzene-\( d_1 \) after spin-lock cross-polarization experiments (Fig. 2) between the protons and the deuterium nuclei in this sample. The destructions are measured as function of the off-resonance frequency \( \Delta \nu \) of the deuterium irradiation field. The rf field intensities \( v_{1S} \) and \( v_1 \) on the \( S \)- and the \( I \)-spin systems, respectively, were kept constant. \( \Delta \nu \) was measured from the deuterium Larmor frequency. According to the Hartmann-Hahn condition \( v_{1S}^2/v_0^2 + (1 + 4\Delta \nu^2) = v_1^2/v_0^2 \), the expected maxima in the destruction spectra are for \( v_{1S} = 8 \) kHz and \( v_1 = 10 \) kHz at \( \Delta \nu = 4.9 \) kHz and for \( v_{1S} = 6.7 \) kHz and \( v_1 = 7.5 \) kHz at \( \Delta \nu = 1.7 \) kHz. For the values \( v_{1S} = 20 \) kHz and \( v_1 = 10 \) kHz the Hartmann-Hahn condition can not be fulfilled and the maximum destruction is expected at \( \Delta \nu = 0 \). The agreement between experiment and theory is excellent.

FIG. 12. Relative destructions of the proton signals of solid benzene-\( d_1 \) after cross-polarization spin-lock experiments on the deuterium double-quantum transition. The destructions were measured as function of the deuterium irradiation field strength \( v_{1S} \) for two constant values of the proton irradiation field intensity. According to the Hartmann-Hahn condition \( v_{1S}^2/v_0^2 = v_1^2/v_0^2 \) the maximum destruction is expected for \( v_1 = 6.2 \) kHz at \( v_{1S} = 14.8 \) kHz and for \( v_1 = 10.5 \) kHz at \( v_{1S} = 19.2 \) kHz. This is in excellent agreement with the experimental results.

FIG. 14. The experiment in Fig. 13 with \( v_{1S} = 8 \) kHz and \( v_1 = 10 \) kHz is repeated here for positive and negative values of \( \Delta \nu \). The asymmetry in the destruction spectrum is discussed in the main text.
which is equal to $\nu_{1f}$.

The asymmetry in $d_{DQ}(\Delta \nu)$ can be explained, if we take into account the initial condition of the deuterium-spin density matrix, before cross polarization occurs. In all cases of Sec. III, we assumed that the initial $S$-spin temperature coefficient $\beta_{S1}$ is zero. This assumption is justified if the direction of effective rf irradiation field in the rotating frame on the $S$ spins is perpendicular to the direction of the Zeeman field, $\delta \omega \approx 0$. Then, at the moment the irradiation field is applied, the $S$ spins are in a state defined by

$$\rho_{eq,S} = Z S + (1 + \beta_L \omega_{0S} S)$$

and the effective irradiation Hamiltonian on the double-quantum transition [Eq. (3.23)] is

$$H_{DQ} = \omega_{DQ} S (1 + 2 \beta_L \omega_{0S} S)^{-3}.$$

According to the spin temperature approximation in the rotating frame, the initial $S$-spin density matrix is then equal to

$$\rho_{init,S} = Z S + (1 - \beta_{S1} H_S) = Z S.$$

However, if the irradiation field is not perpendicular to the Zeeman field and

$$H_S = \omega_{DQ} S (1 + 2 \beta_L \omega_{0S} S)^{-3} - 2 \delta \omega S^3$$

the initial $S$-spin density matrix becomes

$$\rho_{init,S} = Z S + (1 + (2 \delta \omega \omega_{0S}^{-3}) S - 2 \delta \omega \beta_L H_S),$$

where $\omega_{0S}^{-3}$ is defined in Eq. (4.22). Physically, this means that the $S$ spin begins with a slight positive or negative polarization (temperature) dependency on whether we are above or below resonance. The initial value for $\beta_{S1}$ is thus different from zero and equals

$$\beta_{S1} = \frac{-4 \delta \omega \omega_{0S}^{-3}}{(\omega_{0S}^{-3})^2} \beta_L.$$  \hspace{1cm} (5.12)

The final spin temperature coefficient $\beta_f$ in Eq. (3.50) must be modified and becomes

$$\beta_f = \frac{\beta_{DQ} C_f + \beta_{S1} C_{S1}}{C_f + C_{S1}} = \beta_f (1 - \epsilon_p) + \beta_{S1} \epsilon_D.$$  \hspace{1cm} (5.13)

Now the relative destruction $d_{DQ}$ must be calculated from Eq. (2.48) and gets the form

$$d_{DQ}(\Delta \nu) = \frac{\beta_f - \beta_f (1 - e^{-t/T_{1S}})}{\beta_f (1 - e^{-t/T_{1S}})},$$

where we used the expression for $\beta_f$ from Eq. (2.19) and in general $\nu = \omega/2\pi$. With the Hartmann-Hahn condition $\nu_{1f}^3 = \nu_{1f}$ we obtain

$$d_{DQ}(\Delta \nu) = \frac{\beta_f + 4 \Delta \nu H_{DQ}}{\nu_{1f}^3 + 3 \gamma_{DQ}} (1 - e^{-t/T_{1S}}).$$

The ratio between the values of $d_{DQ}$ for positive and negative $\Delta \nu$ is

$$\frac{d_{DQ}(\Delta \nu)}{d_{DQ}(-\Delta \nu)} = \frac{4 \Delta \nu}{\gamma_{1f}^3 + 3 \gamma_{DQ}}.$$

This ratio equals 1.6 for the experimental parameters of Fig. 14. The experimental result for this ratio is 1.5.

For the ADRF case in Fig. 15 we obtain the same asymmetry in $d_{DQ}(\Delta \nu)$ as for the SL case. The rf irradiation intensity on the deuterons in this experiment is $\nu_{1f} = 14.7$ kHz and the experimental values for the maximum destruction are $\Delta \nu = \pm 3$ kHz. Insertion of these values in Eq. (5.14) results in a value of 1.5 for the ratio between the maxima. The experimental value equal is 1.4.

C. Cross-polarization dynamics

Until now we assumed that for all our experiments the spin-lattice relaxation times of the proton and the deuterium spins were much longer than the experimental mixing time $t$. In these cases it is sufficient to describe the spin temperature coefficients of these $I$ and $S$ spins by the rate equations given in Eq. (4.13). However, if we monitor the behavior of the spin system during cross polarization for long mixing times, these equations must
be extended. In this subsection we consider an ADRF experiment on the double-quantum transition. We show that from the deuterium signal intensity, as a function of the mixing time, it is possible to obtain the value of $T_{1D}$. These experiments also measure the value of the ratio $\rho_2$ between the spin heat capacities of the double-quantum deuterium transition and the protons.

The spin–lattice relaxation time for the deuterium $S=1$ during an ADRF experiment is $T_{1D}$. This is the relaxation time of the deuterons during a spin-lock experiment on their double-quantum transition. The relaxation time of the protons $T_{1D}$ equals the relaxation time of the protons $(t = \frac{1}{2})$ after an adiabatic demagnetization in the rotating frame of these nuclei. Taking into account the relaxation times, the rate equation for the spin temperature coefficients $\beta_j$ and $\beta_2$ are given by

$$\frac{d}{dt} \beta_j = \frac{-\varepsilon_j (\beta_j - \beta_{S1})}{T_{1S}^{1D}},$$

$$\frac{d}{dt} \beta_{S1} = \frac{-\varepsilon_{S1} (\beta_{S1} - \beta_2)}{T_{1S}^{1D}}.$$  (5.18)

The solution of these coupled equations is calculated in Appendix B and with the initial conditions for the spin temperature coefficients $\beta_j(0) \neq 0$ and $\beta_{S1}(0) = 0$ it becomes

$$\beta_{S1}(t) = \beta_j(0) g(t) = (\omega_{S1}/\omega) \beta_j g(t),$$  (5.19)

with $g(t)$ given in Appendix B. The corresponding density matrix of the $S$ spins can be represented by Eq. (3.56)

$$\rho_{02}(t) = Z^1 [1 - \beta_{S1}(t) H_{S1}]$$

$$= Z^1 [1 + \beta_{S1}(t)(\omega_{S1}/\omega) S_{z}^{1S}]$$

$$= Z^1 [1 + \beta_{L} \omega_{S1}(\omega_{S1}/\omega) S_{z}^{1S}] g(t).$$  (5.20)

The time behavior of $\beta_{S1}(t)$ can be monitored by measuring the $S$-spin signal intensity after cross polarization as a function of $t$. Before we present the experimental result of the deuterium signal intensity in the ADRF experiment we show how the $T_{1D}$ and $T_{1S}$ relaxation times were measured.

$T_{1D}$ experiment

The $T_{1D}$ relaxation time of the deuterium spins can be measured by a double-quantum spin-lock experiment. In such an experiment the spins are locked to the effective rf irradiation field of the double-quantum transition by a 45° phase shift on this rf field. In our case we obtained the same result by a cross polarization of the deuterium double-quantum transition with the protons. In Fig. 16 the experimental scheme for this measurement is represented. The deuterium spins are polarized by an ADRF experiment and after the mixing time the proton dipolar order is destroyed by a 45° pulse. After this pulse the double-quantum coherence of the deuterons is spin locked and will decay with a time $T_{1D}$. This decay can be monitored by measuring the deuterium signal after 7 sec with an additional detection pulse. The result of this experiment is shown in Fig. 17 and the value of $T_{1D}$ obtained is $T_{1D} = 43$ msec.

$T_{1S}$ measurement

The relative deuterium signal intensity as a func-
The measurement of the proton local field spin-lattice relaxation time $T_{1p}$ of solid benzene-$d_4$.

The points in this graph are the relative proton signal intensities $M_I^2/M_2^2$ as function of the time $\tau$ between the creation of proton dipolar order by an ADRF pulse sequence (Fig. 2) and the transformation of this order to a measurable signal by a 45° pulse. From these measurements we get $T_{1p}=300$ msec.

The experimental result of Fig. 19 together with the values of $T_{1D}$ and $T_{1S}$ must be compared with Eq. (5.21). A computer program was written to minimize the deviation between the experimental and theoretical result by changing the parameters $\epsilon_p$ and $T_{1S}$. The results of this calculation with $\eta = 0.95$ are $\epsilon_p = 0.85 \pm 0.05$ and $T_{1S} = 77.6$ msec. Insertion of these values in Eq. (5.22) results in the solid line in Fig. 19. To compare the obtained value of $\epsilon_p$ with its theoretical value, we calculated $\epsilon_p$ from Eq. (3.52) with $N_p/N_F = 0.2$ and replaced $\omega_p$ by $\omega_p$. The local field strength $\omega_p$ in frequency units of the protons was calculated from the linewidth $\delta_g$ of the proton spectrum of benzene-$d_4$. Assuming a Gaussian shape for this line, the $\omega_p$ value was taken as $\omega_p = \delta_g/1.18 = 2.75$ kHz and $\epsilon_p = 1.18$. This is in reasonable agreement with the experimental value 0.85.

**VI. SUMMARY**

The motivation of this paper has been to provide a theoretical framework and experimental results for various cross-polarization experiments between abundant $I = \frac{1}{2}$ and rare $S = 1$ spins. In particular, cross polarization between the $I = \frac{1}{2}$ and the $S$ double-quantum transition has been treated. The double-quantum transition has previously been shown to be extremely useful for high-resolution $^2$D and $^{14}$N NMR in solids and the results of the present experiments indicate that such spectroscopy can also be done with very good sensitivity. The theory for cross-polarization thermodynamics and dynamics between $I = \frac{1}{2}$ and $S = 1$ was developed for both spin locking and adiabatic demagnetization in the rotating frame. This is a generalization of the familiar $I = S = \frac{1}{2}$ case. When $\omega_i \ll \omega_q$ a modified Hartmann-Hahn condition for the simplest case of double-quantum cross polarization $\omega_i^2/\omega_q = \omega_i$ emerges. Experiments were performed, showing the validity of the approach both for the thermodynamics and dynamics of the cross-polarization process for double-quantum transitions. By an indirect detection the double-quantum free-induction decay of $S = 1$ can be mapped point by point. Such further experiments on $^2$D and $^{14}$N and other nuclei are underway.

**ACKNOWLEDGMENT**

This work was supported by the Division of Materials Sciences, Office of Basic Sciences, U.S. Department of Energy. Partial support for S.V. was provided by a grant from the United States-Israel Binational Science Foundation, Jerusalem, Israel.

**APPENDIX A**

To transfer the total double-quantum coherence after cross polarization...
where \( \rho_{DQ} = a_{x}^{-3}S_{-}^{z} \) to single-quantum coherence, we apply a strong 90° pulse \( \omega_{Q} \gg \omega_{S} \) on the S spins, 45° out of phase with the mixing pulse. In this Appendix we calculate the effect of this pulse on \( \rho_{DQ} \) and we evaluate the signal intensity measured after this pulse.

The Hamiltonian of the rf pulse in the rotating frame with \( \omega_{Q} = \omega_{Q}(S_{z} + S_{-}) \)

\[
H_{p} = -(1/\sqrt{2})\omega_{Q}(S_{z} + S_{-}),
\]

(A2)

The effect of a \( \tau_{S} \) second pulse with \( \omega_{S}\tau_{S} = \pi/2 \) on \( \rho_{DQ} \) is calculated by

\[
\rho_{DQ}^{0} = P^{-1}\rho_{DQ}P,
\]

(A3)

with

\[
P = e^{i\pi/2}\rho_{S} = e^{i\pi/2(S_{z} + S_{-})},
\]

(A4)

In the actual calculation we make use of the commutation relations in Eq. (2.6) of Ref. 17. The expression for \( \rho_{DQ}^{0} \) is obtained as follows:

1) Transfer \( \rho_{DQ}^{0} \) and \( H_{p}\tau_{S} \) with

\[
U_{p} = \exp(-i\pi S_{z}) = \exp(-i\pi S_{+}^{2})
\]

(A5)

and obtain

\[
\rho_{DQ}^{0} (t) = \exp[-i(1/\sqrt{2})\omega_{Q}(S_{z}^{-} + S_{-}^{-})t]\rho_{DQ}^{0} \exp[i(1/\sqrt{2})\omega_{Q}(S_{z}^{+} + S_{+}^{+})t]
\]

\[
= -(1/\sqrt{2})a_{x}^{-3}[S_{z}^{-} \cos(\omega_{Q}t + 1/4\pi) - S_{-}^{-} \sin(\omega_{Q}t + 1/4\pi) + S_{z}^{+} \cos(\omega_{Q}t + 1/4\pi) - S_{-}^{+} \sin(\omega_{Q}t + 1/4\pi)].
\]

(A14)

The signal intensity corresponding to this density matrix equals

\[
M_{S} = \text{Tr}[\rho_{DQ}^{0}(t)S_{+}] = \sqrt{2}\text{Tr}[\rho_{DQ}^{0}(t)(S_{z}^{+} + S_{-}^{+})]
\]

\[
= -a_{x}^{-3}\cos(\omega_{Q}t + 1/4\pi)
\]

(A15)

and the full double-quantum coherence \( a_{x}^{-3} \) is transferred to the single-quantum signal intensity. A 45° pulse at a phase angle of 90° with respect to the mixing pulse transfers only half of the double-quantum coherence to single-quantum coherence. In this case we must calculate

\[
\rho_{DQ}^{45} = P^{-1}\rho_{DQ}P
\]

(A16)

with

\[
P = \exp(-i\pi S_{z}) = \exp[-i(\pi/2\sqrt{2})(S_{z}^{+} + S_{-}^{+})].
\]

(A17)

Transformation of \( \rho_{DQ}^{45} \) and \( P \) with \( U_{S}^{1/2} \) in Eq. (A8) results in

\[
\rho_{DQ}^{T} = (U_{S}^{1/2})^{-1}\rho_{DQ}^{45}U_{S}^{1/2}
\]

\[
= a_{x}^{-3}S_{-}^{z} - \frac{1}{2}a_{x}^{-3}[S_{z}^{+} + S_{-}^{+}]
\]

(A17)

and

\[
P^{T} = \exp(-i\pi S_{z}^{+})
\]

(A18)

With these equations we obtain

\[
\rho_{DQ}^{T} = U_{S}^{-1}\rho_{DQ}U_{S} = -a_{x}^{-3}S_{-}^{z} \]

(A6)

\[
H_{S}\tau_{S} = -\frac{\pi}{2}S_{z} = -(\pi/\sqrt{2})(S_{z}^{+} + S_{-}^{+})
\]

(A7)

(2) Perform an additional transformation with

\[
U_{S}^{1/2} = \exp(-i\pi S_{z}^{+})
\]

(A8)

and use Eq. (2.9) in Ref. 17:

\[
\rho_{DQ}^{T} = \rho_{DQ}^{0},
\]

(A9)

\[
H_{S}\tau_{S} = (U_{S}^{1/2})^{-1}H_{S}U_{S}^{1/2} \tau_{S} = -\pi S_{z}^{+}.
\]

(A10)

(3) In this new representation calculate Eq. (A3):

\[
\rho_{DQ}^{T}(90) = (P^{T})^{-1}\rho_{DQ}^{T}P^{T} = \frac{1}{2}a_{x}^{-3}S_{x}^{+}.
\]

(A11)

(4) The transformation of \( \rho_{DQ}^{T} \) back to the rotating frame yields

\[
\rho_{DQ}^{T}(90) = -(1/\sqrt{2})a_{x}^{-3}(S_{z}^{-} - S_{-}^{-})
\]

(A12)

and

\[
\rho_{DQ}^{45} = -\frac{1}{2}a_{x}^{-3}(S_{z}^{+} + S_{-}^{+} - S_{z}^{-} - S_{-}^{-}).
\]

(A13)

This result is used in Eq. (3.57).

The density matrix after the pulse will evolve, due to the quadrupolar interaction, as

\[
\rho_{DQ}^{T}(t) = \exp[-i(1/\sqrt{2})\omega_{Q}(S_{z}^{+} + S_{-}^{+})t] \rho_{DQ}^{T}\exp[i(1/\sqrt{2})\omega_{Q}(S_{z}^{+} + S_{-}^{+})t]
\]

(A14)

The rate equations for the spin temperature coefficients \( \beta_{g} \) and \( \beta_{s} \) can be written in matrix form

\[
\frac{d}{dt} \beta = -\Gamma \beta + \alpha,
\]

(B1)

with
DOUBLE QUANTUM CROSS-POLARIZATION NMR IN SOLIDS

\[
\beta = \left[ \begin{array}{c} \beta_I \\ \beta_H \end{array} \right], \quad \alpha = \beta_L \left[ \begin{array}{c} R_{1D} \\ R_{2p} \end{array} \right],
\]

(B2)

\[
\Gamma = \left[ \begin{array}{cc} \epsilon R_{1S} + R_{1D} & -R_{1S} \\ -R_{1S} & R_{1S} + R_{1p} \end{array} \right]
\]

(B3)

and in general \( R_i \equiv T_i \).

To solve Eq. (B1) we diagonalize \( \Gamma \) and get

\[
\Lambda = D^T \Gamma D,
\]

with

\[
\Lambda = \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix}
\]

(B5)

and

\[
D = \begin{bmatrix} \cos \theta & \epsilon \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix}
\]

(B6)

This expression was used in the computer program to fit the dynamics and the value of \( \epsilon_d \) in the cross-polarization experiments.


