Selective cross-polarization in solution state nuclear magnetic resonance of scalar coupled spin \( \frac{1}{2} \) and quadrupolar nuclei

Thomas R. Eykyn, David J. Philp, and Philip W. Kuchel

School of Molecular and Microbial Biosciences, University of Sydney, NSW 2006, Australia

(Received 11 November 2002; accepted 27 January 2003)

Semiselective heteronuclear cross-polarization for achieving coherence transfer between a spin \( I = \frac{1}{2} \) scalar coupled to a spin \( S \geq \frac{1}{2} \) in isotropic solution is considered. The expansion of the density operator as products of irreducible tensor operators provides a compact formalism for describing cross-polarization involving scalar coupled quadrupolar nuclei. An analytical description of cross-polarization is presented in the limit of strong radio-frequency (rf) fields, with respect to the scalar-coupling constant. Numerical simulations show that reducing the rf field amplitudes does not have a detrimental effect on the efficiency of the transfer provided they are comparable to or greater than the scalar-coupling constant. The use of weak rf fields largely circumvents the reduced efficacy due to Hartmann–Hahn mismatch. Applications of the method for selective observation of scalar-coupled quadrupolar nuclei are considered and experimental results are presented for a mixture of beryllium fluoride complexes. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1560955]

I. INTRODUCTION

Quadrupolar nuclei are becoming increasingly important in a wide variety of applications. The study of relaxation and exchange processes involving quadrupolar nuclei in both the laboratory and rotating frames has yielded a wealth of information on molecular motions. This has yielded novel insights into ordered environments in biological systems. Quadrupolar nuclei are being increasingly recognized as useful spin probes in magnetic resonance imaging, and for studying surface properties of porous media.

The ability to transfer coherences between different nuclei in homo- and heteronuclear spin systems is one of the cornerstones of nuclear magnetic resonance (NMR). The transfer of polarization from \( I = \frac{1}{2} \) to \( S = \frac{1}{2} \) nuclei has become routine. In solution the majority of these methods employ free-precession type techniques such as INEPT (insensitive nucleus enhancement by polarization transfer) where polarization transfer from one spin to another is mediated via the scalar coupling. The majority of these techniques are designed for spin-half systems and have shown particular utility in the study of structure and dynamics of biomolecules labeled with \( ^{13}\text{C} \) and \( ^{15}\text{N} \). The use of INEPT for achieving polarization transfer in systems of scalar coupled quadrupolar nuclei has also been investigated.

An alternative class of experiments employ cross-polarization to transfer coherence between two species. Widely used in solid state NMR, the transfer is driven by the dipolar coupling. This is usually carried out under magic angle sample spinning conditions and a number of techniques have been proposed to improve the efficiency of cross-polarization (CP) under these conditions, including amplitude modulation, frequency modulation, or ramping the rf fields adiabatically through the Hartmann–Hahn condition. Important applications of CP include heteronuclear correlation experiments and the measurement of internuclear distances.

Cross-polarization has also been shown to be applicable for coherence transfer in solution state, where the dipolar interaction is motionally averaged to zero. The transfer is therefore usually driven by the scalar coupling interaction, and in some circumstances by the interaction with the rf fields. The scalar coupling is in general at least two orders of magnitude smaller than the dipolar interaction rendering the method susceptible to rf mismatch. Cross-polarization in solution state is therefore a less attractive method than its free precession counterparts. Methods developed for mismatch compensation in the solid state have been shown to be applicable to solution state NMR. It has recently been shown that employing rf fields whose amplitudes are of the same order as the scalar coupling interaction can largely circumvent this obstacle. The use of weak rf fields makes cross-polarization an ideal tool for selective experiments in both solution and solid state.

In this paper we consider the possibility of achieving coherence transfer in a scalar-coupled two-spin system \( IS \) in isotropic solution under the influence of continuous-wave (cw) radio-frequency fields where \( I = \frac{1}{2} \) and \( S \geq \frac{1}{2} \). A theoretical framework in the limit of strong rf fields is presented. The use of weak rf field amplitudes that are at least of the same order as the scalar-coupling constant does not have a detrimental effect on the efficiency of the transfer and reduces the sensitivity to Hartmann–Hahn mismatch, in analogy with spin-half systems. Cross-polarization is shown to be a useful tool for enhancing the sensitivity to detection of low-gyromagnetic ratio quadrupolar nuclei. Experimental re-
results are presented for complexes of beryllium fluoride in isotropic solution.

II. HETERONUCLEAR COHERENCE TRANSFER

We first outline the analytical procedures for predicting the transfer functions for cross-polarization between two scalar-coupled spins $I$ and $S$. The mechanism of cross-polarization for $I=\frac{1}{2}$, $S=\frac{1}{2}$ is well known but less so for $S>\frac{1}{2}$. The following discussion is limited to isotropic solution where rotational reorientation averages the quadrupolar interaction to zero. However this may not be the case for anisotropic motion, such as in liquid-crystal solvents, and partially aligned bicelle solutions, where the dynamics of cross-polarization will be influenced by the presence of a residual quadrupolar interaction. These effects are not considered further here. Throughout the following discussion relaxation will be neglected.

Figure 1 shows the pulse sequence that can be used to achieve cross-polarization between $I$ and $S$. A $(\pi/2)_y$ pulse applied to the $I$ spins prepares an initial state of $I_x$, transverse magnetization. Coherence transfer is achieved by applying two simultaneous rf fields. The evolution function of the density operator for a system of two spins-1/2 under the influence of the above-mentioned Hamiltonian can be solved analytically for arbitrary rf field strengths and scalar coupling constant, as shown in the Appendix. For a spin $I$ scalar coupled to a spin $S$ these analytical expressions become extremely cumbersome.

III. THE STRONG FIELD LIMIT

For coherence transfer between two scalar coupled spins $I$ and $S$ where $I=\frac{1}{2}$ and $S>\frac{1}{2}$ the solution of the Liouville-\-von Neumann equation remains amenable to numerical integration but an analytical solution becomes intractable in the doubly rotating frame. This occurs because the Hamiltonian is non-diagonal and the rf-field terms do not commute with the scalar-coupling term.

To proceed, we recast the Hamiltonian in Eq. (3) into the reference frame of the RF fields. Employing the following series of transformations

$$\mathcal{H}^{RF} = \mathcal{H} - \mathcal{H}_0$$

where $\mathcal{H} = U_0^{-1}\mathcal{H}^{DR}U_0$ with $U_0 = \exp(-i\mathcal{H}_0 t)$ and $\mathcal{H}_0 = \omega_{1y} J_{1y} + \omega_2 J_{2y}$, and assuming that the Hartmann–Hahn condition is fulfilled $\omega_1 = \omega_2 = \omega_0$, the rotating tilted Hamiltonian RT is transformed into a rotating tilted rotating frame (RTR)

$$\mathcal{H}^{RTR} = \pi J S (1 + \cos(2\omega t)) + I_z S_x \sin(2\omega t)$$

For very strong rf fields (2$\omega t \gg \pi J S$) we may neglect the oscillating components in Eq. (4) by invoking the secular approximation, to give

$$\mathcal{H}^{RTR} = \pi J S (I_z S_x + I_z S_y)$$

We turn our attention to the mechanism of cross-polarization for $S>\frac{1}{2}$. It is important to note that although the above-mentioned Hamiltonian has been derived in the basis of Cartesian operators it is completely general for scalar coupled IS systems where $I=\frac{1}{2}$ and $S>\frac{1}{2}$. The Cartesian product operator formulism does not provide a particularly intuitive description of coupling to quadrupolar nuclei. To proceed we recast the density operator as products of irreducible tensor operators, as follows.

IV. IRREDUCIBLE TENSOR OPERATORS

To calculate the coherent evolution of a given operator under the influence of a particular Hamiltonian it is necessary to express the density matrix in terms of a suitable orthonormal basis set. For a single spin-half nucleus the most convenient representation is in terms of Cartesian spin operators $I_x$, $I_y$, and $I_z$, with the half-identity operator $\frac{1}{2}I$ completing the basis.

\[
\langle B \rangle = \text{Tr} \{ U(\tau) A \ U^{-1}(\tau) B \},
\]

where the propagator is given by $U(\tau) = \exp(-iH\tau)$. The success of this approach therefore relies on the ability to calculate this latter matrix exponential of the Hamiltonian.
than one spin the density operator is expanded as direct products of these single spin operators. The density operator may also be recast in terms of shift operators and polarization operators that in turn lead to the more general notion of single-transition operators. These provide a particularly elegant description of selective experiments in complicated spin systems. The product operator basis for a general spin can be extended for \( I > \frac{1}{2} \) although the manipulation of such expressions is not intuitive. An alternative description that proves more convenient in the description of multiple-quantum NMR of \( I \geq \frac{1}{2} \) is to expand the density operator in terms of irreducible tensors given by

\[
\sigma(t) = \sum_{l=0}^{2S} \sum_{l=-l}^{l} b_{lp}^S(t) T_{lp}^S,
\]

where \( T_{lp}^S \) is an irreducible tensor operator of rank \( l \) and coherence order \( p \). The Cartesian basis of product operators, and rotations thereof, can be interpreted in terms of vectors. The rotational properties of tensor operators are the same as those of their corresponding spherical harmonics. The matrix representations of these tensor operators are well established. The definitions and corresponding normalization factors employed throughout this work are those of Müller et al.

The representation of the Hamiltonian, whilst quite general for any spin, has been cast in terms of Cartesian operators. To proceed we must recast the representation of the Hamiltonian in terms of spherical tensor operators. The relationship between these tensor operators and their Cartesian counterparts are as follows.

The identity operator is given by

\[
E = \lambda_0 T_{00},
\]

where \( \lambda_0 = \sqrt{2}, \sqrt{3}, \sqrt{4} \) for \( I = \frac{1}{2}, 1, \frac{3}{2} \) respectively.

The operator corresponding to Zeeman order is given by

\[
S_z = \lambda_1 T_{10},
\]

where \( \lambda_1 = 1/\sqrt{2}, \sqrt{2}, \sqrt{5} \) for \( I = \frac{1}{2}, 1, \frac{3}{2} \) respectively.

An awkward feature of tensor operators is that the individual operators are not Hermitian (except for \( p = 0 \)). Coherences are represented by the following linear combinations of irreducible tensor operators:

\[
T_{11,x} = (T_{1,-1} - T_{1,1})/\sqrt{2},
\]

\[
T_{11,y} = i(T_{1,-1} + T_{1,1})/\sqrt{2},
\]

\[
S_x = \lambda_1 T_{11,x},
\]

\[
S_y = \lambda_1 T_{11,y}.
\]

For single-quantum coherences the notation of the phase as \( x \) and \( y \) is chosen due to the direct correspondence with Cartesian operators. For \( p \neq 0 \) it is useful to define a Hermitian density operator component as

\[
T_{lp,\phi} = \frac{1}{\sqrt{2}} \left[ \cos(\phi) (T_{l,-p} + (-1)^p T_{l,+p}) + i \sin(\phi) (T_{l,-p} - (-1)^p T_{l,+p}) \right].
\]

Explicit inclusion of the phase in the term on the left-hand side yields a particularly convenient notation for the description of higher-order coherences.

For an isolated spin-\( \frac{1}{2} \) the complete basis set is represented by the four tensor operators: \( T_{00} \) (identity), \( T_{10} \) (Zeeman order), \( T_{11,0} \) and \( T_{11,\pi/2} \) (rank-one, single quantum coherences). For an isolated spin 1 the complete basis set is composed of nine tensor operators. In addition to the previous four operators one requires: \( T_{20} \) (quadrupolar order), \( T_{21,0} \) and \( T_{21,\pi/2} \) (rank-two, single quantum coherences), \( T_{22,0} \) and \( T_{22,\pi/4} \) (rank-two, double quantum coherences). For an isolated spin \( \frac{3}{2} \) the complete basis set is composed of 16 tensor operators. In addition to the previous nine operators we require: \( T_{30} \) (octopolar order), \( T_{31,0} \) and \( T_{31,\pi/2} \) (rank-three, single quantum coherences), \( T_{32,0} \) and \( T_{32,\pi/4} \) (rank-three, double quantum coherences), \( T_{33,0} \) and \( T_{33,\pi/6} \) (rank-three, triple quantum coherences).

In complete analogy with the product operator description of Cartesian operators for coupled spin systems it has been shown that it is possible to represent the density operator as products of the irreducible tensor operators of each individual spin. For an IS spin system the density operator can be represented by

\[
\sigma(t) = \sum_{l_1,l_2,p_1,p_2} b^{IS}_{l_1l_2p_1p_2}(t) T_{l_1p_1}^S T_{l_2p_2}^S.
\]

The matrix representation of a product of tensor operators can therefore be formed in the usual way as a direct product of the individual spin tensors

\[
T_{l_1p_1}^l T_{l_2p_2}^p = T_{l_1p_1}^l \otimes T_{l_2p_2}^p.
\]

Employing direct products and the previously defined tensor operators we can derive matrix representations of the tilted rotating frame Hamiltonian in Eq. (5). The relevant components of the density operator can be derived in an analogous fashion.

### V. Heteronuclear Cross-Polarization From \( I = \frac{1}{2} \) to \( S = \frac{3}{2} \)

Matrix representations of Hamiltonian operators in the rotating tilted rotating (RTR) interaction frame of Eq. (5) can be derived by calculating direct products of the relevant tensor operators.

For \( I = \frac{1}{2} \) and \( S = \frac{3}{2} \) the Hamiltonian of Eq. (5) is given by

\[
\mathcal{H}^{RTR} = \frac{\pi J_{IS}}{2} (T_{11,x} T_{11,x} + T_{11,y} T_{11,y}).
\]

The matrix representation of the RTR Hamiltonian in Eq. (13) is
VI. HETEROUCLEAR CROSS-POLARIZATION FROM $I=\frac{1}{2}$ TO $S=1$

The matrix representation of the Hamiltonian operator in the RTR interaction frame of Eq. (5) for $I=\frac{1}{2}$ and $S=1$ is given by

$$\mathcal{H}_{\text{RTR}}^{\text{RTR}} = \pi J_{IS}(T_{11,x}T_{11,y} + T_{11,y}T_{11,x}).$$  \hspace{1cm} (16)

The matrix representation of the RTR Hamiltonian in Eq. (16) is

$$\mathcal{H}_{\text{RTR}}^{\text{RTR}} = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{\sqrt{2}} \pi J_{IS} & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} \pi J_{IS} & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{\sqrt{2}} \pi J_{IS} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}.$$  \hspace{1cm} (17)

Note again that the Hamiltonian matrix in Eq. (17) is block diagonal. The mechanism of cross-polarization for $I=\frac{1}{2}$ and $S=1$ in the limit of $2\omega_1 \gg \pi J_{IS}$ corresponds to two independent rotations in the subspaces $|2\rangle,|4\rangle$ and $|3\rangle,|5\rangle$ whilst the subspace $|1\rangle,|6\rangle$ remains invariant.

For exact Hartmann–Hahn match and in the limit of strong rf field strengths, the expectation value of the observable $S$ spin coherence is given by

$$\langle S_x \rangle(t) = \frac{1}{2}(1 - \cos(\pi J_{11} t)).$$  \hspace{1cm} (15)

The coherence transfer is driven by the scalar coupling with a maximum efficiency of $\langle S_x \rangle(t) = 1$ that occurs with the duration $t = J_{11}^{-1}$.

Figure 2 shows simulations carried out for a two spin-$\frac{1}{2}$ system. The solid lines correspond to the theoretical high rf field limit of Eq. (15). The dashed line is a numerical simulation for the transfer functions when the rf fields were set equal in amplitude to the scalar coupling. The dotted line corresponds to the transfer function under the influence of rf field amplitudes that were set much weaker than the scalar coupling. Note that the efficiency of the transfer rapidly decreases in the latter case as the two components of the IS doublet are no longer efficiently locked.

FIG. 2. Analytical solution and numerical simulations for a two-spin $I=\frac{1}{2}$, $S=\frac{1}{2}$ system. The build-up of $\langle S_x \rangle$ is plotted as a function of the duration of cross-polarization for an initial density operator $\sigma(0) = |I\rangle$. The solid line corresponds to the strong rf field limit of Eq. (15) with an optimum duration of $\tau = 1/J_{11}$. The dashed line corresponds to rf field strengths that are equal to the scalar-coupling constant $\omega_{12}/2\pi = \omega_{12}/2\pi = J_{11}$. The dotted line corresponds to rf field strengths that are much weaker than the scalar-coupling constant $\omega_{12}/2\pi = \omega_{12}/2\pi = 0.2J_{11}$.
The maximum transfer efficiency is 
\[ \langle S_x \rangle(t) = \frac{1}{\sqrt{6}}(1 - \cos(\sqrt{2}\pi J_{IS}t)). \]  
(18)

The maximum transfer efficiency is \( \langle S_x \rangle(t) = 2/\sqrt{6} \sim 0.816 \) that occurs when the duration of cross-polarization is \( t = (\sqrt{2}J_{IS})^{-1} \).

Figure 3 shows simulations carried out for a two-spin system \( I = \frac{1}{2}, S = 1 \). The solid lines correspond to the theoretical high rf field limit of Eq. (18). The dashed line is a numerical simulation for the transfer functions when the rf fields were set equal in amplitude to the scalar coupling. The dotted line corresponds to the transfer function under the influence of rf field amplitudes that were set to be much weaker than the scalar coupling. Note that the efficiency of the transfer rapidly decreases in the latter case, as the three components of the \( I \) spin triplet and the two components of the \( S \) spin doublet are no longer efficiently locked.

Note again that the Hamiltonian in Eq. (20) is block diagonal. The mechanism of cross-polarization for \( I = \frac{1}{2} \) and \( S = 3/2 \) in the limit of \( 2\omega_0 \gg \pi J_{IS} \) corresponds to three independent rotations in the subspaces \( \{|2\rangle,|5\rangle\}, \{|3\rangle,|6\rangle\} \) and \( \{|4\rangle,|7\rangle\} \) whilst the subspace \( \{|1\rangle,|8\rangle\} \) is invariant.

For exact Hartmann–Hahn match, and in the limit of high field strengths, the expectation value of the observable \( S_\| \) spin coherence is given by
\[ \langle S_x \rangle(t) = \frac{1}{\sqrt{6}} \left( \frac{3}{4} - \frac{1}{2} \cos(\sqrt{3}\pi J_{IS}t) \right) \cos(2\pi J_{IS}t). \]  
(21)

The maximum transfer efficiency is \( \langle S_x \rangle(t) \sim 0.663 \) that occurs when the duration of cross-polarization is \( t = 0.547/J_{IS} \).

Figure 4 shows simulations carried out for a two-spin system consisting of \( I = \frac{1}{2}, S = 3/2 \). The solid lines correspond to the theoretical high rf field limit of Eq. (21). The dashed line is a numerical simulation of the transfer functions when the rf fields are equal in amplitude to the scalar coupling. The dotted line corresponds to the transfer function under the influence of rf field amplitudes that are much weaker than the scalar coupling constant. Note again that the efficiency of the transfer rapidly decreases in the latter case as the four components of the \( I \) spin quartet and the two components of the \( S \) spin doublet are no longer efficiently locked.

Again the maximum efficiency is less than 100% for the conversion from \( I_x \) to \( S_x \), due to the accessibility of higher rank coherences.

VIII. SENSITIVITY TO MISMATCH

The effect of rf mismatch on the efficiency of cross-polarization can be calculated by recasting Eq. (3) in the following form:
\[ \mathcal{H}^{\text{RT}} = \frac{\omega_S}{2} (I_z + S_z) + \frac{\omega_A}{2} (I_z - S_z) + 2\pi J_{IS} I_x S_x, \]  
(22)
where the sum of the rf fields is \( \omega_S = \omega_I + \omega_S \) and the rf
mismatch is \( \omega_\Delta = \omega_1^I - \omega_5^S \). The Hamiltonian in Eq. (22) is recast in terms of the relevant direct products of tensor operators as previously.

The effect of rf mismatch, \( \omega_\Delta \), was investigated in Fig. 5, for cross-polarization from \( I = \frac{3}{2} \) to \( S = \frac{3}{2} \). The expectation value \( \langle S_x \rangle \) for an optimum duration of \( t = 0.547 J_{1S} \) is plotted as a function of the sum of the rf field strengths, \( \omega_5 \). The solid line corresponds to a perfect Hartmann–Hahn match. The dashed and dotted lines correspond to a 10% and 20% mismatch, respectively, with respect to the sum of the rf field strengths. The curves converge for low rf field strengths, consequently cross-polarization becomes insensitive to rf mismatch. We note that for efficient transfer, the amplitude of the sum of the rf fields should be at least of the order of three times the scalar coupling constant, \( \omega_5 / 2 \pi \).

\[ \omega_\Delta = \omega_1^I - \omega_5^S \]

\( \langle S_x \rangle \) is plotted as a function of \( \tau J_{1S} \). The dashed line corresponds to a 10% and 20% mismatch with respect to the sum of the rf fields, respectively.

FIG. 4. Analytical solution and numerical simulations for a two-spin \( I = \frac{1}{2}, S = \frac{1}{2} \) system. The build-up of \( \langle S_x \rangle \) is plotted as a function of the duration of cross-polarization for an initial density operator \( \sigma(0) = \langle I_x \rangle \). The solid line corresponds to the strong rf field limit of Eq. (21) with an optimum duration of \( \tau = 0.547 J_{1S} \). The dashed line corresponds to rf field strengths that are equal to the scalar-coupling constant \( \omega_1^I / 2 \pi = \omega_5^S / 2 \pi = J_{1S} \). The dotted line corresponds to rf field strengths that are much weaker than the scalar-coupling constant \( \omega_1^I / 2 \pi = \omega_5^S / 2 \pi = 0.2 J_{1S} \).

FIG. 5. Efficiency of polarization transfer from \( I_1 \) to \( S_5 \), for an \( I = \frac{3}{2}, S = \frac{1}{2} \) spin system as a function of the sum of the rf fields \( \omega_2 \) (in units of \( J_{1S} \)). Three different mismatch conditions are displayed. The solid line corresponds to perfect matching conditions. Dashed and dotted lines correspond to a 10% and 20% mismatch with respect to \( \omega_5 \), respectively.

The effect of rf mismatch in the case of a spin system \( I = \frac{3}{2} \) and \( S = \frac{1}{2} \) is qualitatively similar. In this case however, to achieve maximum efficiency the sum of the rf fields should be at least of the order of the scalar-coupling constant, \( \omega_5 / 2 \pi = J_{1S} \). In the case of a spin system \( I = \frac{5}{2} \) and \( S = 1 \) maximum transfer efficiency is achieved when the sum of the rf fields is at least of the order of twice the scalar coupling constant, \( \omega_5 / 2 \pi \approx 2 J_{1S} \).

IX. CROSS-POLARIZATION IN MULTISPIN SYSTEMS \( I_nS \)

The expansion of the density operator as direct products of tensor operators can be easily extended to describe polarization transfer in multispin systems \( I_nS \) where \( n \geq 1 \). For Fig. 6 numerical simulations were carried out for coherence transfer between \( I = \frac{1}{2} \) and \( S = \frac{3}{2} \) for the extended spin systems \( I_nS \), where \( n = 1, \ldots, 4 \). The expectation value \( \langle S_x \rangle \) is plotted as a function of the cross-polarization contact duration for an initial density operator \( \sigma(0) = I_x \). The intensity scale was normalized with respect to the maximum in the transfer function. The solid line, dotted line, dashed line, and dot-dashed lines correspond to an \( IS \), \( I_2S \), \( I_3S \), and \( I_4S \) spin systems, respectively. Note that while the transfer functions are qualitatively similar, the optimal duration of CP decreases as the number of coupling partners increases.

X. EXPERIMENTS

Beryllium fluoride complexes are an excellent test sample for a scalar coupled system \( I = \frac{1}{2} \) and \( S = \frac{3}{2} \). Both \(^{19}\)F and \(^{9}\)Be have a natural abundance of 100%. Furthermore the
high sensitivity of fluorine and the relative insensitivity of beryllium yields a enhancement factor of 0.663 $\gamma_F / \gamma_{\text{Be}} = 4.45$.

Beryllium fluoride complexes are known to act as phosphate analogues that bind to adenosine diphosphate (ADP). Fluoride complexes of beryllium and aluminum have been shown to activate a number of proteins, including G-proteins, microtubules, F-actin, and other phosphotransfer enzymes. Furthermore, they are known to give separate resonances. Spectra in the 19 F spectrum they are degenerate in the 9 Be spectrum. Spectra in the 19 F spectrum they are degenerate in the 9 Be spectrum. Spectra in the 19 F spectrum they are degenerate in the 9 Be spectrum.

An aqueous mixture of beryllium fluorides was prepared containing 100 mM NaF and 10 mM BeSO$_4$. At these concentrations the major species are BeF$_3^-$ and BeF$_4^{2-}$. All experiments were performed on a Bruker DRX 400 MHz spectrometer equipped with a broadband double-resonance probe, at 298 K. The $^1$H channel was detuned to the 19 F resonance frequency (376.4 MHz) and the X nucleus tuned to 9 Be (56.2 MHz). The Hartmann–Hahn condition was calibrated by keeping one of the rf field amplitudes constant while the other was varied to achieve optimal transfer. The rf amplitudes employed were $\omega_1^F/2\pi = \omega_1^F/2\pi = 170$ Hz (closed circles) and 85 Hz (open circles). The optimum transfer duration was 12 ms. The solid line corresponds to a numerical simulation for an IS system whereas the dotted line corresponds to the analytical solution for an IS spin system given in Eq. (21). Each experimental point was acquired with 8 scans.

![Figure 7](image1.png)

**FIG. 7.** Experimental transfer functions for cross-polarization between 19 F and 9 Be in the complex BeF$_3^-$ and BeF$_4^{2-}$. The rf amplitudes employed were $\omega_1^F/2\pi = \omega_1^F/2\pi = 170$ Hz (closed circles) and 85 Hz (open circles). The optimum transfer duration was 12 ms. The solid line corresponds to a numerical simulation for an IS system whereas the dotted line corresponds to the analytical solution for an IS spin system given in Eq. (21). Each experimental point was acquired with 8 scans.

![Figure 8](image2.png)

**FIG. 8.** (a) Conventional 19 F 1D spectrum of a mixture of BeF$_3^-$ and BeF$_4^{2-}$. The scalar coupling constants are $J_{\text{hf}}(\text{BeF}_3^-) = 33.9$ Hz and $J_{\text{hf}}(\text{BeF}_4^{2-}) = 37.4$ Hz. (b) 9 Be 1D spectrum. Note that assignment of the two different species is difficult due to the degeneracy of the beryllium resonances. (c) 9 Be spectrum acquired with the carrier frequencies positioned at the center of the BeF$_3^-$ multiplets. (d) 9 Be spectrum acquired with the carrier frequencies positioned at the centers of the BeF$_4^{2-}$ multiplets. To enable comparison (b)–(d) were acquired with identical acquisition parameters and are displayed with the same intensity scale. The rf amplitudes employed in (c) and (d) were $\omega_1^F/2\pi = \omega_1^F/2\pi = 85$ Hz.

intensity scale was normalized with respect to the maximum transfer efficiency.

Figure 8 shows spectra recorded for the above-mentioned mixture of beryllium fluoride complexes. The conventional 19 F and 9 Be 1D spectra is shown in (a) and (b). Note that while the two species are well separated in the 19 F spectrum they are degenerate in the 9 Be spectrum. Spectra in (c) and (d) are of 9 Be acquired with the pulse sequence of Fig. 1. The carrier frequencies were positioned at the centers of the BeF$_3^-$ and BeF$_4^{2-}$ multiplets, respectively. To enable a direct comparison the spectra (b)–(d) were acquired with identical acquisition parameters and are displayed with the same intensity scale. The ratio of the peak integrals in (b)–(d) is 1:0.7:1.7. Thus a factor of 2.4 sensitivity enhancement was achieved over the conventional pulse-acquire experiment. This value is less than the theoretical maximum as the transfer is affected by relaxation.

**XI. CONCLUSIONS**

We have shown that cross-polarization in solution state can be an efficient technique for the selective excitation of scalar coupled quadrupolar nuclei. Given the increasing im-
portance of quadrupolar nuclei as probes of the local dynamics in structured environments it is likely that this technique will be applicable to a variety of systems in liquid state NMR.

ACKNOWLEDGMENTS

This work was supported by a grant from the Australian Research Council to P.W.K. T.R.E. acknowledges a University of Sydney Sesqui Research Fellowship and thanks Dr. F. Ferrage for valuable discussions. Dr. Bill Bubb is thanked for help with the NMR spectrometers and Bill Lowe for technical assistance.

APPENDIX: ANALYTICAL SOLUTION FOR $I = \frac{1}{2}$, $S = \frac{1}{2}$, AND ARBITRARY rf FIELD STRENGTH

The Hamiltonian in the tilted reference frame of Eq. (3) may be expressed in terms of single-transition operators\(^{36,37}\) that span the zero and double quantum subspaces:

$$\hat{H}_{RT}^{(x)} = \left( \omega_x I_{1x}^{(x)} + \pi J_{1S} I_{1S}^{(x)} \right) + \left( \omega_x I_{z}^{(x)} + \pi J_{1S} I_{1S}^{(x)} \right),$$

(A1)

where $\omega_x = \omega_x^0 + \omega S$ and $\omega_{1S} = \omega_1 - \omega S$. The zero-quantum (ZQ) and double-quantum (DQ) single-transition operators are defined by

$$I_{1x}^{(x)} = \frac{1}{2}(I_x + S_x) = DQ_x, \quad I_{z}^{(x)} = \frac{1}{2}(I_x - S_x) = ZQ_x,$$

$$I_{1x}^{(x)} = (I_x S_x - I_x S_x) = DQ_x, \quad I_{z}^{(x)} = (I_x S_x + I_x S_x) = ZQ_x,$$

(A2)

where $I_{1S}^{(x)} (\xi = x,y,z)$ refers to coherences and to differences in populations between the eigenstates $|\rho\rangle$ and $|s\rangle$. To calculate the efficiency of the transfer from $I_x$ to $S_x$ in the rotating frame we need to calculate the transfer from $I_x$ to $S_x$ in the tilted frame RT in Eq. (A1). Consider an initial density operator $\sigma(0) = I_x$ (equivalent to $I_z$ in the tilted reference frame):

$$\sigma'(0) = I_x = I_{1x}^{(x)} + I_{z}^{(x)}.$$

(A3)

Note the prime to indicate the tilted reference frame to distinguish it from the normal rotating frame. The two components evolve independently since the zero and double quantum subspaces commute. The evolution in the zero quantum subspace is described by a rotation about the axis $\{ \pi J_{1S}, 0, \omega_{1S} \}$ whilst in the double quantum subspace it is described by a rotation about the axis $\{ \pi J_{1S}, 0, \omega_S \}$.

The expectation value of the observable $\hat{S}_z$ spin magnetization $\sigma(t) = S_z$ (equivalent to $\sigma'(t) = S_z = I_{1z}^{(x)} - I_{z}^{(x)}$ in the tilted reference frame) is given by\(^{33}\)

$$\langle S_z \rangle(t) = \frac{1}{2} \left[ \frac{\omega_\Sigma^2 + \pi J_{1S} \cos(\omega_{1S} t)}{\omega_{\Sigma}^2} - \frac{\omega^2 + \pi J_{1S} \cos(\omega_{1S} t)}{\omega_{\Delta}^2} \right],$$

(A4)

where $\omega_{\Sigma} = \sqrt{\omega_x^2 + \pi J_{1S}^2}$, $\omega_{1S} = \sqrt{\omega_x^2 + \pi J_{1S}^2}$, $\omega_{\Sigma}$ and $\omega_{\Delta}$ are as defined below Eq. (A1). In the limit of strong rf fields the transfer function in Eq. (A4) simplifies to Eq. (15).