Numerical Design of Composite Pulses for Polycrystalline Samples in Pulsed NQR Spectroscopy *

A. Ramamoorthy [a] and P. T. Narasimhan [b]

Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India

Z. Naturforsch. **45a**, 581–586 (1990); received August 24, 1989; in revised form December 6, 1989

The density matrix approach along with fictitious spin-1/2 or tensor operator formalisms were employed to obtain general expressions for $\langle I_x \rangle$ and thus the signal induced in a coil in the case of physically equivalent non-interacting spin $I=1$ and 3/2 nuclei in a single crystal with a three-pulse composite pulse. The corresponding powder averages were then obtained and the dependence of the signal on the i-th pulse flip angle (θ_i) and phase (ϕ_i) studied. A numerical procedure established the optimum "$\pi/2$" composite pulse for polycrystalline samples as $(90)_0$–$(70)_{45}$–$(20)_{25}$, where the quantity in parentheses denotes the flip angle and the subscript the phase. A two-pulse composite pulse of the form $(126)_0$–$(300)_{80}$ was also inferred, but the three-pulse composite pulse is superior. These composite pulses are shown to have general validity for other spin I values.

Key words: Composite pulses, NQR spectroscopy, Polycrystalline samples, Numerically designed pulses.

Introduction

A composite pulse is a sequence of phase-shifted radio frequency (rf) pulses with no delays within the sequence. The importance of composite pulses (abbreviated to comp-pulses) for uniform excitation over a wide band of resonance frequencies independent of rf field inhomogeneity and off-set has been realized by NMR spectroscopists, and applications of comp-pulses abound in the NMR literature [1]. In general, comp-pulses have been shown to perform better in NMR than their single pulse counterparts. The area of coherent optics [2, 3] has also benefited by the introduction of comp-pulses. However, similar applications of comp-pulses in the area of NQR spectroscopy are conspicuous by their absence. Realizing this situation, we recently initiated a program of research on comp-pulses for NQR spectroscopy.

Using the Magnus expansion approach [4–6] and the fictitious spin-1/2 operator formalism [7] we were able to express [8] the NQR signal amplitude for two- and three-pulse comp-pulses in the case of a single crystal containing physically equivalent non-interacting $I=1$ spins in the absence of a Zeeman field. The electric field gradient (efg) inhomogeneity leads to a distribution $\Delta\omega_Q$ in NQR frequency. The inhomogeneity $\Delta\omega_1$ in the rf field and $\Delta\omega_Q$ were treated as perturbations in the appropriately transformed frames of the NQR Hamiltonian [8] and the evolution operator [9] was obtained in the spirit of the Magnus expansion approach. Only the zeroth-order term was considered in our treatment, and two- and three-pulse comp-pulses were designed for compensating for $\Delta\omega_1$ and $\Delta\omega_Q$ in the context of broad band excitation. We were thus led to propose [8] the $(90)_0$–$(300)_{90}$ NQR composite $\pi/2$ pulse for compensating efg inhomogeneity and the $(90)_0$–$(0)_{90}$–$(90)_0$ NQR composite π pulse which compensates better for efg inhomogeneity when θ lies between 90° and 270°. $(\theta)_\phi$ in a comp-pulse represents a pulse with flip angle θ and rf phase ϕ. In designing these comp-pulses, we decided to limit the phases of these pulses to either 0° or 90° on account of the experimental simplicity associated with the generation of such pulses. The computer simulation of the theoretically calculated responses showed that these comp-pulses perform, in general, better than single rf pulses. In the spin $I=1$ case, considering an allowed

---

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

[a] Present address: Laboratory of Chemical Physics, Central Leather Research Institute, Adayaru, Madras-600 020, India.

[b] Huntington Medical Research Institutes, Magnetic Resonance Spectroscopy Unit & Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, USA.

Reprint requests to Prof. Dr. P. T. Narasimhan, Huntington Medical Research Institutes, 660 S. Fair Oaks, Pasadena, California 91105 USA.

0932-0784 / 90 / 0300-0581 $ 01.30/0. – Please order a reprint rather than making your own copy.

transition, we noticed that the structure of the comp-pulses is independent of the asymmetry parameter of the efg. Unlike NMR, it is not feasible to employ a large number of pulses within a comp-pulse in NQR, on account of the shorter transverse relaxation time, T_2. Consequently, we have limited our treatment to comp-pulses having at most three pulses.

In our recent work [10], we investigated the use of comp-pulses consisting of phase-alternated pulses and were able to show that for non-interacting physically equivalent $I=1$ and $I=3/2$ nuclei in a single crystal in the absence of a magnetic field it is possible to design comp-pulses that can yield broad band excitation in NQR with compensation for efg and rf field inhomogeneities. We used the tensor operator formalism [11, 12] to represent the operators involved in the $I=3/2$ case. The pulses comprising the comp-pulses have their rf phase either 0° or 180°. The procedure adopted in designing the comp-pulses for $I=3/2$ is similar to the one mentioned above for $I=1$ [8]. Some of the $\pi/2$ pulses obtained by us are: (a) $\overline{22.5}$ 112.5, (b) $\overline{45}$ 135, (c) $\overline{60}$ 150, (d) $1\overline{14}.3$ 318.6$1\overline{14}$.3, (e) 385 $\overline{320}$ 25. Some of the π pulses obtained by us are: (a) $\overline{22.5}$ 225 $\overline{22.5}$, (b) $\overline{45}$ 270 $\overline{45}$, (c) $\overline{60}$ 300 $\overline{60}$, (d) 90 $\overline{180}$ 90, (e) 260 $\overline{160}$ 80 and (f) 315 $\overline{225}$ 90. A bar over a pulse of flip angle θ denotes an rf phase shift of 180° with respect to a pulse without a bar. These comp-pulses were arrived at via the Magnus expansion route and considering only the zeroth order term [5, 6] $V^{(0)}$ in the expansion, i.e. we consider comp-pulses for which $V^{(0)}=0$. Since the Magnus expansion approach is a perturbation approach, inclusion of higher order terms may alter the convergence as well as extend the range of the performance of the composite pulses. However, it is generally noted that consideration of higher order terms entails an increase in the number of pulses in a comp-pulse. As noted earlier, the short T_2 behavior in NQR, as contrasted to NMR, prohibits the design of longer sequences for NQR comp-pulses. In designing the composite pulses we also used another criterion, namely, $[V^{(0)}, \varrho^{(0)}] = 0$, i.e. the zeroth order Magnus expansion term commutes with the initial density matrix. This is a less stringent condition and allows the consideration of a larger number of comp-pulses for which $V^{(0)} \neq 0$ and nevertheless may show useful excitation characteristics. One point that we noted in our work [8, 10] was that while some of the comp-pulses mentioned in the NMR literature may perform well in the NQR context, the correspondence is not one-to-one.

In the present work we examine the design of optimum two- and three-pulse comp-pulses which would be the equivalent of a "$\pi/2$" rf pulse in the case of powders. In order to avoid the perturbation approximation involved in the Magnus expansion approach we decided to handle the problem of optimizing the "$\pi/2$" comp-pulses by direct calculation of the signal response using the density matrix approach and examining the dependence of the calculated response as a function of the various flip angles and phases involved in the comp-pulse. We now discuss the details of the theoretical procedure adopted for the design of such two- and three-pulse comp-pulses.

Theory

We illustrate the procedure using the $I=1$ case as our example. The results can be shown to be similar for the $I=3/2$ case. The quadrupolar Hamiltonian, $\mathscr{H}_Q$, is given in the usual notation [13] as

$$\mathscr{H}_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I^2 - \eta(I_x^2 - I_y^2)] \qquad (1)$$

with the asymmetry parameter η defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} . \qquad (2)$$

V_{ii} are the components of the efg with $V_{zz} = eq$ and $|V_{xx}| \leqq |V_{yy}| \leqq |V_{zz}|$. The eigen functions and energy levels associated with this $\mathscr{H}_Q$ for the $I=1$ case are well-known [13]. Following Cantor and Waugh [14] and using the fictitious spin-1/2 operator formalism [7] we write $\mathscr{H}_Q$ as

$$\mathscr{H}_Q = \frac{e^2 q Q}{2} [I_{x3} - I_{y3} - \eta I_{z3}]$$

$$= \omega_p I_{p3} + \omega'_p I_{p4}; \quad p = x, y, z . \qquad (3)$$

I_{pl}'s represent the fictitious spin-1/2 operators with p having three components x, y, and z, and for each p there is a sub-space characterized by $l=1, 2, 3$ obeying the commutation relations (4)

$[I_{p1}, I_{p2}] = i I_{p3}$ (or) cyclic permutations of 1, 2, 3 .

As shown in [9], considering one of the allowed transitions, viz.

$$|0\rangle \leftrightarrow \frac{1}{\sqrt{2}} [|+1\rangle + |-1\rangle] ,$$

we can write

$$\mathscr{H}_Q = \omega_Q I_{x3} + \omega'_Q I_{x4}\,, \tag{5}$$

where

$$\omega_Q = \frac{e^2 q Q}{4}\,[\eta + 3] \tag{5a}$$

and

$$\omega'_Q = \frac{e^2 q Q}{4}\,[\eta - 1]\,. \tag{5b}$$

We consider next the rf Hamiltonian $\mathscr{H}_{rf}$. We assume that the single crystal quadrupole principal axis system (QPAS) is oriented with its V_{xx} axis making an angle α with the rf coil axis. The laboratory axes x, y, z are oriented such that the lab x axis coincides with the rf coil axis. $\mathscr{H}_{rf}$ for an rf pulse of frequency ω_Q and phase ϕ can be written as

$$\mathscr{H}_{rf} = -2\omega_1 \cos(\omega_Q t + \phi(t)) \cdot [I_x \cos\alpha + I_y \sin\alpha \sin\beta + I_z \sin\alpha \cos\beta]\,, \tag{6}$$

where $\omega_1 = \gamma H_1$ (rad/sec) denotes the strength of the rf pulse and β denotes the angle between the projection of V_{xx} axis and the lab z axis on the lab z-y plane. Using the fictitious spin-1/2 operator formalism $\mathscr{H}_{rf}$ can be written as

$$\mathscr{H}_{rf} = -4\omega_1 \cos(\omega_Q t + \phi(t)) \cdot [I_{x1} \cos\alpha + I_{y1} \sin\alpha \sin\beta + I_{z1} \sin\alpha \cos\beta]\,. \tag{7}$$

Note that $I_p = 2I_{p1}$ when we represent the familiar spin angular momentum operator I_p in the fictitious spin-1/2 operator formalism.

The total Hamiltonian can be written as

$$\mathscr{H}(t) = \mathscr{H}_Q + \mathscr{H}_{rf}\,. \tag{8}$$

Our goal is to calculate the density matrix $\varrho(t)$ at the end of the comp-pulse by solving the equation of motion

$$\frac{d\varrho(t)}{dt} = i\,[\varrho(t), \mathscr{H}(t)]\,. \tag{9}$$

The time development of our model system will be described by following the time evolution of the reduced density matrix $\varrho(0)$ at the beginning of the comp-pulse. In the quadrupole interaction frame (QIF) [15] defined by the unitary operator $U_Q = \exp(-i\mathscr{H}_Q t)$ we have

$$\tilde{\varrho} = U_Q^{-1}\,\varrho\,U_Q\,, \tag{10}$$

and the time development in this frame is governed by the equation of motion

$$d\tilde{\varrho}/dt = i\,[\tilde{\varrho}(t), \tilde{\mathscr{H}}_{rf}]\,, \tag{11}$$

where

$$\tilde{\mathscr{H}}_{rf} = U_Q^{-1}\,\mathscr{H}_{rf}\,U_Q\,. \tag{12}$$

Note that operators in QIF are denoted with a tilde. It is worth remembering at this juncture the relation between the fictitious spin-1/2 operators in the starting frame and the transformed interaction frame (QIF).

$$\tilde{I}_{x1} = U_Q^{-1}\,I_{x1}\,U_Q = I_{x1}\cos(\omega_Q t) - I_{x2}\sin(\omega_Q t), \tag{13}$$
$$\tilde{I}_{y1} = U_Q^{-1}\,I_{y1}\,U_Q = I_{y1}\cos(\omega_Q t/2) + I_{y2}\sin(\omega_Q t/2),$$
$$\tilde{I}_{z1} = U_Q^{-1}\,I_{z1}\,U_Q = I_{z1}\cos(\omega_Q t/2) + I_{z2}\sin(\omega_Q t/2).$$

Making use of these relations and truncating the high frequency terms [14] we get

$$\tilde{\mathscr{H}}_{rf} = -2\omega_1 \cos\alpha\,[I_{x1}\cos\phi - I_{x2}\sin\phi]. \tag{14}$$

In the QIF the system evolves under the evolution operator $U_{rf} = \exp(-i\tilde{\mathscr{H}}_{rf} t)$. The density matrix at the end of an rf pulse of duration t_1 can be written as

$$\begin{aligned}\tilde{\varrho}(t_1) &= U_{rf}\,\tilde{\varrho}(0)\,U_{rf}^{-1} = \exp(-i\,\tilde{\mathscr{H}}_{rf}\,t_1)\,\tilde{\varrho}_0\exp(i\,\tilde{\mathscr{H}}_{rf}\,t_1)\\ &= \exp(-i\,\tilde{\mathscr{H}}_{rf}\,t_1)\,\varrho_0\exp(i\,\tilde{\mathscr{H}}_{rf}\,t_1)\\ &= \omega_Q[I_{x3}\cos(2\omega_1 t_1\cos\alpha) - I_{x2}\sin(2\omega_1 t_1\cos\alpha)].\end{aligned} \tag{15}$$

The NQR signal is proportional to the x-component of the angular momentum operator, I_x. Choosing a suitable reference phase we get the expectation value of I_x as

$$\begin{aligned}\langle I_x\rangle &= \mathrm{Tr}\,\{\tilde{\varrho}(t_1)\,\tilde{I}_x \sin\omega_Q t\}\\ &= (\omega_Q/kT)\sin(2\omega_1 t_1\cos\alpha).\end{aligned} \tag{16}$$

The fraction of crystallites with their QPAS x-axis pointing at an angle between α and $\alpha + d\alpha$ with respect to coil axis is

$$\frac{2\pi\sin\alpha\,d\alpha}{4\pi} = -\tfrac{1}{2}\,d(\cos\alpha). \tag{17}$$

The expression for the NQR signal immediately following a single rf pulse from a polycrystalline sample can be obtained by averaging over all possible α values and noting that the induced signal in the coil

is proportional to $\cos\alpha$. Thus

$$\langle \bar{I}_{\text{coil}} \rangle \propto -\frac{\omega_Q}{2kT} \int_0^{\pi} \cos\alpha \sin(2\omega_1 t_1 \cos\alpha)\, \mathrm{d}(\cos\alpha)$$

$$= \frac{\omega_Q}{kT} \frac{1}{\theta_1^2} [\sin\theta_1 - \theta_1 \cos\theta_1], \tag{18}$$

where θ_1 is the flip angle of the rf pulse defined as $\theta_1 = 2\omega_1 t_1$. It will be seen from (18) that the signal amplitude as a function of θ_1 is modulated by the first order Bessel function $J_1(\theta_1)$. The signal maximum is obtained not at $\theta_1 = 90°$ but at $0.66\pi = 119°$ in the case of a powdered specimen, a result familiar to many NQR spectroscopists. Similarly, the value for the "180°" pulse is $1.43\pi = 256°$.

After this slight digression let us continue further and consider the signal response at the end of a three-pulse comp-pulse which we denote as $(\theta_1)_{\phi_1} - (\theta_2)_{\phi_2} - (\theta_3)_{\phi_3}$. Our aim is to calculate $\langle I_x \rangle$ and thus $\langle \bar{I}_{\text{coil}} \rangle$ at the end of the comp-pulse and optimize this value by varying pulse widths and phases. For a three-pulse comp-pulse we have, in all, six variables to handle. By setting $\phi_1 = 0$ and referring all phases to the phase of the first pulse we can reduce the number of variables to five. In general, for an N-pulse comp-pulse we will have $2N-1$ independent variables. However, we do not propose to consider comp-pulses consisting of more than three pulses due to the following considerations. Firstly, as mentioned earlier, the short T_2 values typical of NQR make larger numbers of pulses within a comp-pulse difficult to handle experimentally. Secondly, as the number of pulses increases the number of variables increases and a purely numerical approach of optimization can take prohibitively long time in a computer. Thirdly, at the high rf levels used in pulsed NQR, longer duration sequences can cause sample heating and thus lead to a change in the NQR frequency. We, therefore, limited ourselves here to a consideration of three-pulse sequences only. We shall next present the expression obtained for $\langle I_x \rangle$ at the end of a three-pulse comp-pulse following essentially the same procedure as outlined above for the single pulse. $\langle I_x \rangle$ is thus expressed as a function of five variables, namely, θ_1, θ_2, θ_3 and ϕ_2 and ϕ_3. Using this expression for $\langle I_x \rangle$ we could obtain the expression for $\langle \bar{I}_{\text{coil}} \rangle$ at the end of the comp-pulse for the powder specimen analogous to (18) and by a numerical search procedure we found the optimum values of the five variables that lead to a maximum value of $\langle \bar{I}_{\text{coil}} \rangle$.

Results

At the end of a three-pulse comp-pulse, the signal intensity from a single crystallite can be written as

$$\text{Signal intensity} \propto \langle I_x \rangle \propto \frac{\omega_Q}{kT} \Big\{ \frac{\sin\theta_1}{2} (1-\cos\theta_2)(\cos\theta_3 - 1)(\sin 2\phi_2) \sin\phi_3 \cos\phi_3$$
$$- \cos\theta_1 \sin\theta_2 [\cos\theta_3 \cos(\phi_1 - \phi_2) \cos\phi_3$$
$$+ \sin\phi_3 \sin(\phi_3 - \phi_2)]$$
$$- \sin\theta_1 (\sin^2\phi_2 + \cos\theta_2 \cos^2\phi_2) \tag{19}$$
$$\cdot (\cos\theta_3 \cos^2\phi_3 + \sin^2\phi_3)$$
$$+ \sin\theta_3 \cos\phi_3 (\sin\theta_1 \sin\theta_2 \cos\phi_2 - \cos\theta_1 \cos\theta_2) \Big\}.$$

Here, $\theta_n = 2\omega_1 t_n$ with t_n being the duration of the n-th pulse. Using this result we could get the expression for $\langle \bar{I}_{\text{coil}} \rangle$ by averaging over all orientations in a manner analogous to the derivation of (18). Thus we obtained

$$\langle \bar{I}_{\text{coil}} \rangle \propto \frac{\omega_Q}{2kT} [X + Y], \tag{20}$$

where X and Y are quantities involving the trigonometrical functions of θ's and ϕ's. Since these expressions are rather lengthy they are not reproduced here. It can be seen, however, that the problem of maximizing $\langle \bar{I}_{\text{coil}} \rangle$ is a non-linear one. We searched for the maximum of this function using a computer program in which the flip angles and phases are first varied steps of 3° and regions around the maxima searched in 1° steps. In order to test the computational feasibility of this scheme we first tried to optimize a two-pulse comp-pulse and then went over to the three-pulse case. The results are summarized in Table 1.

Table 1. Two- and three-pulse numerically optimized composite pulses for powder specimen ($I = 1$).

Number of pulses in comp-pulses	Sequence	Signal intensity*
2	$(126)_0 - (300)_{80}$	44
3	$(90)_0 - (70)_{45} - (20)_{25}$	64

* Signal at the end of the comp-pulse in arbitrary units. In comparison, for a single 90° pulse the signal intensity is 43.6.

We used the tensor operator formalism in the $I=3/2$ case and obtained the expression for $\langle \bar{I}_{\text{coil}} \rangle$. The result was identical to the $I=1$ case except for the altered definition of the flip angle as $\theta_n = \dfrac{\omega_1(3+\eta)}{\sqrt{[3+\eta^2]}}\, t_n$, where t_n is the duration of the pulse. Thus the sequences arrived at are applicable to the $I=3/2$ case also.

Discussion

By limiting ourselves to a maximum of three pulses we have been able to design by a numerical procedure comp-pulses for maximum excitation of a powdered specimen containing $I=1$ or $3/2$ nuclei. We have seen that the definition of the flip angle θ varies depending on the nucleus under consideration. It will be noticed that if the asymmetry parameter is small the values of optimum ω_1 and t_n are not very different from those for the case of $\eta=0$. In the case of $I=5/2$ with $\eta=0$ there are two allowed NQR transitions, namely $|\pm\tfrac{1}{2}\rangle \leftrightarrow |\pm\tfrac{3}{2}\rangle$ and $|\pm\tfrac{3}{2}\rangle \leftrightarrow |\pm\tfrac{5}{2}\rangle$. Referring to these as ν_1 and ν_2 respectively, it is known that the ratio of these two frequencies $\nu_1 : \nu_2$ is 1 : 2. If we irradiate one of the allowed transitions only at a time then it can be shown that for a given θ_n the values for the two frequencies will be in the ratio of $\sqrt{8}:\sqrt{5}$. The structure of the comp-pulses remains otherwise unaltered. This constancy of the structure of the comp-pulses is a consequence of the reduction of the excitation problem to that of a two-level case [16] in the presence of radiation that connects only a pair of levels in a multi level system. Equation (18) thus assumes the general form

$$\langle \bar{I}_{\text{coil}} \rangle \propto C J_1(\theta_1)\,, \tag{21}$$

where $J_1(\theta_1)$ is the first-order Bessel function. The specific value of C for some quadrupolar nuclei are presented in Table 2. θ_n in this Table refers to the flip angle for the n-th pulse in the composite pulse.

It must be emphasized here that our present treatment does not take into account any interaction amongst the quadrupolar spins that may be present. However, the comp-pulses reported here should serve as good model comp-pulses on which refinements could be made experimentally when interactions amongst the spins are present. Experimentally, while generation of rf pulses differing in phases by multiples of 90° is relatively simpler, generating rf pulses with arbitrary phase entails more hardware. In this regard comp-pulses with phase-alternated pulses are more attractive. Results [10] obtained by us with ^{35}Cl NQR lines in $NaClO_3$ and $HgCl_2$ powder specimen indicate that two- and three-pulse phase-alternated comp-pulses perform better than single rf pulses as "$\pi/2$" pulses with regard to broad band excitation. A comprehensive report on the experimental results with comp-pulses will be presented elsewhere. From these theoretical and preliminary experimental results obtaind by us it can be safely concluded that composite pulses can be used with advantage in NQR spectroscopy as well.

Table 2. Parameters for composite pulses for various quadrupolar nuclei. $A=(e^2qQ/kT)$.

I		C		θ_n
1		$\left(\frac{1}{4}\right) A(3+\eta)$		$2\omega_1 t_n$
$\frac{3}{2}$		$\left(\frac{\sqrt{3}}{16}\right) A\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}$		$\dfrac{(3+\eta)\,\omega_1 t_n}{\sqrt{3+\eta^2}}$
$\frac{5}{2}$ ($\eta=0$)	(i)	$\left(\frac{1}{40}\right) A$	for $\lvert\pm\tfrac{1}{2}\rangle \leftrightarrow \lvert\pm\tfrac{3}{2}\rangle$	$\sqrt{8}\,\omega_1 t_n$
	(ii)	$\left(\frac{\sqrt{5}}{20}\right) A$	for $\lvert\pm\tfrac{3}{2}\rangle \leftrightarrow \lvert\pm\tfrac{5}{2}\rangle$	$\sqrt{5}\,\omega_1 t_n$
$\frac{7}{2}$ ($\eta=0$)	(i)	$\left(\frac{9\sqrt{15}}{56}\right) A$	for $\lvert\pm\tfrac{1}{2}\rangle \leftrightarrow \lvert\pm\tfrac{3}{2}\rangle$	$\sqrt{15}\,\omega_1 t_n$
	(ii)	$\left(\frac{3\sqrt{12}}{7}\right) A$	for $\lvert\pm\tfrac{3}{2}\rangle \leftrightarrow \lvert\pm\tfrac{5}{2}\rangle$	$\sqrt{12}\,\omega_1 t_n$
	(iii)	$\left(\frac{11\sqrt{7}}{28}\right) A$	for $\lvert\pm\tfrac{5}{2}\rangle \leftrightarrow \lvert\pm\tfrac{7}{2}\rangle$	$\sqrt{7}\,\omega_1 t_n$

Acknowledgements

We thank the authorities of I.I.T., Kanpur for providing the facilities and the staff of the computer center for their valuable cooperation. We also thank Jennifer Bellinger for secretarial assistance. P.T.N. wishes to thank Dr. Brian D. Ross, Prof. John D. Roberts, Prof. J. H. Richards, and Mr. William Opel for their kind interest. A presentation of this work at the X-th ISNQRS at Takayama, Japan, was made possible by funds from the Huntington Medical Research Institutes, Pasadena.

[1] M. H. Levitt, Progr. NMR Spectry. **18,** 61 (1984).
[2] W. S. Warren and A. Zewail, J. Chem. Phys. **78,** 2279, 3583 (1983).
[3] J. C. Diels and S. Besnainou, J. Chem. Phys. **85,** 6347 (1986).
[4] W. Magnus, Commun. Pure Appl. Math. **7,** 649 (1954).
[5] U. Haeberlen, High Resolution NMR in Solids: Selective Averaging, Academic Press, New York 1976.
[6] M. Mehring, Principles of High Resolution NMR in Solids, 2nd edition, Springer, New York 1983.
[7] S. Vega and A. Pines, J. Chem. Phys. **66,** 5624 (1977).
[8] A. Ramamoorthy and P. T. Narasimhan, J. Mol. Struct. **192,** 333 (1989).
[9] R. Tycko, Phys. Rev. Lett. **51,** 775 (1983).
[10] A. Ramamoorthy and P. T. Narasimhan, Abstract. **M 44,** 30th ENC, Asilomar, Pacific Grove, California, USA (April 1989).
[11] a) G. J. Bowden and W. D. Hutchison, J. Magn. Reson. **67,** 403 (1986). – b) G. J. Bowden, W. D. Hutchison, and J. Khachan, J. Magn. Reson. **67,** 415 (1986).
[12] R. Reddy and P. T. Narasimhan, Mol. Phys. (submitted 1989).
[13] T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Phys. Suppl. 1, Academic Press, New York 1958.
[14] R. S. Cantor and J. S. Waugh, J. Chem. Phys. **73,** 1054 (1980).
[15] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Oxford Univ. Press, Oxford 1970.
[16] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.