Cross-polarization efficiency in I_NS systems using adiabatic RF sweeps

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The theory describing nuclear magnetic resonance cross-polarization using adiabatic sweeps of the rf spin-lock fields through the Hartmann–Hahn matching condition is extended to small homonuclear coupled systems of the type I_NS. In particular, the connection is made between such experiments and the associated theoretical limits on polarization transfer—the ''unitary bounds''—demonstrating that these techniques can achieve the maximum transfer of polarization from the I spins to the S spins, subject to the constraint of angular momentum conservation imposed by spin-locking. Factors such as permutation symmetry of the spins, imperfect adiabaticity of individual crossings and fast sample spinning are shown to have no fundamental impact on the validity of these results. © *1997 American Institute of Physics.* [S0021-9606(97)00445-5]

I. INTRODUCTION

Cross polarization (CP) from high-γ nuclei (conventionally labeled I spins) to low-γ nuclei (S spins) is an essential step in the majority of solid-state nuclear magnetic resonance (NMR) experiments. Usually this is achieved by spin-locking the transverse magnetization, using continuous rf irradiation, such that the field strengths on the two spin species, ω_I and ω_S, satisfy the Hartmann–Hahn matching condition,[1] $|\omega_I|=|\omega_S|$. Such cross polarization leads to a sensitivity enhancement of γ_I/γ_S, which may be increased further by increasing the repetition rate if $T_{1\rho}$ of the I spins is shorter than that of the S spins. The efficiency of the experiment can be improved by adiabatically sweeping the amplitude of one (or both) of the rf fields through the Hartmann–Hahn match such that the condition is satisfied at the approximate midpoint of the experiment. This approximately doubles the maximum possible efficiency relative to simple Hartmann–Hahn matching (*vide infra*), as well as reducing the difficulty of achieving the matching condition and suppressing transient oscillations. This technique has been successfully applied in liquid-state spectroscopy for J-coupled systems[2,3] and in solids, under the acronym APHH (adiabatic passage through the Hartmann–Hahn condition) for both static[4] and spinning samples.[5] Other modifications of the Hartmann–Hahn matching condition to include quasiadiabatic sweeps of the rf have also been reported.[6,7]

The theoretical description of the APHH experiment has been presented for isolated IS spin systems.[4,5] The current paper extends this theory to systems of the form I_NS, that is, systems of isolated S spins coupled to N I spins, which may themselves be coupled by the homonuclear dipolar interaction. The results are compared with the efficiency of Hartmann–Hahn matching experiments and general theoretical constraints on the degree of polarization transfer.

II. ADIABATIC PASSAGE IN THE I_2S SYSTEM

Before considering the general I_NS system, it is useful to consider as a specific example the behavior of the I_2S system under the conditions of the adiabatic passage at the Hartmann–Hahn condition (APHH) experiment. In the simulation of Fig. 1 the spin-lock field on I is fixed ($\omega_I/2\pi = 20$ kHz), while the rf strength on the S nucleus is swept through the Hartmann–Hahn condition. The time-dependent offset of the S spin rf is given by[4]

$$\Delta(t)=\omega_S(t)-\omega_I=d_{\mathrm{est}}\tan\alpha\left(\frac{\tau}{2}-t\right)\quad 0\leqslant t\leqslant\tau, \tag{1}$$

$$\alpha=\frac{2}{\tau}\arctan\frac{\Delta(0)}{d_{\mathrm{est}}}, \tag{2}$$

where d_{est} is an estimated dipolar linewidth (simply the heteronuclear coupling in an IS system), τ is the total contact time, and $\Delta(0)/d_{\mathrm{est}}$ is the ratio of the initial offset to the dipolar linewidth. This tangential time-dependence ensures that the rf is swept relatively slowly through the approximate matching condition; this functional form is a compromise between linear rf sweeps which compensate well for variations in the match condition[8] (e.g., due to rf inhomogeneities) and other forms which optimize the adiabaticity[9] but are less tolerant of mismatch.

In Fig. 1 there is a single heteronuclear coupling between the S spin and one of the (coupled) I spins, and APHH successfully transfers half the I spin magnetization to the S spin, which is the maximum possible polarization transfer in this system, cf. Sec. III A. Although the homonuclear coupling has no effect on the efficiency of transfer, it clearly modifies the matching condition; for this example, the homonuclear coupling exceeds the heteronuclear linewidth, and the polarization transfer occurs in two distinct steps separated by the homonuclear interaction strength. Note that only a single crystallite orientation has been simulated and in a powder sample, this splitting of the matching condition will be washed out by the orientation dependence of the coupling constants. The variation of the apparent matching condition

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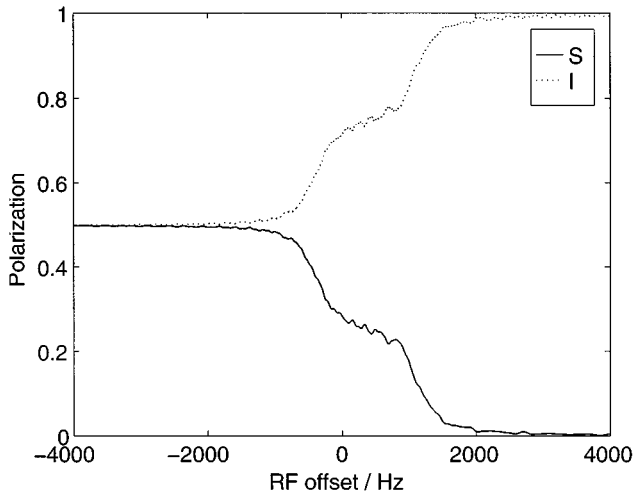

FIG. 1. Simulations of the APHH experiment for a static I_2S system. The hetero- and homonuclear couplings are 500 and 1500 Hz, respectively. The polarization is initially on the I spins and the rf offset, $\Delta/2\pi$, is swept from a positive value through the Hartmann–Hahn condition (i.e., right to left in the figure). The parameters used to set the shape of the tangential rf sweep, cf. Eq. (1), were $\omega_I/2\pi=20$ kHz, $d_{\text{est}}/2\pi=1200$ Hz, $\Delta(0)/2\pi=7200$ Hz and $\tau=30$ ms.

with orientation requires that both the initial rf offset, $\Delta(0)$, and the width over which the rf is swept slowly, be increased if the adiabaticity conditions are to be satisfied.

Clearly, the homonuclear coupling must be included in any theoretical analysis of this system. In the doubly rotating tilted frame (in which the quantisation axis, z, for both spins lies along the spin-lock fields) the Hamiltonian for the I_2S system is

$$H(t)=H_{\text{rf}}(t)+\Omega_S S_x+\sum_i \Omega_i I_{xi}+2\sum_i d_i I_{xi}S_x + D(2I_{x1}I_{x2}-I_{y1}I_{y2}-I_{z1}I_{z2}), \tag{3}$$

$$H_{\text{rf}}(t)=\omega_I(t)(I_{z1}+I_{z2})+\omega_S(t)S_z, \tag{4}$$

where Ω_S and Ω_i are the chemical shifts of spin S and the I spins respectively, $\omega_I(t)$ and $\omega_S(t)$ denote the time-dependent rf on the I and S spins, respectively, d_i is the (orientation dependent) heteronuclear coupling constant between the S spin and the I_i spin, and D is the (similarly orientation dependent) homonuclear coupling between the I spins.

It is convenient to keep one spin-lock field constant, say ω_I, and sweep the S spin field through the Hartmann–Hahn condition, i.e., $\omega_S(t)=\omega_I+\Delta(t)$ where $\Delta(t)$ is the time-dependent offset from match. Hence the rf contribution to the Hamiltonian can be simplified to

$$H_{\text{rf}}(t)=\omega_I(F_z+S_z)+\Delta(t)S_z, \tag{5}$$

where F_z is the sum z operator for the I spins, $I_{z1}+I_{z2}$ for I_2S.

Assuming that the rf is strong, i.e., $\omega_I \gg d_i, D, \Omega_i$, this diagonal term will dominate the Hamiltonian which can then be divided into blocks of the same total magnetic quantum number, $\langle F_z+S_z\rangle$. Assuming that all spins are spin-1/2, this results in four diagonal blocks, $\langle F_z+S_z\rangle=\pm 1/2,\pm 3/2$. The isolated $1\times 1\langle F_z+S_z\rangle\pm 3/2$ blocks can be ignored as they will not lead to evolution of the initial density matrix, leaving the two 3×3 blocks corresponding to $\langle F_z+S_z\rangle=\pm 1/2$. Removing the diagonal terms in ω_I, which are proportional to the identity matrix and therefore not important in describing the dynamics of the system, these blocks are given by

$$\begin{pmatrix} -D/4\mp\Delta/2 & d_1/2 & d_2/2 \\ d_1/2 & D/4\pm\Delta/2 & D/4 \\ d_2/2 & D/4 & D/4\pm\Delta/2 \end{pmatrix}. \tag{6}$$

The adiabatic passage occurs in the eigenbasis of these Hamiltonians. In the limit of $\Delta \gg D,d$, which is the case at the beginning and end of the rf sweep, Eq. (6) is diagonalized straightforwardly giving the eigenvalues and eigenvectors:

$$\begin{aligned} &\text{(i)} && \mp\Delta/2-D/4 && (1,0,0), \\ &\text{(ii)} && \pm\Delta/2+D/2 && (0,1/\sqrt{2},1/\sqrt{2}), \\ &\text{(iii)} && \pm\Delta/2 && (0,-1/\sqrt{2},1/\sqrt{2}). \end{aligned} \tag{7}$$

Applying the similarity transformation defined by the eigenvectors (i)–(iii) to Eq. (6),

$$\begin{pmatrix} -D/4\mp\Delta/2 & d_+/2 & \pm d_-/2 \\ d_+/2 & D/2\pm\Delta/2 & 0 \\ \pm d_-/2 & 0 & \pm\Delta/2 \end{pmatrix}, \tag{8}$$

where $d_\pm=(d_1\pm d_2)/\sqrt{2}$.

The density matrix following the initial $(\pi/2)_y$ pulse, is proportional to F_z in the tilted rotating frame (assuming the usual high temperature approximation). This commutes with the similarity transform of Eq. (7), which fulfills the first criterion for an adiabatic exchange,[9,10] i.e., that the density matrix must commence in a pure state of the Hamiltonian. If $H(t)$ changes sufficiently slowly, then the eigenstates of the density matrix will smoothly follow the eigenstates of Eq. (8), i.e., no transitions are induced between eigenstates. Figure 2 plots these eigenvalues as a function of Δ, revealing which initial eigenstates cross into which final states. Unless d_+ and d_- are both zero (in which case cross polarization is impossible) state (i) will cross over into state (ii) or (iii). The choice of final eigenstate depends on which crossing is encountered first (which in turns depends on the sign of D, and whether Δ approaches zero from below or above), and on whether the first crossing is avoided (i.e., whether $d_\pm$ is negligibly small).

The result of the adiabatic transfer is to exchange the corresponding diagonal elements of the density matrix in the Eq. (7) eigenbasis, ρ', e.g., for the $\langle F_z+S_z\rangle=1/2$ block with transfer occurring between states (i) and (ii), linked by the d_+ matrix element,

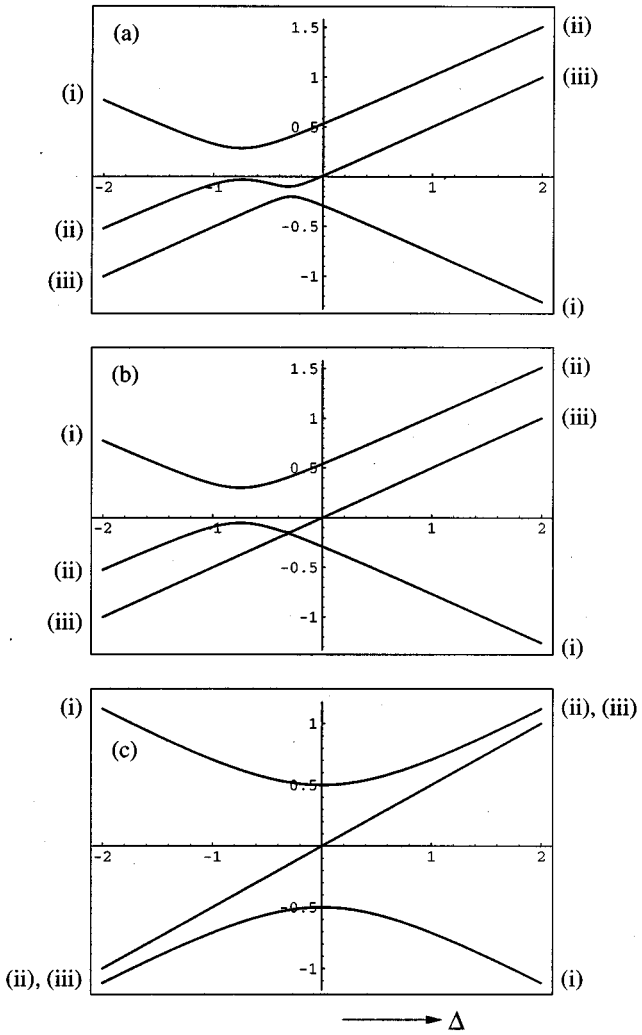

FIG. 2. Eigenvalues of Eq. (6), $\langle F_z+S_z\rangle=1/2$: (a) $|d_1|\neq|d_2|$, $D\neq0$, (b) $d_1=d_2$, $D\neq0$, and (c) $D=0$. The labels (i)–(iii) correspond to the limiting eigenstates of Eq. (7). The horizontal scale is Δ/D for (a) and (b), and $\Delta/\sqrt{d_1^2+d_2^2}$ for (c).

$$\rho'(0)=F_z=\begin{pmatrix}1/2 & & \\ & -1/2 & \\ & & -1/2\end{pmatrix}$$

$$\rightarrow\rho'(\tau)=\begin{pmatrix}-1/2 & & \\ & 1/2 & \\ & & -1/2\end{pmatrix}. \tag{9}$$

The similarity transform of Eq. (7) commutes with S_z, hence $\langle S_z\rangle=\mathrm{Tr}(\rho S_z)=\mathrm{Tr}(\rho' S_z)$. As a result, the final S spin polarization is independent of which states exchange populations. Which crossing is taken will, however, affect the rf field at which the transfer occurs. For example, if d_+ and d_- are nonzero and D is positive, decreasing the rf offset Δ will lead first to a crossing in the block of the density matrix corresponding to $\langle F_z+S_z\rangle=-1/2$ at $\Delta=3D/4$, Fig. 2(a), followed by a subsequent crossing at $\Delta=-D/4$ in the $\langle F_z+S_z\rangle=1/2$ block. These crossings will only be distinct if $|d_\pm|<|D|$ with the separation of the eigenvalues at the crossing given by twice the connecting matrix element, $|d_\pm|$. If, on the other hand, $|D|\ll|d_\pm|$, Fig. 2(c), two of the three states are effectively degenerate and there is a single crossing point at $\Delta=0$ with the separation of states given by $\sqrt{d_1^2+d_2^2}$.

We can describe the effect of imperfect adiabaticity in terms of the parameter θ which describes the rotation applied to the fictitious spin-1/2 I_z operator appropriate to the transition cf. Sec. III B. At the end of a truly adiabatic passage $\theta=\pi$ corresponding to a full inversion of the populations of the states involved. Other values of θ correspond to imperfect inversion with the limit of $\theta=0$ corresponding to a sudden transition in which no population is transferred. If we consider the subsystem above starting in the pure state with only level-1 populated, $\rho'_{11}(0)=1$, the total population of the 2 and 3 levels after passage through the 1-2 and 1-3 transitions can be straightforwardly shown to be

$$\rho'_{22}(\tau)+\rho'_{33}(\tau)=\tfrac{3}{4}-\tfrac{1}{4}\cos\,\theta^{1\text{-}2}-\tfrac{1}{4}\cos\,\theta^{1\text{-}3}-\tfrac{1}{4}\cos\,\theta^{1\text{-}2}\cos\,\theta^{1\text{-}3}. \tag{10}$$

If any $\cos\theta^{i-j}=-1$, this expression has the value 1, corresponding to full exchange of population between level 1 and the 2/3 levels. Only if *both* transitions are nonadiabatic is the population exchange reduced.

III. ADIABATIC TRANSFER IN I_NS

A. Unitary bounds on polarization transfer

If the density matrix is initially in a pure state, B, the transfer of this coherence into another state, A (which commutes with B) can be represented

$$B\rightarrow aA+bB+\cdots. \tag{11}$$

The maximum efficiency is, therefore, given by the maximum coefficient of A, $|a|$. The requirement that the square-norm of the density matrix be conserved leads to the so-called entropy or thermodynamic bound on a

$$a_{\max}^{\text{entropy}}=\frac{\|B\|^2}{\|A\|^2}. \tag{12}$$

In NMR experiments, however, the only transformations that can be applied directly to the density matrix are unitary ones. As shown by Sørensen and co-workers,[11–15] this further restricts $a_{\max}$ to

$$a_{\max}^{\text{unitary}}=\frac{\Lambda(A)\cdot\Lambda(B)}{\Lambda(A)\cdot\Lambda(A)}, \tag{13}$$

where $\Lambda(X)$ denotes the vector of the ordered eigenvalues of X.

A unitary transform cannot change the eigenvalues of ρ, and the maximum value of a corresponds to maximising the projection of the eigenvalue vector of A on to the eigenvalue vector of B. Only if the eigenvalues of B match those of A (in which case A and B are related directly by a unitary transform) will the unitary bound equal the entropy bound

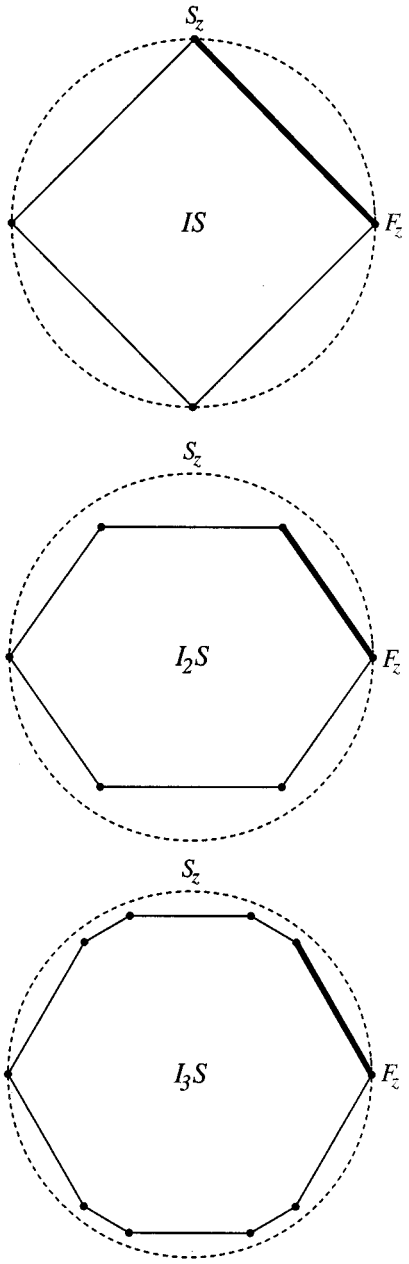

FIG. 3. Unitary bound (area enclosed by solid lines) for the transfer of coherence from F_z to S_z for I_NS, $N=1,2,3$. The vertical axes are scaled by $1/\sqrt{N}$ so that the entropy bound (dashed) line remains circular. The thickened segments correspond to states for which $\langle F_z+S_z\rangle=1$. Only states corresponding to points within the unitary bound can be accessed by a density matrix starting in F_z and subjected to purely unitary transforms.

derived on the basis of the conservation of spin order. The unitary bound can only be circumvented by invoking nonunitary process such as relaxation.[16]

The cross-polarization experiment can be conveniently visualized in terms of the two-dimensional (2D) generalization of the unitary bound,[14] that is, a plot of the accessible values of a and b for a transfer between two states, $B\rightarrow A$. The 2D unitary bounds on the $F_z\rightarrow S_z$ transfer are shown for IS, I_2S and I_3S in Fig. 3, see Ref. 14 for other such diagrams for I_NS_M. These bounds are traced out by swapping eigenvalues of the density matrix so as to maximize the increase in the projection on to S_z for a given decrease in the projection on to the initial state, F_z. For I_NS and $S=1/2$, the eigenvalues of F_z can be ordered

$$(M^{\alpha}_{g(M)},(M-1)^{\alpha}_{g(M-1)},\ldots,(-M+1)^{\alpha}_{g(M-1)},(-M)^{\alpha}_{g(M)},$$
$$M^{\beta}_{g(M)},(M-1)^{\beta}_{g(M-1)},\ldots,(-M+1)^{\beta}_{g(M-1)},(-M)^{\beta}_{g(M)}), \tag{14}$$

where $(m)^{\alpha}_{n}$ denotes an eigenvalue m repeated n times with the superscript indicating the state of the S spin. M is the maximum value of $\langle F_z\rangle$, and $g(m)$ is the degeneracy of the m state of F_z. Note that this applies to I spins of arbitrary spin quantum numbers although, in practice, the strong quadrupolar interactions of spins $I>1/2$ cannot be effectively spin-locked in this frame of reference.

The problem of choosing which eigenvalues should be exchanged can be formulated generally. If **d** and **f** denote the initial and target eigenvalue vector, respectively, and **e** the current state, and using e_n to denote the nth element of **e**, etc., the changes in projection, ΔL, caused by swapping elements m and n are given by

$$\Delta L(\mathbf{d})=\left(d_me_n+d_ne_m+\sum_{i\neq m,n}d_ie_i\right)-\sum_i d_ie_i$$
$$=(d_m-d_n)(e_n-e_m), \tag{15}$$

$$\Delta L(\mathbf{f})=\cdots=(f_m-f_n)(e_n-e_m). \tag{16}$$

Hence, we need to maximize

$$\left|\frac{\Delta L(\mathbf{f})}{\Delta L(\mathbf{d})}\right|=\left|\frac{f_m-f_n}{d_m-d_n}\right| \quad (e_n\neq e_m). \tag{17}$$

In the case of $S=1/2$, $|f_m-f_n|$ can only take the value 1. The smallest nonzero difference of **d** values is also 1 (the spacing of angular momentum levels), hence $|\Delta L(\mathbf{f})/\Delta L(\mathbf{d})|=1$. The 2D bounds thus commence from a state of maximum polarization with a line of unit gradient ($\langle F_z\rangle=1-\langle S_z\rangle$), the thickened segments of Fig. 3. Note that several pairs of states may have the same **f** and **d** eigenvalues; the corresponding segment of the 2D bound is traced out by exchanging all of these pairs.

It is important to note that neither the Hartmann–Hahn matching experiment nor APHH (or related experiments) reach the simple one-dimensional bound on the maximum coefficient of S_z given by Eq. (13). This is a result of the strong spin-lock fields which imply that $\langle S_z\rangle$ and $\langle F_z\rangle$ remain good quantum numbers throughout the experiment, resulting in the conservation of $\langle F_z+S_z\rangle$. This constrains the projection of the density matrix on to the F_z,S_z plane to lie on the line $\langle F_z+S_z\rangle=1$,[17] which coincides with the first segment of the unitary bound derived above. The maximum coefficient of S_z corresponds to the point where shape of the unitary bound diverges from this line, that is the ends of the thickened segments in Fig. 3. For IS and I_2S, the APHH experiment reaches this point, with $\langle S_z\rangle(\tau)=\langle F_z\rangle(0)$ and $\langle S_z\rangle(\tau)=\langle F_z\rangle(0)/2$, respectively. In contrast, the Hartmann–Hahn matching experiment results in a quasiequi-

librium state of the density matrix.[18] This point corresponds to a S spin magnetization of about half that of the adiabatic transfer experiments, cf. Sec. IV.

If $\langle F_z+S_z\rangle$ is not conserved, more complete polarization transfer is possible cf. the optimal sequences developed for I_NS cross polarization in liquids.[11] This limitation can, for instance, be avoided using multiple-quantum transitions, i.e., flipping more than one I spin for each S spin flop.[19] The practicality of such gedanken experiments has yet to be demonstrated, and so the polarization transfers corresponding to the remaining segments of the 2D unitary bound are not considered further. It is also important to note that the ADRF/ARRF experiment is not subject to this limitation and can, potentially, achieve full polarization transfer, within the limit of the unitary bound.[20] This experiment involves adiabatically demagnetizing the I spins in the rotating frame (ADRF), followed by remagnetization of the S spins.[21] The ordering of the eigenstates during the adiabatic passage is, however, strongly dependent on the details of the homonuclear and heteronuclear coupling network and full polarization transfer cannot always be achieved. The reordering of states under the influence of homonuclear couplings is probably a better explanation for the often poor performance of ADRF than the supposition of fast relaxation of the intermediate dipolar order.

It is instructive to examine in general under what conditions an adiabatic sweep can achieve the limit set by the unitary bound. This involves determining the evolution of the density matrix as a result of the APHH experiment. The Hamiltonian is truncated by the strong rf term (F_z+S_z) and so evolution of the density matrix can only occur within blocks of the same total spin quantum number, $\langle F_z+S_z\rangle$, i.e., between $(m-1)^\alpha$ and $(m)^\beta$ states. Each $(m-1)^\alpha-(m)^\beta$ block of the initial density matrix, proportional to F_z, can be represented schematically

$$\begin{pmatrix} m\mathbf{I}_{g(m)} & \mathbf{0} \\ \mathbf{0} & (m-1)\mathbf{I}_{g(m-1)} \end{pmatrix}, \tag{18}$$

where $\mathbf{I}_n$ is an identity matrix of order n.

When the rf is strong and $|\Delta(t)|$ is large, the corresponding portion of the Hamiltonian, Eq. (3), is truncated by H_{rf}, Eq. (5), to

$$\begin{pmatrix} \mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} \end{pmatrix}, \tag{19}$$

where $\mathbf{A}$ and $\mathbf{B}$ consist of diagonal rf terms, $(m-1/2)\omega_I \mp \Delta/2$, and homonuclear coupling terms; the off-diagonal heteronuclear coupling blocks are eliminated by the truncation. The component proportional to the identity, $(m-1/2)\omega_I\mathbf{I}$, although responsible for the truncation, is irrelevant to the evolution of the subsystem and can be dropped, leaving the secular terms $\mp\Delta/2$. The eigenvectors of this block-diagonal matrix fall into two sets: $g(m-1)$ eigenvectors within $\mathbf{A}$, corresponding to α S states, and $g(m)$ β eigenvectors in $\mathbf{B}$.

The evolution of the system can be followed in the eigenbasis which diagonalizes the rf Hamiltonian. This initial density matrix commutes with this transformation and so the evolution of the density matrix can be reduced to the exchange of the diagonal population elements with correspond to the eigenstates of the Hamiltonian. Provided the evolution is adiabatic, i.e., the passage through avoided crossings of the Hamiltonian is sufficiently slow that that no transitions between eigenstates occur, then it is only necessary to determine which eigenstates of the final Hamiltonian correspond to which eigenstates of the initial Hamiltonian.

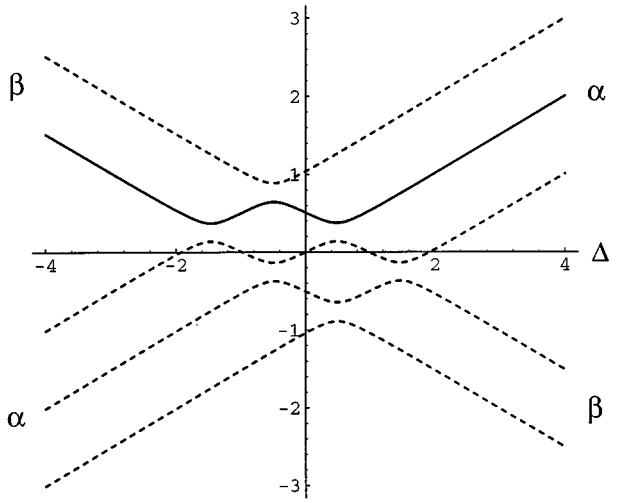

FIG. 4. Eigenvalues of Eq. (21) as a function of Δ for $D=1$, $d=0.2$.

For general rf offsets, Δ, the partially-diagonalized Hamiltonian has the form

$$\begin{pmatrix} \mathbf{B}' & \mathbf{d}' \\ (\mathbf{d}')^\dagger & \mathbf{A}' \end{pmatrix}, \tag{20}$$

where $\mathbf{A}'$ and $\mathbf{B}'$ are the diagonal forms of $\mathbf{A}$ and $\mathbf{B}$, and $\mathbf{d}'$ is the transformed matrix of heteronuclear couplings. Equation (20) is the schematic generalization of Eq. (8). Assuming that the crossings between the α eigenstates and the β eigenstates are avoided, then $g(m)$ α eigenstates will exchange with β eigenstates, leaving $(g(m-1)-g(m))$ β eigenstates localized in the $\mathbf{B}$ submatrix cf. Figs. 2 and 4. In terms of the density matrix, this corresponds to an exchange of the $g(m-1)$ diagonal terms of $\mathbf{A}$ with $g(m-1)$ of the diagonal terms of $\mathbf{B}$. This is equivalent to the exchange of eigenvalues used to find the 2D unitary bound earlier. This density matrix must then be transformed from the eigenbasis of the rf Hamiltonian into the initial frame of reference. This generally results in off-diagonal terms in the final density matrix, but since this similarity transform commutes with S_z, the final S spin polarization, $\mathrm{Tr}(\rho S_z)$, is unaffected. The assumption that $g(m)\leqslant g(m-1)$ is, of course, only valid for $m>0$; analogous arguments apply, however, for $m<0$.

The completeness of this polarization transfer requires that all $g(m)$ α eigenstates cross into β eigenstates. Clearly if there is no coupling pathway between an l spin and the S spin, then no polarization transfer is possible from that spin, and so the number of spins, N, should only include spins with at least one coupling pathway to the S spin. In the large

Δ limit, the plot of the eigenvectors as a function of Δ consists of two sets (α and β) of states corresponding to $\langle S_z \rangle = \pm 1/2$. With the degeneracy of the states lifted by finite homonuclear couplings and in the absence of symmetry (which is discussed in more detail below), each β eigenstate must cross into a state of α character. Even if this state crosses with another β state, it in turn must encounter another α state into which it can cross, since $g(m) \leqslant g(m-1)$. Note that there are $g(m-1)-g(m)$ states which remain α states through the manifold crossing. This is illustrated in Fig. 4 for the eigenvalues of a matrix of the form

$$\begin{pmatrix} -\Delta/2-D/2 & 0 & d & d & d \\ 0 & -\Delta/2+D/2 & d & d & d \\ d & d & \Delta/2-D & 0 & 0 \\ d & d & 0 & \Delta/2 & 0 \\ d & d & 0 & 0 & \Delta/2+D \end{pmatrix}. \tag{21}$$

Note how the eigenstate marked by the solid line connects the α ($\Delta/2$) manifold at $\Delta \rightarrow \infty$ with the β ($-\Delta/2$) manifold at $\Delta \rightarrow -\infty$.

It is possible that small couplings between eigenstates may result in nonadiabatic transfer. As shown earlier for the specific I_2S case, such crossing failures do not, however, preclude full polarization transfer. Only if there are no crossings at all between one of the α states and any of β states is the polarization transfer guaranteed to be incomplete. In practice, crossings will often fall in the intermediate regime where the crossing is not so fast that it is missed entirely (the sudden approximation), nor sufficiently slow to be truly adiabatic. In these cases the α eigenstate polarization may cross into more than one β state. Of course, any α polarization that remains untransferred to β states corresponds to a loss of efficiency but for systems where there are several possible crossings, the adiabaticity of individual crossings may be quite poor without the polarization loss becoming unacceptably high. If polarization is transferred into multiple β states, the final density matrix will no longer be in a pure state of the rf Hamiltonian and will oscillate (Rabi oscillations) between states at frequencies determined by their energy separation. $\mathrm{Tr}(\rho S_z)$, however, is independent of the population distribution of these states at large $|\Delta|$, and this break-down of adiabaticity is only observable as transient oscillations of the plot of $\langle S_z \rangle$ vs time around the crossings (where the eigenstates of the total Hamiltonian are not eigenstates of the rf Hamiltonian). These oscillations are visible in Fig. 1, where the sweep is still sufficiently slow that the overall polarization transfer is complete.

B. Adiabaticity of crossings

For a passage through a crossing of states to be truly adiabatic, two conditions must be fulfilled. The density matrix at the start and end of the passage must be in an eigenstate of the Hamiltonian and the rate of change of the density matrix must be small. These conditions can be conveniently expressed for a crossing of two states in terms of fictitious spin-1/2 operators[22,23] for the two levels involved.[4] The density matrix at time t is proportional to

$$I_z \cos\,\theta(t) + I_x \sin\,\theta(t), \tag{22}$$

where $\theta(t)$ is the angle between the density matrix at time t and I_z,

$$\tan\,\theta(t) = d_i/\Delta_i(t), \tag{23}$$

where Δ_i is the offset of the rf from the ith crossing and d_i is the separation of the states at ith crossing (equal to the coupling between the states).

With the initial density matrix proportional to I_z, adiabatic inversion requires firstly that $\theta_i(0)=0$ and $\theta_i(\tau)=\pi$, corresponding to $\Delta_i(0) = -\Delta_i(\tau) = \infty$, and secondly that

$$Q(t) = \sqrt{\Delta_i(t)^2 + d_i^2} \Big/ \frac{d\theta(t)}{dt} \gg 1, \tag{24}$$

where $Q(t)$ is the adiabaticity factor.[9]

Failure to start the sweep in an eigenstate of the Hamiltonian [i.e., using an initial offset, $\Delta(0)$, that is too small] leads to oscillations which may persist through the transfer. It is noteworthy that these oscillations are most noticeable in IS systems and tend to be suppressed by homonuclear couplings. Since the eigenvalues are continuous, the requirement that the density matrix begins each crossing in an eigenstate is automatically fulfilled provided that the density matrix begins in pure eigenstates of the Hamiltonian and subsequent crossings are close to adiabatic. As seen above, these conditions can be relaxed if, as is invariably the case, we only require adiabaticity of the overall $F_z \rightarrow S_z$ transfer rather than adiabaticity of individual crossings.

Where the crossings in a multilevel system are well-separated or involve independent states, each crossing can be considered separately and the overall adiabaticity can be assumed to be limited by the minimum value of $Q_i(t)$ for any crossing i. Assuming that $\Delta(t)$ is adjusted so that it follows a suitable functional form for each crossing, then $Q_i(t)$ will generally have its minimum value at the crossing point of the states involved. This is certainly true for a matched tangential sweep since $d\theta/dt$ is a constant for this form of $\Delta(t)$.[4] Hence it is usually sufficient to assume that the maximum sweep rate is limited by $|d_i|$, the minimum separation of the states.

Some general conclusions about the separation of eigenstates and hence the adiabaticity of crossings can be drawn in the two limiting cases of $\omega_D \ll \omega_d$ and $\omega_D \gg \omega_d$, where ω_D and ω_d denote the linewidths of the homonuclear and heteronuclear couplings, respectively. When $\omega_D \gg \omega_d$, e.g., Figs. 2(a) and 2(b), then the separation of eigenstates is found by the diagonalization of the α and β blocks of the Hamiltonian. In the notation of Eq. (20), the couplings between the $g(m)$ α and $g(m-1)$ β states given by the $g(m) \times g(m-1)$ matrix $\mathbf{d}'$. Figures 2(a) and 4 illustrate the usual pattern of crossings that result. Symmetry may result in some nonavoided crossings, e.g., Fig. 2(b).

As shown in the Appendix, when $\omega_D \gg \omega_d$ the eigenvalues of the Hamiltonian $m>0$ blocks can be divided into two

sets: a $(g(m-1)-g(m))$ degenerate level of noninteracting α eigenstates and $g(m)$ pairs of eigenvalues given by

$$\gamma_i = \pm\sqrt{\Delta^2/4+\lambda_i^2}, \tag{25}$$

where λ_i are the singular values of the matrix of heteronuclear couplings **d**. These pairs of states all cross at $\Delta=0$ with a separation of $2|\lambda_i|$, cf. Fig. 2(c). Hence the condition that all the α eigenstates cross into β states reduces to whether **d** is of full rank, that is whether rank(**d**)$=g(m)$.

When the hetero- and homonuclear couplings are of similar strengths, the crossings may be strongly overlapped and can no longer be treated as simple two-level systems.

C. Effects of permutation symmetry

Additional symmetry of the Hamiltonian may result in states failing to interact as a result of their belonging to different symmetry representations. It is important to examine whether such further blocking of the Hamiltonian interferes with polarization transfer, especially as some permutation symmetries have been shown to affect the unitary bounds[24] and are relevant to cross-polarization in scalar coupled systems.[3] In the context of solid-state NMR where the dominant dipolar interactions are strongly orientation dependent (in contrast with the scalar J couplings which dominate liquid-state NMR), orientation-independent symmetry of the couplings is relatively unusual. The only common example is inversion symmetry and so equivalence of all spins is only possible in I_2S, which has been considered in some detail already in Sec. II. Fast motion, however, may also render spins equivalent, e.g., freely rotating methyl groups (I_3S) and in liquid crystals where only the projection of the couplings on to the director axis survives the averaging due to rapid motion about this axis.[25]

If each subset of identical spins is transformed into its coupled representation, the Hamiltonian for the complete I_N system can be formed as usual from the direct product of these representations to form a mixed coupled-uncoupled representation in which only identical spins are coupled. For instance, an I_2I_3 system (a five spin-1/2 system made up of one pair and one triplet of identical spins) will contain a block which can be denoted $A(1,2)E(3,4,5)$, i.e., a 2×2 block resulting from the direct product of the $I=0$ block from the coupling of spins 1 and 2, and one of the $I=1/2$ blocks from the coupling of spins 3, 4, and 5. Only transfers between blocks of the same symmetry are permitted.

It is important to note that each symmetry block, such as $A(1,2)E(3,4,5)$, is itself the representation of an angular momentum operator. In particular $g_n(m)\leqslant g_n(m-1)$ $(m>0)$, where m denotes the spin quantum number and n is used to distinguish the blocks. This implies that for each state with quantum number m, within the manifold of degeneracy $g(m)$, there exists a state of the same symmetry within the $m-1$ manifold. This is significant since this is exactly the condition required for complete polarization transfer between two levels connected by the heteronuclear dipolar interaction. Only if a level is isolated, that is $g_n(m)>0$ and $g_n(m-1)=0$, can the polarization of m level be completely prevented from exchanging with that of the $m-1$ level. This is consistent with previously published results[24] which showed that magnetic equivalence of the I spins did not affect the 2D unitary bound for I_2S. In contrast, permutation symmetry of all the spins did change the shape of the 2D bound, for instance for an I_3 system in which polarization was being transferred from one I spin to the two other identical spins. This is not relevant, however, for heteronuclear CP.

The problem simplifies if all the I spins are identical.[2,3] In this case, the states in the coupled basis can be simply labelled $|L,M,\alpha\rangle$ ($|L,M,\beta\rangle$ for the corresponding βS state), where L and M are the quantum numbers for the coupled states. There is no mixing between states of different symmetry (including those with identical L values), and so cross polarization is reduced to population inversion between all the pairs of states $|L,M-1,\alpha\rangle$, $|L,M,\beta\rangle$. The effective heteronuclear coupling between these states is scaled by a factor of $\sqrt{L(L+1)-M(M-1)}$ relative to the coupling between S and the individual I nuclei.

D. APHH under MAS

Since (high-speed) sample spinning does not significantly change the nature of the APHH transfer, the generalisation of the theory of APHH for cross polarization of IS under MAS[5] need only be presented in outline. The central portion of the Floquet Hamiltonian[26–28] corresponding to Eq. (3) for an I_NS system can be written schematically as

$$\begin{array}{c} \\ \langle\beta 1| \\ \langle\alpha 1| \\ \langle\beta 0| \\ \langle\alpha 0| \\ \langle\beta -1| \\ \langle\alpha -1| \end{array} \begin{array}{c} \ddots \quad |\beta 1\rangle \qquad |\alpha 1\rangle \qquad |\beta 0\rangle \qquad |\alpha 0\rangle \qquad |\beta -1\rangle \qquad |\alpha -1\rangle \\ \left(\begin{array}{cccccc} \mathbf{Z}_\beta+\mathbf{D}_0+\omega_R & \mathbf{d}_0 & \mathbf{D}_1 & \mathbf{d}_1 & \mathbf{D}_2 & \mathbf{d}_2 \\ \mathbf{d}_0 & \mathbf{Z}_\alpha+\mathbf{D}_0+\omega_R & \mathbf{d}_1 & \mathbf{D}_1 & \mathbf{d}_2 & \mathbf{D}_2 \\ \mathbf{D}_{-1} & \mathbf{d}_{-1} & \mathbf{Z}_\beta+\mathbf{D}_0 & \mathbf{d}_0 & \mathbf{D}_1 & \mathbf{d}_1 \\ \mathbf{d}_{-1} & \mathbf{D}_{-1} & \mathbf{d}_0 & \mathbf{Z}_\alpha+\mathbf{D}_0 & \mathbf{d}_1 & \mathbf{D}_1 \\ \mathbf{D}_{-2} & \mathbf{d}_{-2} & \mathbf{D}_{-1} & \mathbf{d}_{-1} & \mathbf{Z}_\beta+\mathbf{D}_0-\omega_R & \mathbf{d}_0 \\ \mathbf{d}_{-2} & \mathbf{D}_{-2} & \mathbf{d}_{-1} & \mathbf{D}_{-1} & \mathbf{d}_0 & \mathbf{Z}_\alpha+\mathbf{D}_0-\omega_R \end{array}\right) \\ \ddots \end{array}, \tag{26}$$

where $\mathbf{Z}$ (labelled by S spin state) is used to represent the rf terms, ω_R is the rotation frequency, and $\mathbf{d}_n$ and $\mathbf{D}_n$ are matrices corresponding to the nth Fourier components of the hetero- and homonuclear couplings, respectively. Under the conditions of fast spinning at the magic angle, i.e., $\omega_R, \|\mathbf{Z}\| \gg \|\mathbf{d}_i\|, \|\mathbf{D}_i\|$, the Floquet matrix diagonalizes into blocks with similar diagonal terms (the secular approximation). For arbitrary values of ω_I, ω_S and ω_R, these blocks correspond to the individual $\mathbf{Z}$ submatrices and no polarization transfer is possible. At various resonance conditions, however, these blocks may be connected via the $\mathbf{d}_n$ or $\mathbf{D}_n$ matrices. In general, these resonances occur at

$$\Delta_I \omega_I + \Delta_S \omega_S + \Delta_N \omega_R = 0, \tag{27}$$

where Δ_I, Δ_S, and Δ_N are the differences in F_z eigenvalue, S_z eigenvalue and N eigenvalue for any pair of $\mathbf{Z}$ diagonal terms. Note that resonance phenomena can occur when ω_R and ω_I (and ω_S) are rational multiples of each other. This effect has been used to allow double-quantum transitions in experiments to restore the dipolar interaction under MAS[29] and similar effects have recently been observed in the spin-locking of quadrupolar nuclei,[30] but this complication need not be considered further.

The heteronuclear dipolar interaction is a flip–flop interaction, corresponding to $\Delta I = -\Delta S = \pm 1$, with Fourier components at $\Delta N = 0, \pm 1, \pm 2$ and so the resonance condition is simply

$$\omega_S = \omega_I + k\omega_R \quad k = 0, \pm 1, \pm 2. \tag{28}$$

Under these conditions, and assuming fast spinning (which also disallows the $k=0$ condition for magic angle spinning), the Floquet matrix reduces to blocks of the form

$$\begin{pmatrix} \mathbf{Z}_\beta + \mathbf{D}_0 & \mathbf{d}_k \\ \mathbf{d}_{-k} & \mathbf{Z}_\alpha + \mathbf{D}_0 \end{pmatrix} + \begin{pmatrix} n\omega_R & 0 \\ 0 & n\omega_R \end{pmatrix}. \tag{29}$$

The resulting Hamiltonian is identical in form to the static Hamiltonian, cf. Eq. (20), and so the dynamics are identical,[5] with the effective coupling constants being scaled by the appropriate second-order reduced Wigner rotation matrix element $d^{(2)}_{k0}$. More significantly, the homonuclear coupling vanishes, since $d^{(2)}_{00}$ and hence $\mathbf{D}_0$ vanishes at the magic angle. This implies that, to this order of approximation, the degree of spin order transfer cannot be improved by exploiting homonuclear interactions to otherwise uncoupled spins.

IV. EFFICIENCY OF APHH VS HARTMANN–HAHN MATCHING

Under Hartmann–Hahn matching, a quasiequilibrium state is reached which corresponds to an equilibration of the populations of matching α and β manifolds[18,31] before spin-lattice relaxation returns the spin system to full equilibrium. It is useful to calculate the projection on to S_z of this state and compare it to the limit from the APHH experiment.

Consider population exchange between two manifolds with the same eigenvalue of $F_z + S_z$, e.g., the $|1/2,\alpha\rangle$ and $|3/2,\beta\rangle$ levels in I_3S. The initial diagonal of the appropriate subblock of the density matrix (proportional to F_z), can be represented

$$1/2,\ 1/2,\ 1/2,\quad 3/2. \tag{30}$$

After APHH, the $|3/2,\beta\rangle$ population has exchanged with that of one of the $|1/2,\alpha\rangle$ states, e.g.,

$$1/2,\ 3/2,\ 1/2,\quad 1/2. \tag{31}$$

The final population of the $|m,\alpha\rangle$ level is given by

$$\begin{aligned} P^m_\alpha &= g(m+1)(m+1) + [g(m) - g(m+1)]m \\ &= g(m+1) + g(m)m. \end{aligned} \tag{32}$$

In general, the final total populations of the m level are given by

$$P^m_a = \begin{cases} g(m)m + g(m+1) & m \geqslant 0, \\ g(m)(m+1) & m < 0 \end{cases} \tag{33}$$

$$P^m_\beta = \begin{cases} g(m)(m-1) & m \geqslant 0, \\ g(m)m - g(m-1) & m < 0. \end{cases} \tag{34}$$

Note that $g(m) = 0$ for values of m outside the range of F_z eigenvalues $(M, \ldots, -M)$ and the sign of m is significant since it affects the relative values of $g(m)$ and $g(m+1)$.

Hence the projection on to S_z is given by

$$\langle S_z \rangle_{\mathrm{APHH}} = \frac{1}{2} \sum_m P^m_\alpha - P^m_\beta \tag{35}$$

$$= \mathscr{N} - \begin{cases} g(1/2) & 2M \text{ odd}, \\ g(0) & 2M \text{ even}, \end{cases} \tag{36}$$

where $\mathscr{N} = \Sigma^M_{-M} g(m)$ is the total number of states in the I spin-system (2^N for $I = 1/2$).

The Hartmann–Hahn match is slightly different, since the populations are equilibrated rather than completely exchanged (implying that the maximum efficiency of a Hartmann–Han matching is always smaller than the maximum efficiency of the APHH experiment). Unlike the APHH case where I spin symmetry has no effect on the degree of polarization transfer, symmetry operations which further block-diagonalize the $F_z + S_z$ blocks will slightly modify the final degree of polarization transfer. It is worth noting that symmetry operations which reduce the number of states in $|m,\beta\rangle$ with which $|m-1,\alpha\rangle$ can equilibrate ($m > 0$) will reduce the extent of polarization transfer between β and α S_z states. Indeed, the quasiequilibrium state has a complex dependence on the details of the coupling network.[18] For simplicity, however, we will ignore the effects of homonuclear and heteronuclear coupling and assume complete equilibration[31] between all $g(m-1)$ states of $|m,\alpha\rangle$ and the $g(m)$ states of $|m,\alpha\rangle$.

For the levels of Eq. (30), the final population distribution will be

$$3/4,\ 3/4,\ 3/4,\quad 3/4 \tag{37}$$

and in general

$$\frac{P_{\alpha}^{m-1}}{g(m-1)}=\frac{P_{\beta}^{m}}{g(m)}=\frac{g(m-1)(m-1)+g(m)m}{g(m-1)+g(m)}$$

$$=m-1+\frac{g(m)}{g(m-1)+g(m)}. \tag{38}$$

Note how each $|m-1,\alpha\rangle$, $|m,\beta\rangle$ pair effectively has its own spin temperature which depends on the degeneracies of the levels involved. Semiclassical calculations based on spin thermodynamics are clearly inappropriate for such small spin systems.

The quasiequilibrium S_z polarization is then

$$\langle S_z\rangle_{\mathrm{HH}}=\frac{1}{2}\sum_{m=-M}^{M} g(m)\left(1+\frac{g(m+1)}{g(m)+g(m+1)}-\frac{g(m)}{g(m-1)+g(m)}\right). \tag{39}$$

In the limit of a large number of spins, $g(m-1)\approx g(m)\approx g(m+1)$ and the fractional terms of Eq. (39) will cancel (i.e., a common spin temperature becomes a good approximation). Hence, the ratio of Eqs. (36) and (39) gives

$$\lim_{M\to\infty}\frac{\langle S_z\rangle_{\mathrm{HH}}}{\langle S_z\rangle_{\mathrm{APHH}}}=\frac{1}{2}. \tag{40}$$

V. SUMMARY

The theory of cross polarization via adiabatic sweeps through the Hartmann–Hahn matching condition (APHH) has been extended to cover I_NS systems, including the effects of homonuclear coupling between the I spins. In general terms, the presence of homonuclear coupling increases the range of the offset from match over which the rf must be swept to maintain adiabaticity and ensure maximum polarization transfer. For example, in I_2S systems in which the homonuclear coupling is larger than the heteronuclear coupling, the polarization transfer occurs in two distinct steps. This broadening of match condition (which must be carefully distinguished from inhomogeneous effects such as spatial variations of the match condition) might seem entirely unwelcome. If, however, not all the I spins are directly coupled to the S spin, homonuclear couplings which connect otherwise isolated spins to I spins which are coupled to S may permit greater polarization transfer. A useful compromise in such systems might be to scale the linewidth of the homonuclear coupling to within that of the heteronuclear coupling, e.g., using off-resonance decoupling.[32] Experimental attempts to observe APHH in the presence of extensive homonuclear coupling have been unsuccessful.[5] It is unclear, however, whether this is a fundamental problem or a failure to maintain a strong spin-lock over the wide offset range required for an adiabatic transfer. In fast MAS experiments, the homonuclear coupling is eliminated to first order and it is unlikely that the residual homonuclear coupling could noticeably improve the degree of polarization transfer. Quantitative studies of the efficiency of adiabatic passage experiments under MAS are underway in other laboratories.

For experiments where F_z+S_z is a constant of the motion, APHH allows the maximum possible transfer of I to S magnetization in I_NS systems. This is true for both static and spinning samples, for systems where symmetry considerations restrict which states can interact, and even in cases where the adiabaticity conditions are not strictly maintained. Of course, this only represents a maximum efficiency and does not guarantees that this efficiency can be achieved, nor even that different techniques will not perform better in practice than APHH. Analysis of cross polarization in terms of unitary bounds does, however, provide a target for experimental practice to strive for.

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APPENDIX

When the homonuclear couplings are negligibly small in comparison with the heteronuclear couplings, the F_z+S_z blocks of the Hamiltonian can be approximated by

$$\begin{pmatrix} -\Delta/2\,\mathbf{I}_{g(m)} & \mathbf{d} \\ \mathbf{d}^{\dagger} & \Delta/2\,\mathbf{I}_{g(m-1)} \end{pmatrix}, \tag{A1}$$

where $\mathbf{d}$ is the matrix of heteronuclear couplings and $\mathbf{I}_n$ an identity matrix of order n.

This matrix can be factored using the singular value decomposition[33] of $\mathbf{d}$, that is,

$$\mathbf{d}=\mathbf{V}^{\dagger}\mathbf{\Lambda}\mathbf{U}, \tag{A2}$$

where $\mathbf{V}$ and $\mathbf{U}$ are unitary matrices of order $g(m)$ and $g(m-1)$, respectively, and $\mathbf{\Lambda}$ is the $g(m)\times g(m-1)$ matrix containing the $g(m)$ singular values of $\mathbf{d}$, λ_i,

$$\mathbf{\Lambda}=\begin{pmatrix} \lambda_1 & 0 & \cdots & 0 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & 0 & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_{g(m)} & 0 & \cdots & 0 \end{pmatrix} \quad (m>0). \tag{A3}$$

Equation (A1) can then be written

$$\begin{pmatrix} -\Delta/2\,\mathbf{I}_{g(m)} & \mathbf{d} \\ \mathbf{d}^{\dagger} & \Delta/2\,\mathbf{I}_{g(m-1)} \end{pmatrix} = \begin{pmatrix} \mathbf{V}^{\dagger} & 0 \\ 0 & \mathbf{U}^{\dagger} \end{pmatrix}\begin{pmatrix} -\Delta/2\,\mathbf{I}_{g(m)} & \mathbf{\Lambda} \\ \mathbf{\Lambda}^{\dagger} & \Delta/2\,\mathbf{I}_{g(m-1)} \end{pmatrix}\begin{pmatrix} \mathbf{V} & 0 \\ 0 & \mathbf{U} \end{pmatrix} = \mathbf{X}^{\dagger}\mathbf{Y}\mathbf{X}. \tag{A4}$$

The eigenvalues of Eq. (A1) can then be found by diagonalizing matrix $\mathbf{Y}$. $\mathbf{Y}$ separates into a diagonal matrix $\Delta/2\,\mathbf{I}_{g(m-1)-g(m)}$, the eigenstates of which form a $g(m-1)-g(m)$ degenerate level of noninteracting β eigenstates and $g(m)$ 2×2 matrices of the form

$$\begin{pmatrix} -\Delta/2 & \lambda_i \\ \lambda_i & \Delta/2 \end{pmatrix} \tag{A5}$$

with eigenvalues

$$\gamma_i = \pm\sqrt{\Delta^2/4+\lambda_i^2}. \tag{A6}$$

The eigenvalues of Eq. (A1) can be expressed more simply if $g(m)=1$ $(m>0)$. The eigenvalues, γ, are given by the solution of

$$\begin{vmatrix} -\Delta/2-\gamma & d_1/2 & \cdots & d_{g(m-1)}/2 \\ d_1/2 & \Delta/2-\gamma & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ d_{g(m-1)}/2 & 0 & \cdots & \Delta/2-\gamma \end{vmatrix} = 0 \tag{A7}$$

and so

$$\gamma = \pm\sqrt{\Delta^2/4+\sum_j d_j^2/4} \tag{A8}$$

plus $g(m-1)-1$ repeated roots, $\gamma=\Delta/2$. This corresponds to a single avoided crossing with an effective coupling given by

$$d_{\mathrm{eff}}^2 = \sum_j^{g(m-1)} d_j^2. \tag{A9}$$

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