

Composite pulses in nuclear quadrupole resonance

By S. Z. AGEEV, D. J. ISBISTER† and B. C. SANCTUARY
Department of Chemistry, McGill University, Montreal, Quebec,
Canada H3A 2K6

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It is shown in this paper that composite pulses optimized for NMR situations can be used also for NQR experiments. Specifically identical composite pulses can be used in both cases and are most effective for single crystal NQR experiments. A number of composite pulses used for NMR are calculated exactly for the NQR case and shown to be as good as or better than existing pulses designed exclusively for NQR.

1. Introduction

A composite pulse is a sequence of closely spaced radiofrequency (RF) pulses of rectangular shape which are phase shifted with no time evolution between pulse elements in the sequence. Composite pulses have been studied extensively for the nuclear magnetic resonance (NMR) case and have found numerous applications [1]. Composite pulses are rather insensitive to offset π pulses and $\pi/2$ pulses for relatively simple examples. In particular, composite pulses are useful for nonlinear situations where the intensity of RF fields differs from one region to another (RF inhomogeneity) and where it is necessary to excite spins over a range of chemical shifts (resonance offset). A variety of methods have been developed to produce composite pulse sequences. These include the Magnus expansion [1–3], similarity transformations [4], recursive expansions [1, 5, 6], and the multipole approach [7, 8].

Recently, several reports on nuclear quadrupole resonance (NQR) pulses have appeared in the literature [9–11]. Pure NQR of solids is characterized by broad lines of the order of a few kilohertz due to various internal interactions such as electric field inhomogeneity and dipole–dipole interactions present in the system, which create multiple spectral lines. These interactions are not averaged as in the NMR case, and thus the spin–spin relaxation time T_2 and spin–lattice relaxation time T_1 are much shorter than those in NMR cases. Consequently, long pulse sequences are not desirable for NQR. A single short RF pulse, however, does not excite the broad NQR spectra uniformly. It is possible to overcome this problem by increasing the RF power, but this, in turn, can cause difficulties in practice. In addition, the response to a single RF pulse is sensitive to RF inhomogeneity. These problems can be resolved partially by using composite pulses of short durations. Up to date the design of composite pulses for NQR has relied heavily on the Magnus expansion. This approach offers both advantages and disadvantages. First, composite pulses can be constructed regardless of the initial conditions of the density matrix. On the other

† Permanent address: Department of Physics, University of NSW, University College, ADFA, Canberra, ACT 2600, Australia.

hand, the Magnus expansion converges slowly and the extension of the range of compensation is difficult without increasing the length of the sequence [11]. In addition, a separate numerical optimization of pulse lengths and phases must be performed if pulses have rotation angles different from 90° and 180° . Ramamoorthy's approach to the design of NQR composite pulses is based on the Magnus approximation. One of the major results of our approach is to recognize that NQR composite pulses for half integer spins basically reduce to the study of spins of $1/2$. As such we can use composite pulses derived for NMR. We find, in fact, that such composite pulses work very well for NQR crystal studies, but less well for powders.

In actual calculation of NQR composite pulses, Ramamoorthy *et al.* [10] essentially use spin $1/2$ operators. Our approach is to recognize that a pulse in NQR is selective, being between two pairs of levels. These are treated as rotations, since selective excitation between neighbouring pairs of levels has zero effective quadrupole while the pulse is applied [12, 13]. In addition, we are able to solve much of this problem by the use of matrix computer algebra, particularly the program Maple. This allows us easily to diagonalize the quadrupole Hamiltonian when $\eta \neq 0$ and to calculate the Baker–Campbell–Hausdorff (BCH) formula analytically for integer and half integer spins.

In this paper it is shown that NMR composite pulses are directly applicable to the pure NQR problem for half integer spins in the case of single crystals. The effects of composite pulses of short durations are obtained using a multipole approach in NMR [8] and applied to the NQR case. Powders are also considered.

2. Single pulses

The pure quadrupole Hamiltonian for spin I in the quadrupole principal axis system (QPAS) is given by

$$H_Q = \frac{\hbar e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2) \right], \quad (1)$$

where $e^2 q Q$ is the nuclear quadrupole coupling constant and η is the asymmetry parameter. Much interest has centred on the evolution of the density matrix $\sigma_1(t)$ as it responds to a pulse sequence of 1, 2 or 3 pulses applied to a system of isolated spins I . These spins are initially prepared at thermal equilibrium as characterized by temperature T at time $t = 0$. The equilibrium density matrix can be expressed in the high temperature limit as

$$\sigma_1(0) = \frac{1}{(2I+1)} [E_I - \beta \mathbf{H}_Q], \quad (2)$$

where $\beta = 1/kT$ is the Boltzmann factor and E_I is the $(2I+1) \times (2I+1)$ identity matrix. We shall illustrate our analysis for $\sigma_1(t)$ with a simple $I = 3/2$ example, using it to detail the various steps in our approach which can be then followed for other half integer spin values. The equilibrium density matrix $\sigma_{3/2}(0)$ for spin $3/2$ can be

expressed in the customary $|IM\rangle$ basis in the following matrix form

$$\sigma_{3/2}(0) = \frac{1}{4}(E_{3/2} - \beta H_Q) = \frac{1}{4} \left\{ E_{3/2} - \frac{\beta \hbar e^2 q Q}{4} \begin{pmatrix} 1 & 0 & \frac{\eta}{\sqrt{3}} & 0 \\ 0 & -1 & 0 & \frac{\eta}{\sqrt{3}} \\ \frac{\eta}{\sqrt{3}} & 0 & -1 & 0 \\ 0 & \frac{\eta}{\sqrt{3}} & 0 & 1 \end{pmatrix} \right\}. \quad (3)$$

The quadrupolar Hamiltonian of equation (3) can be diagonalized by means of the unitary transformation defined by S where

$$S = \begin{pmatrix} \cos \theta & 0 & \sin \theta & 0 \\ 0 & \cos \theta & 0 & -\sin \theta \\ -\sin \theta & 0 & \cos \theta & 0 \\ 0 & \sin \theta & 0 & \cos \theta \end{pmatrix} \quad (4)$$

and $\tan 2\theta = \eta/\sqrt{3}$.

In this new basis $|\Psi\rangle$, $|\Psi\rangle = S^{\dagger}|IM\rangle$, the equilibrium density matrix is

$$\sigma_{3/2}^{\Psi}(0) = \frac{1}{4}\{E_{3/2} - \beta H_Q^{\Psi}\}, \quad (5)$$

where

$$H_Q^{\Psi} = \frac{\hbar\omega_Q}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

is used and

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

The basis vectors in the $|\Psi\rangle$ basis are $|+3/2\rangle$, $|+1/2\rangle$, $|-1/2\rangle$ and $|-3/2\rangle$. If a RF pulse is applied along the x axis of the QPAS, the RF Hamiltonian in the $|IM\rangle$ basis is customarily written as

$$H_{\text{RF}} = -2\hbar\omega_1 \cos(\omega t - \phi) I_x, \quad (6)$$

where ω_1 is the RF amplitude, ω is the carrier frequency and ϕ is the arbitrary phase associated with the RF pulse. In the $|\Psi\rangle$ basis, H_{RF} can be written in matrix form as

$$H_{\text{RF}}^{\Psi} = -\hbar\omega_1 \cos(\omega t - \phi) \begin{pmatrix} 0 & A & 0 & B \\ A & 0 & C & 0 \\ 0 & C & 0 & A \\ B & 0 & A & 0 \end{pmatrix}, \quad (7)$$

where

$$A = \frac{\sqrt{3 + \frac{\eta}{\sqrt{3}}}}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}$$

$$B = 1 + \frac{\eta - 1}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}$$

$$C = 1 + \frac{1 - \eta}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}.$$

Following Pratt [14], the interaction picture of the evolving density matrix allows significant simplification enabling one to follow the von Neumann equation in this frame. This is achieved by the transformation operator Π defined as

$$\Pi = \exp\left(-\frac{iH_Q^\Psi}{\hbar\omega_Q} \omega t\right). \quad (8)$$

Transforming H_{RF}^Ψ of equation (7) into the interaction picture and omitting high frequency terms [14], lengthy but straightforward algebra leads to a dramatic simplification of the radiofrequency Hamiltonian H_{RF}^Ψ in which only the RF phase variable ϕ plays a leading role,

$$\tilde{H}_{\text{RF}}^\Psi = -\frac{\hbar\omega_1 A}{2} \begin{pmatrix} 0 & e^{-i\phi} & 0 & 0 \\ e^{i\phi} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{i\phi} \\ 0 & 0 & e^{-i\phi} & 0 \end{pmatrix}. \quad (9)$$

The total Hamiltonian containing the quadrupole interaction of equation (3) and RF field of equation (6) can therefore be written in the interaction representation as

$$\tilde{H} = \tilde{H}_1 + \tilde{H}_2 = \begin{pmatrix} h_1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & h_2 \end{pmatrix}, \quad (10)$$

where the block matrices h_1 and h_2 consist of off-resonant constant terms $(\omega_Q - \omega)$ and elements depending on only the RF pulse characteristics $(\omega_1, \phi$ and $\eta)$, viz:

$$h_1 = \frac{\hbar(\omega_Q - \omega)}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\hbar\omega_1}{2} \frac{3 + \eta}{(3 + \eta^2)^{1/2}} \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix}$$

$$h_2 = -\frac{\hbar(\omega_Q - \omega)}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\hbar\omega_1}{2} \frac{3 + \eta}{(3 + \eta^2)^{1/2}} \begin{pmatrix} 0 & e^{i\phi} \\ e^{-i\phi} & 0 \end{pmatrix}.$$

In the interaction representation the equilibrium density matrix at $t = 0$ can be decomposed similarly into 2×2 block form as

$$\sigma_{3/2}^\Psi(0) = \frac{1}{4} \left\{ E_{3/2} - \frac{\beta\hbar\omega_Q}{2} \rho(0) \right\}, \quad (11)$$

where

$$\rho(0) = \rho_1(0) + \rho_2(0) = \begin{pmatrix} \tilde{\rho}_1(0) & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \tilde{\rho}_2(0) \end{pmatrix}$$

and

$$\tilde{\rho}_1(0) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tilde{\rho}_2(0) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Note that the Hamiltonians \tilde{H}_1 and \tilde{H}_2 of equation (10) and the density matrices $\tilde{\rho}_1(0)$ and $\tilde{\rho}_2(0)$ commute.

The evolution of the system under the Hamiltonian \tilde{H}_Q^Ψ in the interaction representation is given by the density matrix

$$\tilde{\sigma}_{3/2}^\Psi(t) = \frac{1}{4} \left\{ E_{3/2} - \frac{\beta \hbar \omega_Q}{2} \begin{pmatrix} \tilde{\rho}_1(t) & 0 \\ 0 & \tilde{\rho}_2(t) \end{pmatrix} \right\}, \quad (12)$$

where

$$\tilde{\rho}_1(t) = \exp(-ih_1 t/\hbar) \tilde{\rho}_1(0) \exp(ih_1 t/\hbar)$$

$$\tilde{\rho}_2(t) = \exp(-ih_2 t/\hbar) \tilde{\rho}_2(0) \exp(ih_2 t/\hbar).$$

Note that h_1 and h_2 are SU(2) Hamiltonians for the elementary spin 1/2 problem. Under a single RF pulse applied along the x axis of the QPAS, the $|1/2\rangle \rightarrow |3/2\rangle$ and $|-1/2\rangle \rightarrow |-3/2\rangle$ transitions are uncoupled and independent. The only approximation used so far involves the omission of the nonsecular terms in H_{RF}^Ψ of equation (9) which, if retained, would lead to Bloch–Siegert order corrections [15]. Equations (10–12) can be interpreted as follows. The transition $|1/2\rangle \rightarrow |3/2\rangle$ is caused by the Hamiltonian h_1 with $|-1/2\rangle \rightarrow |-3/2\rangle$ being caused by the Hamiltonian h_2 . This means the applied RF field is effectively decomposed into two components rotating in opposite senses [16]. The transformation into the quadrupole interaction picture shows that h_1 and h_2 arise from the rotating and counter-rotating components of the applied RF field respectively. In contrast to the treatment of the counter-rotating field in ordinary NMR (where it is dropped in theoretical calculations) both rotating and counter-rotating components are significant in NQR. The transformation to the quadrupole interaction picture in NQR is similar to the rotating frame transformation in NMR.

The propagators $\exp(-ih_1 t/\hbar)$ and $\exp(-ih_2 t/\hbar)$ can be written in terms of the rotational operators [17] $\mathcal{D}(\alpha, \beta, \gamma)$,

$$\begin{aligned} \exp(-ih_1 t/\hbar) &= \mathcal{D}(\alpha^+ + \phi, \beta, \alpha^+ - \phi + \pi) \\ \exp(-ih_2 t/\hbar) &= \mathcal{D}(\alpha^- - \phi, \beta, \alpha^- + \phi + \pi), \end{aligned} \quad (13)$$

where $(\alpha^\pm \pm \phi, \beta, \alpha^\pm \mp \phi + \pi)$ are the Euler angles. These Euler angles are found to be [15]

$$\left. \begin{aligned}
 \alpha^\pm &= \mp \tan^{-1} \left(\frac{\Delta\omega}{\Omega} \tan \left(\frac{\Omega t}{2} \right) \right) - \frac{\pi}{2} \\
 \cos \beta &= \frac{1}{\Omega^2} (\omega_{1\text{eff}}^2 \cos(\Omega t) + \Delta\omega^2) \\
 \Omega &= (\Delta\omega^2 + \omega_{1\text{eff}}^2)^{1/2} \\
 \Delta\omega &= \omega_Q - \omega \\
 \omega_{1\text{eff}} &= \frac{3 + \eta}{(3 + \eta^2)^{1/2}} \omega_1.
 \end{aligned} \right\} \quad (14)$$

Consider the application of a single RF pulse of duration t_1 on an isolated spin 3/2 system. Using the properties of Wigner rotation matrices \mathcal{D} of equation (14) it can be shown that the density matrices are

$$\left. \begin{aligned}
 \tilde{\rho}_1(t_1) &= \left(\begin{array}{cc} \cos \beta_1 & -\sin \beta_1 \exp[-i(\alpha^+ - \phi)] \\ -\sin \beta_1 \exp[i(\alpha^+ - \phi)] & -\cos \beta_1 \end{array} \right) \\
 \text{and} \\
 \tilde{\rho}_2(t_1) &= \left(\begin{array}{cc} -\cos \beta_1 & -\sin \beta_1 \exp[i(\alpha^+ - \phi)] \\ -\sin \beta_1 \exp[-i(\alpha^+ - \phi)] & \cos \beta_1 \end{array} \right)
 \end{aligned} \right\} \quad (15)$$

in the quadrupolar interaction frame. To find the free induction decay we define two magnetization components I_{x0}^Ψ , which is 'in phase', and, I_{x90}^Ψ 'out-of-phase' with the RF field:

$$\left. \begin{aligned}
 I_{x0}^\Psi &= I_x^\Psi \cos(\omega t) \\
 I_{x90}^\Psi &= I_x^\Psi \sin(\omega t).
 \end{aligned} \right\} \quad (16)$$

Transforming equation (16) to the interaction picture and truncating high frequency terms as was done in the derivation of equation (9) leads to

$$\tilde{I}_{x90}^\Psi = \frac{A}{4} i \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \quad \tilde{I}_{x0}^\Psi = \frac{A}{4} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \quad (17)$$

The response of the system in the interaction picture is then defined by averaged 'in phase' and 'out-of-phase' quantities W_1 and W_2 , respectively, where

$$\begin{aligned}
 W_1 &= \text{tr} \{ \tilde{I}_{x0}^\Psi \tilde{\sigma}_{3/2}^\Psi(t) \}, \\
 W_2 &= \text{tr} \{ \tilde{I}_{x90}^\Psi \tilde{\sigma}_{3/2}^\Psi(t) \}
 \end{aligned}$$

and $\text{tr} \{ \dots \}$ indicates the trace of the quantity in $\{ \dots \}$ brackets is to be taken. Using equations (12, 15, 17), W_1 and W_2 can be found for a single RF pulse as

$$\begin{aligned}
 W_1 &= -\sin \beta \cos(\alpha^+ - \phi) \\
 W_2 &= 0,
 \end{aligned}$$

where units of $-\beta\hbar\omega_Q A/8$ are used. It should be emphasized that NQR spectrometers are sensitive to actually measuring the responses W_1 and W_2 of the quadrupolar spin system in the interaction picture.

3. Composite pulses

We now are in a position to solve the problem for the application of composite pulses in NQR. To achieve this goal the \mathcal{D} 's in equation (13) are replaced by products of \mathcal{D} 's, whose arguments are defined by the new values of α^\pm , β and $\omega_{1\text{eff}}$ of equation (14) associated with each new pulse. In general $\tilde{\rho}_1(t)$ and $\tilde{\rho}_2(t)$ in equation (12) for any number of pulses are

$$\begin{aligned}\tilde{\rho}_1(t) &= \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{12}^* & -\sigma_{11} \end{pmatrix} \\ \tilde{\rho}_2(t) &= \begin{pmatrix} -\sigma_{11} & \sigma_{12}^* \\ \sigma_{12} & \sigma_{11} \end{pmatrix}.\end{aligned}\tag{18}$$

Then the response of the system, as measured by W_1 above, is

$$W_1 = \frac{1}{2}(\sigma_{12} + \sigma_{12}^*).$$

For example, for a two pulse experiment we have

$$\begin{aligned}W_1 &= \frac{1}{2}\{-2 \cos \beta_1 \sin \beta_2 \cos(\alpha_2^+ - \phi_2) - \sin \beta_1(1 - \cos \beta_2) \cos(\alpha_1^+ + 2\phi_2 - \phi_1)\} \\ &\quad + \frac{1}{2} \sin \beta_1(1 + \cos \beta_2) \cos(\alpha_1^+ + 2\alpha_2^+ - \phi_1).\end{aligned}$$

The response of the system is clearly analogous to that in the NMR spin 1/2 case evolving under the Hamiltonian h_1 or h_2 [8]. An important difference between the NMR and NQR cases is seen in the vanishing of $\langle I_z \rangle$ for the NQR case,

$$\text{tr}\{\tilde{I}_z^\Psi \tilde{\sigma}_{3/2}^\Psi(t)\} = 0,$$

whereas the NMR counterpart is non-zero. Thus we need a different definition for the inversion pulses to contrast with the NMR case: this is provided by the energy

$$W_3 = \text{tr}\{H_Q^\Psi \tilde{\sigma}_{3/2}^\Psi(t)\}$$

which, according to equation (18), is simply

$$W_3 = \sigma_{11}$$

in units of $-\beta(\hbar\omega_Q)^2/4$. This definition of the inversion pulse is chosen so that the NQR result agrees with that of the corresponding spin 1/2 system.

4. Powder averages

In powders, crystals are randomly oriented. Assuming that the RF coil is oriented in the QPAS system as shown in figure 1 the RF Hamiltonian for the crystal is

$$H_{\text{RF}} = -2\hbar\omega_1 \cos(\omega t - \phi)(\cos \phi_L \sin \theta_L I_x + \sin \phi_L \sin \theta_L I_y + \cos \theta_L I_z).\tag{19}$$

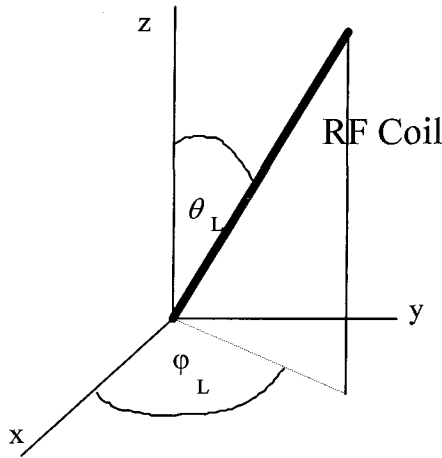


Figure 1. The orientation of the RF field with respect to the QPAS system of the crystal in the powder sample.

In the frame defined by the operator S in equation (4), this becomes

$$\begin{aligned}
 H_{\text{RF}}^{\psi} = -\hbar\omega_1 \cos(\omega t - \phi) & \left\{ \cos \phi_L \sin \theta_L \begin{pmatrix} 0 & A & 0 & B \\ A & 0 & C & 0 \\ 0 & C & 0 & A \\ B & 0 & A & 0 \end{pmatrix} \right. \\
 & + \sin \phi_L \sin \theta_L \begin{pmatrix} 0 & -iA_1 & 0 & iB_1 \\ iA_1 & 0 & -iC_1 & 0 \\ 0 & iC_1 & 0 & -iA \\ -iB_1 & 0 & iA_1 & 0 \end{pmatrix} \\
 & \left. + \cos \theta_L \begin{pmatrix} -D & 0 & E & 0 \\ 0 & -D_1 & 0 & -E \\ E & 0 & D_1 & 0 \\ 0 & -E & 0 & D \end{pmatrix} \right\}, \tag{20}
 \end{aligned}$$

where A, B, C are given by equation (7) and

$$\begin{aligned}
 A_1 &= \frac{\sqrt{3} - \frac{\eta}{\sqrt{3}}}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}} \\
 B_1 &= 1 - \frac{1 + \eta}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}
 \end{aligned}$$

$$C_1 = 1 + \frac{1 + \eta}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}$$

$$D = -1 - \frac{2}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}$$

$$D_1 = 1 - \frac{2}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}$$

$$E = -\frac{\frac{2\eta}{\sqrt{3}}}{\left(1 + \frac{\eta^2}{3}\right)^{1/2}}.$$

Transforming H_{RF}^Ψ of equation (20) into the interaction picture defined by the operator U in equation (8) and neglecting all non-secular terms as was done in deriving equation (9) results in

$$\tilde{H}_{\text{RF}}^\Psi = -\frac{\hbar\omega_1}{2} \left\{ \begin{aligned} &\begin{pmatrix} 0 & \alpha - i\beta & \gamma & 0 \\ \alpha + i\beta & 0 & 0 & -\gamma \\ \gamma & 0 & 0 & \alpha - i\beta \\ 0 & -\gamma & \alpha + i\beta & 0 \end{pmatrix} \cos \phi \\ &+ \begin{pmatrix} 0 & -i\alpha - \beta & -i\gamma & 0 \\ i\alpha - \beta & 0 & 0 & -i\gamma \\ i\gamma & 0 & 0 & i\alpha + \beta \\ 0 & i\gamma & -i\alpha + \beta & 0 \end{pmatrix} \sin \phi \end{aligned} \right\}, \quad (21)$$

where

$$\alpha = A \sin \theta_L \cos \phi_L,$$

$$\beta = A_1 \sin \theta_L \sin \phi_L,$$

$$\gamma = \cos \theta_L E.$$

We now define new operators Q and P such that

$$\tilde{H}_{\text{RF}}^\Psi = -\hbar\omega_{1\text{eff}}(Q \cos \phi + P \sin \phi), \quad (22)$$

where $\omega_{1\text{eff}} = \omega_1(\alpha^2 + \beta^2 + \gamma^2)^{1/2}$. The total Hamiltonian can be then represented as

$$\tilde{H}^\Psi = \hbar(\omega_Q - \omega)R - \hbar\omega_{1\text{eff}}(Q \cos \phi + P \sin \phi), \quad (23)$$

where

$$R = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Note that the operators P , Q and R obey the standard $SU(2)$ algebra commutation relations. The solution for the propagator is

$$\exp(-i\tilde{H}t/\hbar) = \exp[i(\alpha^+ - \phi + \pi)R] \exp(i\beta S) \exp[i(\alpha^+ + \phi)R],$$

where the Euler angles are given by equation (14). The only difference is the new $\omega_{1\text{eff}}$ specified in equation (22) which reflects the arbitrary direction of the RF coil (equation (19)). It is easy at this point to recover the block diagonal form of the total Hamiltonian (contrast to equations (10)) by means of the following change of the basis

$$|\Psi'\rangle = T|\Psi\rangle,$$

where

$$T = \begin{pmatrix} \frac{\gamma}{(\alpha^2 + \beta^2 + \gamma^2)^{1/2}} & 0 & 0 & \frac{\alpha - i\beta}{(\alpha^2 + \beta^2 + \gamma^2)^{1/2}} \\ 0 & 0 & 1 & 0 \\ 0 & -\frac{\gamma}{(\alpha^2 + \beta^2 + \gamma^2)^{1/2}} & \frac{\alpha + i\beta}{(\alpha^2 + \beta^2 + \gamma^2)^{1/2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

such that

$$\tilde{H}_T = T\tilde{H}T^{-1}$$

and

$$\tilde{H}_T = \frac{\hbar(\omega_Q - \omega)}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} - \frac{\hbar\omega_{1\text{eff}}}{2} \begin{pmatrix} 0 & e^{-i\phi} & 0 & 0 \\ e^{i\phi} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{i\phi} \\ 0 & 0 & e^{-i\phi} & 0 \end{pmatrix}. \quad (24)$$

Comparison of equations (24) and (10) shows that these are identical and the equilibrium density matrix is given by equation (11). Thus, all arguments of the previous section can be applied directly to the discussion of the problem of the arbitrary orientation of the RF field with respect to the QPAS of the crystal. The response of the system is given simply by W_1 using the appropriate effective frequency of the RF field, or in terms of the operator Q in the $|\Psi\rangle$ basis

$$W_1 = \text{tr} \{Q\tilde{\sigma}_{3/2}(t)\}.$$

It is clear that, in the case of an arbitrary directed RF coil, the response of the system is analogous to a spin 1/2 system response in the rotating frame. If the distribution

of the crystals is assumed to be random then the averaged signal of the system is [9, 10]

$$\tilde{W}_1 = \int \sin \theta_L W_1(\theta_L, \phi_L) \frac{\sin \theta_L d\theta_L d\phi_L}{4\pi}.$$

For the inversion signal of a single crystal, defined as

$$W_3 = \text{tr} \{R\tilde{\sigma}_{3/2}(t)\},$$

the averaged signal for a powdered sample then is

$$\tilde{W}_3 = \int \sin \theta_L W_3(\theta_L, \phi_L) \frac{\sin \theta_L d\theta_L d\phi_L}{4\pi}.$$

The responses of the system to the various pulse sequences are discussed after consideration of the spin 5/2 system.

5. Generalization for higher order spins

The quadrupolar Hamiltonian matrix for a spin 5/2 in the $|IM\rangle$ basis is [16]

$$H_Q = \frac{\beta\hbar e^2 q Q}{40} \begin{pmatrix} 10 & 0 & \eta\sqrt{10} & 0 & 0 & 0 \\ 0 & -2 & 0 & 3\sqrt{2}\eta & 0 & 0 \\ \eta\sqrt{10} & 0 & -8 & 0 & 3\sqrt{2}\eta & 0 \\ 0 & 3\sqrt{2}\eta & 0 & -8 & 0 & \eta\sqrt{10} \\ 0 & 0 & 3\sqrt{2}\eta & 0 & -2 & 0 \\ 0 & 0 & 0 & \eta\sqrt{10} & 0 & 10 \end{pmatrix}. \quad (25)$$

Assuming that an RF pulse is of the form given in equation (9), in the $|\Psi\rangle$ basis we obtain

$$H_{\text{RF}}^\Psi = -2\hbar\omega_1 \cos(\omega t - \phi) \begin{pmatrix} 0 & A & 0 & B & 0 & D \\ A & 0 & C & 0 & E & 0 \\ 0 & C & 0 & F & 0 & B \\ B & 0 & F & 0 & C & 0 \\ 0 & E & 0 & C & 0 & A \\ D & 0 & B & 0 & A & 0 \end{pmatrix}, \quad (26)$$

where A, \dots, F are specified in terms of the transformation elements U_{ij} as in equation (A 6) (appendix). The energy splittings between pairs of degenerate levels are unequal, and a single pulse acts selectively affecting only a single transition. If the carrier frequency ω of an RF pulse is close to the frequency of the $|\pm 3/2\rangle \rightarrow |\pm 5/2\rangle$ transition, then it is reasonable to define a reduced matrix for the quadrupole and RF Hamiltonians which specifically includes those pairs of states. Other states simply

are not affected by the pulse. Thus the problem reduces from 6×6 to 4×4 . This is realized as H_Q^r , defined as

$$H_Q^r = \frac{\hbar e^2 q Q}{40} \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_3 & 0 & 0 \\ 0 & 0 & E_3 & 0 \\ 0 & 0 & 0 & E_1 \end{pmatrix}. \quad (27)$$

Using the actual frequency of the transition under consideration as $\omega_Q = (e^2 q Q)/40 \times (2E_1 + E_2)$ enables equation (27) to be written as a difference of two matrices

$$H_Q^r = \frac{\hbar \omega_Q}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} - \frac{\hbar e^2 q Q}{40} \frac{E_2}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (28)$$

The second contribution will be dropped as it merely resets the energy reference state. The reduced RF Hamiltonian associated with equation (26) is obtained similarly,

$$H_{\text{RF}}^r = -2\hbar \omega_1 \cos(\omega t - \phi) \begin{pmatrix} 0 & A & 0 & D \\ A & 0 & E & 0 \\ 0 & E & 0 & A \\ D & 0 & A & 0 \end{pmatrix}, \quad (29)$$

where A , D and E are defined in the appendix.

The interaction picture is now defined by the operator Π which uses the reduced Hamiltonian H_Q^r of equation (8)

$$\Pi = \exp\left(-i \frac{H_Q^r}{\hbar \omega_Q} \omega t\right).$$

Transforming the total reduced Hamiltonian into the interaction picture and omitting the high frequency terms gives

$$\tilde{H}^r = \frac{\hbar(\omega_Q - \omega)}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} - \hbar \omega_1 A \begin{pmatrix} 0 & e^{-i\phi} & 0 & 0 \\ e^{i\phi} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{i\phi} \\ 0 & 0 & e^{-i\phi} & 0 \end{pmatrix}.$$

This is exactly the same form as the total Hamiltonian for spin 3/2 in equation (10) provided that $\omega_{1\text{eff}} = 2A\omega_1$. In the case of an arbitrarily directed RF coil (with angles (θ_L, ϕ_L) in the QPAS frame) the total reduced Hamiltonian is given by equation (23) with the following changes

$$\alpha = 2A \sin \theta_L \cos \phi_L$$

$$\beta = 2A_1 \sin \theta_L \sin \phi_L$$

$$\gamma = 2 \cos \theta_L E$$

where A is given by equation (A 6) of the appendix and

$$A_1 = \frac{1}{2}\sqrt{5}U_{11}U_{55} - \sqrt{2}U_{55}U_{13} + \frac{3}{2}U_{53}U_{13} - \sqrt{2}U_{53}U_{15} + \frac{1}{2}\sqrt{5}U_{15}U_{51},$$

$$E = \frac{5}{2}U_{11}U_{15} + \frac{1}{2}U_{31}U_{35} - \frac{3}{2}U_{51}U_{55}.$$

Thus, the response of a spin $5/2$ system to a single RF pulse is of the same form as a spin $3/2$ system with a different effective frequency of RF field. In the case of $\eta = 0$, A reduces to $\sqrt{5/2}$ and $\omega_{1\text{eff}} = \sqrt{5}\omega_1 \sin \theta_L$.

6. Results and discussion

Here we discuss the performance of the composite pulses designed by various NMR methods in the NQR case. As explained in the previous sections, NQR pulses for half integer spins can be described by rotation matrices. The multipole approach to composite pulses uses the fact that a product of rotations is a rotation itself. Recently, several pulse sequences of short duration were designed using this method [8]. In general, for spin I in the case of $\eta = 0$ the effective frequency of the RF field for transition $M \rightarrow M - 1$ is

$$\omega_{1\text{eff}} = [(I + M)(I - M + 1)]^{1/2} \sin \theta_L \omega_1$$

Thus, to obtain universal pictures for a spin I system we need to plot the signal as the function of the offset divided by the factor $[(I + M)(I - M + 1)]^{1/2}$. One example [8] is the composite π pulse of $78_0 - 195_{182} - 318_{12}$. The performance of this sequence is shown in figure 2 for single crystals and powder averages for $\eta = 0$. Figure 2 reveals the fact that this composite pulse sequence has a range between offsets of ± 1.5 , which is relatively flat. This is good not only for single crystals but

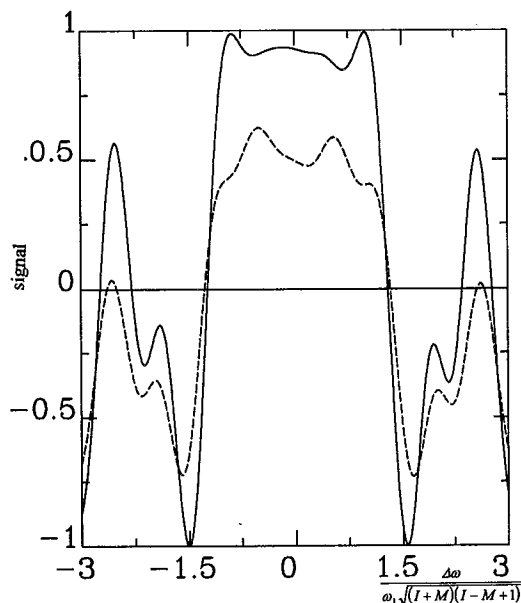


Figure 2. The composite π pulse of $78_0 - 195_{182} - 318_{12}$. The solid line represents a single crystal; the dashed line is used for powders.

also for powders. Other pulse sequences designed for NMR are shown in Figures 3 and 4. Although they work as well for single crystals they are less effective for the case of powders.

Figure 5 shows a $\pi/2$ composite pulse designed by the multipole approach [8]. We found one other pulse sequence which works well not only in the case of single crystals but also in powders. This is $385_{90} - 320_{270} - 25_{90}$ designed using a Magnus expansion [1] (figure 6). It should be noted that the pulse sequences in figures 2 and 6 work better than those presented in [10], using the flatness about zero offset as the criterion. We conclude that composite pulse sequences designed for NMR perform well for NQR in the case of single crystals but less well for powders.

7. Conclusion

We have considered in detail the effect of composite pulses in the case of pure NQR, neglecting relaxation, for half integer spins using spin 3/2 and 5/2 as examples. Mathematically, the difference between NMR and pure NQR cases can be understood in the terms of the corresponding Hamiltonians. In NMR a large static Zeeman field causes equivalent energy splitting between any two adjacent levels. The application of a RF pulse excites all transitions simultaneously. By contrast, in NQR there is no large Zeeman field and the quadrupole interaction causes unequal energy splitting. Thus, pulses in NQR act selectively. The effect of a RF pulse on the pairs of adjacent levels can be described by a $SU(2)$ Hamiltonian, and thus the responses of two different physical systems are found to be similar. The theoretical conclusion that NMR composite pulses can be used with similar effects for NQR should be useful in practice. This conclusion, to date, has not been tested experimentally.

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Appendix

The energy eigenvalues of H_Q of equation (25) are doubly degenerate and obtained as the solution of a cubic secular equation. These are given in detail in [16]. In summary, the energy eigenvalues are E_1 , E_2 and E_3 where

$$\left. \begin{aligned} E_1 &= 2R_1^{1/3} \cos\left(\frac{\theta}{3}\right) \\ E_2 &= 2R_1^{1/3} \cos\left(\frac{\theta + 2\pi}{3}\right) \\ E_3 &= -(E_1 + E_2) = 2R_1^{1/3} \cos\left(\frac{\theta + 4\pi}{3}\right) \end{aligned} \right\} \quad (\text{A } 1)$$

and

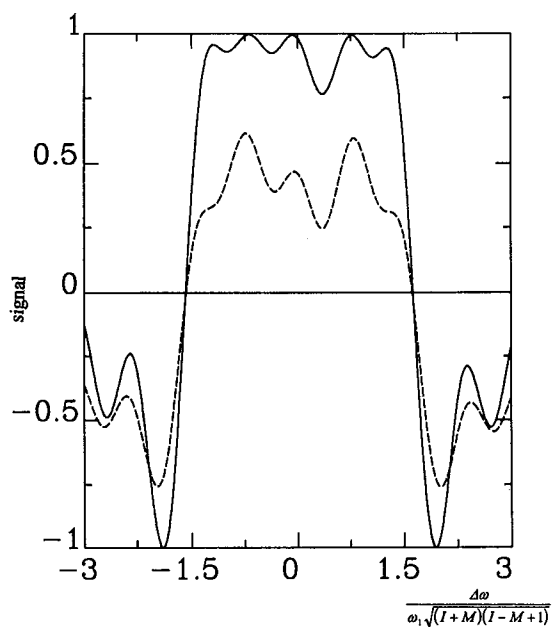


Figure 3. The composite π pulse of $86_0 - 160_{180} - 260_9$. The solid line represents a single crystal; the dashed line is used for powders.

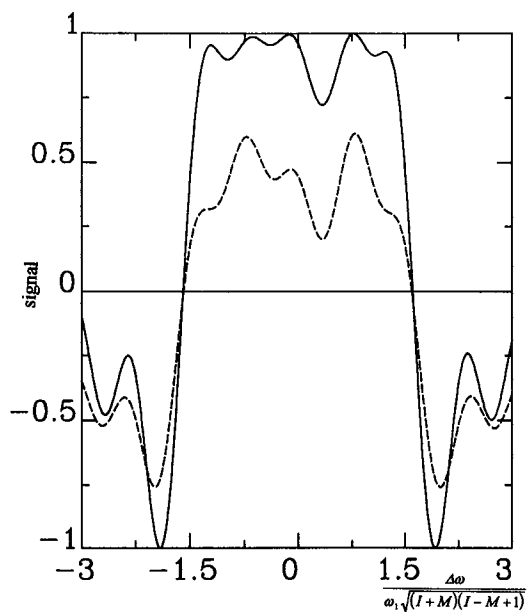


Figure 4. The composite π pulse of $260_0 - 161_{190} - 85_4$. The solid line represents a single crystal; the dashed line is used for powders.

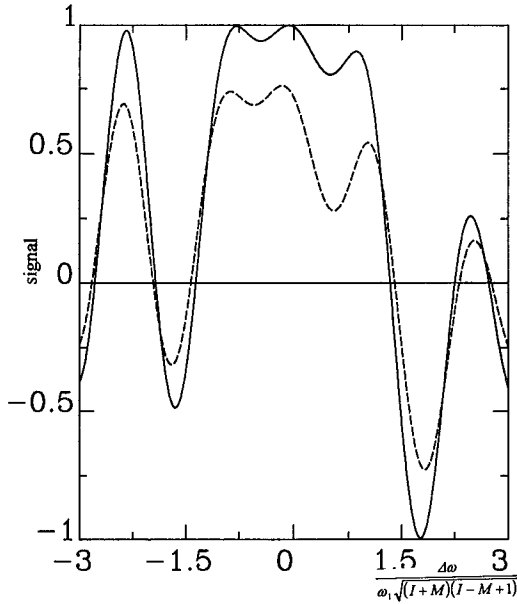


Figure 5. The composite $\pi/2$ pulse of $83_{90} - 233_{191}$. The solid line represents a single crystal; the dashed line is used for powders.

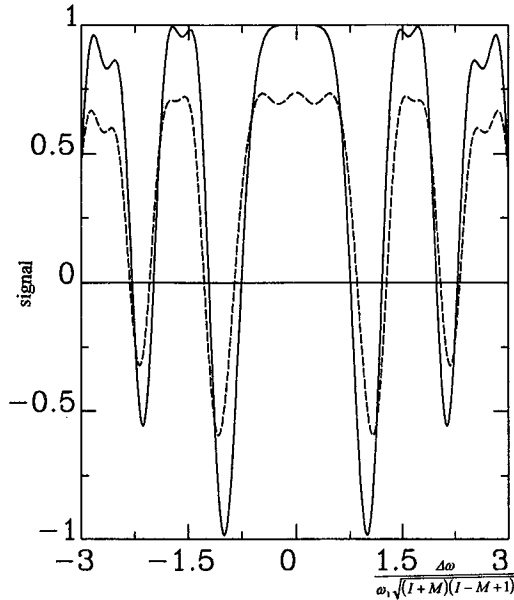


Figure 6. The composite $\pi/2$ pulse of $385_{90} - 320_{270} - 25_{90}$. The solid line represents a single crystal; the dashed line is used for powders.

$$\left. \begin{aligned} R_1^2 &= 80^2(1 - \eta^2)^2 + \frac{64}{81} C_1^2, \\ C_1^2 &= 3(343\eta^6 + 387\eta^4 + 14\,661\eta^6 + 6561), \\ \tan \theta &= \frac{C_1}{90(1 - \eta^2)}. \end{aligned} \right\} \quad (\text{A } 2)$$

In the case of $\eta = 0$ the eigenvalues of the quadrupole Hamiltonian reduce to the simple results $E_1 = 10, E_2 = -8, E_3 = -2$ in units of $(\hbar e^2 q Q)/40$. The matrix which diagonalizes the quadrupole spin 5/2 Hamiltonian [18] is given as:

$$S = \begin{pmatrix} U_{11} & 0 & U_{31} & 0 & U_{51} & 0 \\ 0 & U_{55} & 0 & U_{35} & 0 & U_{15} \\ U_{13} & 0 & U_{33} & 0 & U_{53} & 0 \\ 0 & U_{53} & 0 & U_{33} & 0 & U_{13} \\ U_{15} & 0 & U_{35} & 0 & U_{55} & 0 \\ 0 & U_{51} & 0 & U_{31} & 0 & U_{11} \end{pmatrix} \quad (\text{A } 3)$$

where

$$\left. \begin{aligned} U_{11} &= \frac{1}{N_1}, \\ U_{31} &= \frac{\eta(E_1 + 2)\sqrt{10}}{N_1[(E_1 + 2)(E_1 + 8) - 18\eta^2]}, \\ U_{51} &= \frac{3\eta^2\sqrt{20}}{N_1[(E_1 + 2)(E_1 + 8) - 18\eta^2]}, \\ U_{13} &= \frac{\eta\sqrt{10}}{N_2(E_2 - 10)}, \\ U_{33} &= \frac{1}{N_2}, \\ U_{53} &= \frac{3\eta\sqrt{2}}{N_2(E_2 + 2)}, \\ U_{15} &= -\frac{3\eta^2\sqrt{20}}{N_3[10\eta^2 - (E_3 - 10)(E_3 + 8)]}, \\ U_{35} &= \frac{3\eta(10 - E_3)\sqrt{2}}{N_3[10\eta^2 - (E_3 - 10)(E_3 + 8)]}, \\ U_{55} &= \frac{1}{N_3}. \end{aligned} \right\} \quad (\text{A } 4)$$

The constants N_1, N_2 and N_3 are defined by normalizing each column of the S matrix to unity. The S matrix reduces to the identity matrix when η is equal to zero. In this new representation $|\Psi\rangle H_Q$ takes the diagonal form with elements E_1, E_3, E_2, E_2, E_3 and E_1 .

Assuming a RF pulse is applied along the x axis in the QPAS such that

$$H_{\text{RF}} = -2\hbar\omega_1 \cos(\omega t - \phi)I_x \quad (\text{A } 5)$$

then, in the $|\Psi\rangle$ basis,

$$H_{\text{RF}}^{\Psi} = -2\hbar\omega_1 \cos(\omega t - \phi) \begin{pmatrix} 0 & A & 0 & B & 0 & D \\ A & 0 & C & 0 & E & 0 \\ 0 & C & 0 & F & 0 & B \\ B & 0 & F & 0 & C & 0 \\ 0 & E & 0 & C & 0 & A \\ D & 0 & B & 0 & A & 0 \end{pmatrix}, \quad (\text{A } 6)$$

where

$$\begin{aligned} A &= \frac{1}{2}\sqrt{5}U_{55}U_{11} + \sqrt{2}U_{55}U_{13} + \frac{3}{2}U_{53}U_{13} + \sqrt{2}U_{53}U_{15} + \frac{1}{2}\sqrt{5}U_{15}U_{51}, \\ B &= \frac{1}{2}\sqrt{5}U_{35}U_{11} + \sqrt{2}U_{35}U_{13} + \frac{3}{2}U_{33}U_{13} + \sqrt{2}U_{33}U_{15} + \frac{1}{2}\sqrt{5}U_{15}U_{31}, \\ C &= \frac{1}{2}\sqrt{5}U_{55}U_{31} + \sqrt{2}U_{33}U_{55} + \frac{3}{2}U_{33}U_{53} + \sqrt{2}U_{35}U_{53} + \frac{1}{2}\sqrt{5}U_{35}U_{51}, \\ D &= \sqrt{5}U_{15}U_{11} + 2\sqrt{2}U_{15}U_{13} + \frac{3}{2}U_{13}^2, \\ E &= \sqrt{5}U_{55}U_{51} + 2\sqrt{2}U_{53}U_{55} + \frac{3}{2}U_{53}^2, \\ F &= \sqrt{5}U_{35}U_{31} + 2\sqrt{2}U_{35}U_{33} + \frac{3}{2}U_{33}^2. \end{aligned}$$

References

- [1] LEVITT, M. H., 1986, *Progr. nucl. magn. Reson. Spectrosc.*, **18**, 61. FREEMAN, R., and LEVITT, M. H., 1979, *J. magn. Reson.*, **33**, 473.
- [2] TYCKO, R., SCHNEIDER, E., and PINES, A., 1984, *J. chem. Phys.*, **81**, 680.
- [3] TYCKO, R., 1983, *Phys. Rev. Lett.*, **51**, 775.
- [4] BLUMICH, B., and SPIESS, H. W., 1985, *J. magn. Reson.*, **61**, 356.
- [5] WAUGH, J. S., 1982, *J. magn. Reson.*, **49**, 517.
- [6] SHAKA, A. J., KEELER, J., FREMKIEL, T., and FREEMAN, R., 1983, *J. magn. Reson.*, **52**, 335.
- [7] SANCTUARY, B. C., and COLE, H. B. R., 1987, *J. magn. Reson.*, **71**, 106.
- [8] YANG, X., KENIRY, M. A., and SANCTUARY, B. C., 1994, *J. magn. Reson.*, in press.
- [9] RAMAMOORTHY, A., and NARASIMHAN, P. T., 1989, *J. molec. Struct.*, **102**, 333.
- [10] RAMAMOORTHY, A., CHANDRAKUMAR, N., DUBEY, A. K., and NARASIMHAN, P. T., 1993, *J. magn. Reson. A*, **102**, 274.
- [11] SANITHA BAI, N., RAMAKRISHNA, M., and RAMACHANDRAN, R., 1993, *J. magn. Reson. A*, **104**, 203.
- [12] WU, D., and SANCTUARY, B. C., 1993, *J. magn. Reson. A*, **103**, 171.
- [13] SANCTUARY, B. C., 1983, *Molec. Phys.*, **49**, 785.
- [14] PRATT, J. C., 1977, *Molec. Phys.*, **34**, 539.
- [15] FURMAN, G. B., 1984, *Izv. Vysh. Uchebn. Zaved., Radiofiz.*, **27**, 667, in Russian.
- [16] KRISHNAN, M. S., TEMME, F. P., and SANCTUARY, B. C., 1993, *Molec. Phys.*, **78**, 1385.
- [17] ZHOU, J., GAO, H., and SANCTUARY, B. C., 1993, *J. magn. Reson. A*, **101**, 119.
- [18] KRISHNAN, N. S., unpublished.