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Multipole NMR. VIII. Evidence for Multipole Echoes for $I = 5/2$

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The multipole formulation of NMR is applied to a spin 5/2 in order to study the angle and phase dependence of the second rf pulse in the sequence $(\pi/2)_{\phi_1}-\tau_1-(\beta)_{\phi_2}-\tau_2$. It is shown that the experimental amplitudes of the echoes as a function of β for ^{127}I in KI crystals observed by Weisman and Bennett [*Phys. Rev.* **181**, 1341 (1969)] agree well with the spin dynamic calculation presented here. Only a nuclear quadrupole interaction is included in addition to the usual Zeeman terms. It is shown that by proper choice of β it is possible to suppress, or maximize, certain polarizations giving, for example at $\tau_2 = \tau_1$, a predominantly hexadecapole echo for $\beta = 45°$, $\phi_2 = 90$, $\phi_1 = 0$ in KI.

Since the work of Solomon (*1*), NMR solid echoes have been used to obtain information on the distribution of electric field gradients in solids (*2–7*). These studies usually make use of two-pulse sequences to create the echoes and since nuclear spins with $I \geq 1$ have nuclear electric quadrupole interaction, the name quadrupole echoes is used. In this paper we extend this idea to show that the different multipole *polarizations* contribute to and can dominate the echoes. For $I = 1$, at most quadrupole polarizations can occur; so a $(\pi/2)_0-\tau_1-(\pi/2)_{90}-\tau_2$ pulse sequence refocuses this at $\tau_2 = \tau_1$ which supports the nomenclature of being a quadrupole *polarization* echo. (See Fig. 6 of Ref. (*8*).) For higher I values, however, the same pulse sequence produces higher multipole contribution which can significantly contribute to the echoes. It is therefore of interest to determine whether it is possible to separate out the various multipole polarizations which contribute to echo formation. Stated otherwise, we wish to find pulse sequences which suppress the lower polarizations leaving the higher multipoles to refocus. In this paper we show that for $I = 5/2$ the three echoes produced by a two-pulse sequence can be made to reflect different multipole contributions by varying the second pulse angle.

In this paper, an echo which can be made such that one multipole polarization dominates is called a multipole echo. Hence a solid echo might be a quadrupole echo as in the case for $I = 1, 3/2, 5/2$, etc., subject to a $(\pi/2)_0-\tau_1-(\pi/2)_{90}-\tau_2$ pulse sequence. On the other hand, a $(\pi/2)_0-\tau_1-(\pi/4)_{90}-\tau_2$ pulse sequence completely suppresses quadrupole polarizations and maximized the hexadecapole polarization for the echoes at $\tau_2 = \tau_1/2$ and $2\tau_1$. In consequence these are called hexadecapole echoes.

To verify these ideas, the experimental data of Weisman and Bennett (*7*) are treated within the multipole formalism (*8–13*) and the echoes analyzed. Experimentally it is

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found that by varying the pulse angle β and the phases, ϕ_1 ϕ_2 in the sequence $(\pi/2)_{\phi_1}-\tau_1-(\beta)_{\phi_2}-\tau_2$, the amplitudes and shapes of the echoes change. It is shown that shifting the second pulse by 90° relative to the first, and choosing $\beta = \pi/2$, enhances the echoes at $\tau_2 = \tau_1/2$ and $2\tau_1$ for $^{127}I = 5/2$ in KI crystals while β of 45 and 135° maximizes the $\tau_2 = \tau_1$ echo amplitude. The angle dependence of the two echoes located at $\tau_2 = 2\tau_1$ and $\tau_2 = \tau_1/2$ has been measured (see Fig. 10 of Ref. (*7*).) In this paper we report first the results of a calculation based upon the multipole approach to the spin dynamics for $I = 5/2$. Using the two-pulse sequence above, it is then possible to quantitatively understand the amplitude variation as β changes. Since only an axially symmetric quadrupolar interaction is included together with a homogeneous magnetic field, the good agreement obtained shows that the amplitude changes are due solely to the nuclear electric quadrupole interaction and are not due to dipole–dipole interactions nor magnetic field inhomogeneities.

For a spin $I = 5/2$ the spin density operator is expanded in a multipole operator (*8, 11*) basis

$$\sigma_I(t) = \frac{1}{6}\,[E_I + \sum_{k=1}^{5}\sum_{q=-k}^{k} \mathcal{Y}^{(k)q}(\mathbf{I})\phi_q^k(t)]. \qquad [1]$$

Here $\mathcal{Y}^{(k)q}(\mathbf{I})$ are qth spherical components of kth rank tensor operators irreducible under the rotation group. The polarizations are (*10–12*)

$$\phi_q^k = \mathrm{tr}[\mathcal{Y}_q^{(k)}\sigma(t)] \qquad [2]$$

and the special case of $k = 1$, $q = \pm 1$ describes the magnetization in the xy plane. For $I = 5/2$ the quantity studied by Weisman and Bennett (*7*) is related to the ϕ_q^k's by

$$\phi_1^1(t) = i\sqrt{\frac{12}{35}}\,S(t). \qquad [3]$$

It is assumed that no coupling occurs while the pulse is on. Therefore for a pulse having amplitude, phase, and frequency of, respectively, H_1, ϕ_p and ω, the solutions are simply rotations given by

$$\tilde{\phi}_q^k([\alpha\beta]_{\phi_p}) = \sum_{q} \mathcal{D}_{qq'}^k((\alpha - \phi_p), \beta, (-\alpha + \phi_p))\tilde{\phi}_{q'}^k(0) \qquad [4]$$

where $(\omega_0 = \gamma H_z)$

$$\tilde{\phi}_q^k = e^{-iq\omega_0 t}\phi_q^k \qquad [5]$$

and the angles α and β are given ref. (*11*).

After a resonant $\pi/2$ pulse, the polarization $\phi_0^1(0)$ is transferred to the xy plane and the system develops for a time τ_1 under the influence of the quadrupolar Hamiltonian which is taken to be axially symmetric. In contrast to the effects of rf pulses, the quadrupole causes multipoles of different rank to be mixed. The time development in τ_1 therefore creates higher multipole character which is not observed in the τ_1 time, but which can be refocused in the τ_2 time domain by an appropriate second pulse. The results are

$$\tilde{\phi}_{\pm 1}^1\left[\left(\frac{\pi}{2}\right)_{\phi_1} - \tau_1\right] = \left(2\cos 2\chi_2 + \frac{16}{5}\cos\chi_1 + \frac{9}{5}\right)\frac{e^{\mp i\phi_1}}{7\sqrt{2}} \qquad [6a]$$

$$\hat{\phi}^2_{\pm1}\left[\left(\frac{\pi}{2}\right)_{\phi_1} - \tau_1\right] = \pm\left(\sqrt{10}\sin 2\chi_2 + 4\frac{\sqrt{2}}{5}\sin\chi_1\right)\frac{e^{\mp i\phi_1}}{7\sqrt{2}} \quad [6b]$$

$$\hat{\phi}^3_{\pm1}\left[\left(\frac{\pi}{2}\right)_{\phi_1} - \tau_1\right] = \left(\frac{4}{5}\cos\chi_1 - 2\cos 2\chi_2 + \frac{6}{5}\right]\frac{e^{\mp i\phi_1}}{\sqrt{2\cdot 3\cdot 7}} \quad [6c]$$

$$\hat{\phi}^4_{\pm1}\left[\left(\frac{\pi}{2}\right)_{\phi_1} - \tau_1\right] = \pm 2(\sin 2\chi_2 - 2\sin\chi_1)\frac{e^{\mp i\phi_1}}{7\sqrt{2}} \quad [6d]$$

$$\hat{\phi}^5_{\pm1}\left[\left(\frac{\pi}{2}\right)_{\phi_1} - \tau_1\right] = (\cos 2\chi_2 - 4\cos\chi_1 + 3)\frac{e^{\mp i\phi_1}}{7\sqrt{3}} \quad [6e]$$

where $\chi_1 = \pm 6Q_I\tau_1$, and $\chi_2 = \pm 12Q_I\tau_2$.

It is convenient to represent these polarizations as polar graphs (*8*) whereby the polarizations are written with respect to a spherical harmonic basis.

$$\phi^k = i\sqrt{4\pi}\sum_q \phi^k_q Y_{kq}(\theta\phi). \quad [7]$$

From [6] it is seen that ϕ^k_{-1} and ϕ^k_{-1} differ by at most a sign so that the combinations

$$Y_{kq}(\theta\phi) \pm Y_{k-q}(\theta\phi)$$

occur. With these functions we associate orbital shapes in accordance with the usual nomenclature for atomic orbitals (*8*). Figure 2a shows the orbital shapes following $(\pi/2)_x$–τ_1 pulse which are analytically given in [6]. Figures 2b and 2c show, respectively, the effects of a $(\pi/2)_y$ and $(\pi/4)_y$ pulse on each of those in 2a.

The next part of the pulse sequence requires the application of an rf pulse at resonance for a time such that the polarizations are turned by an angle β having a new phase angle of ϕ_2. For the sequence $\gamma_1 = (\pi/2)_{\phi_1}$–$\tau_1$–$(\beta)_{\phi_2}$ the full density matrix can be analytically calculated, the results being given in Ref. (*13*). Special cases follow by particular choices of β and ϕ. For example the Jeener–Broekaert sequence requires $\beta = \pi/4$, and the phase $\phi_2 = \pi/2$, which gives $\phi^1_0(\gamma_1) = \phi^3_0(\gamma_1) = \phi^5_0(\gamma_1) = 0$ while $\phi^2_0(\gamma_1) \neq 0$, $\phi^4_0(\gamma_1) \neq 0$. These, once produced, require a third $(\pi/4)_{90}$ pulse to transfer ϕ^2_0 and ϕ^4_0 to the xy plane.

In the final τ_2 period in the pulse sequence $\gamma_2 = (\pi/2)_0$–τ_1–$(\beta)_{90}$–τ_2 the only NMR observable is $\phi^1_{\pm1}$ $[\gamma_2]$. This is given by

$$\begin{aligned}\hat{\phi}^1_{\pm1}[\gamma] = {} & [9 + 16\cos\chi_2 + 10\cos 2\chi_2][9 + 16\cos\chi_1 + 10\cos 2\chi_1]\frac{1}{5^2\cdot 7^2\sqrt{2}} \\ & - \left[4\frac{\sqrt{2}}{5}\sin\chi_2 + \sqrt{10}\sin 2\chi_2\right]\left[4\frac{\sqrt{2}}{5}\sin\chi_1 + \sqrt{10}\sin 2\chi_1\right]\frac{A(\beta)}{7^2\sqrt{2}} \\ & + [6 + 4\cos\chi_2 - 10\cos 2\chi_2][6 + 4\cos\chi_1 - 10\cos 2\chi_1]\frac{B(\beta)}{3\cdot 4\cdot 7\cdot 5^2\sqrt{2}} \\ & - [2\sin\chi_2 - \sin 2\chi_2][2\sin\chi_1 - \sin 2\chi_1]\frac{C(\beta)}{2\cdot 7^2\sqrt{2}} \\ & + [3 - 4\cos\chi_2 + \cos 2\chi_2][3 - 4\cos\chi_1 + \cos 2\chi_1]\frac{D(\beta)}{3\cdot 8\cdot 7^2\sqrt{2}} \end{aligned} \quad [8]$$

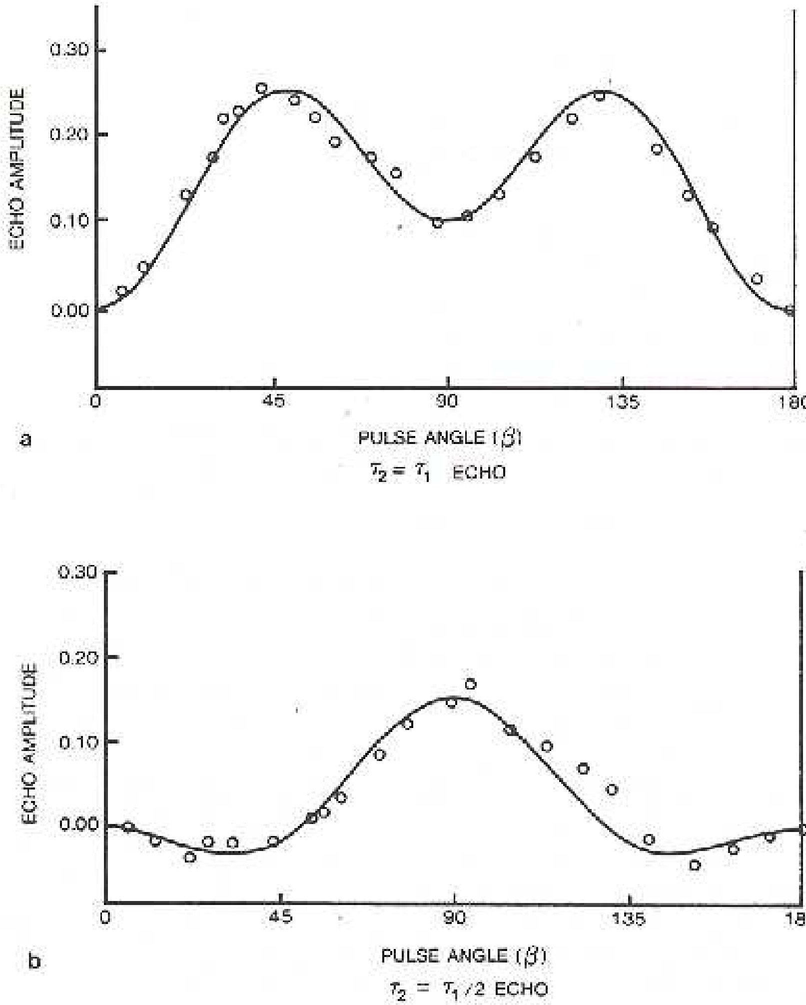

FIG. 1. Comparison between experimental and theoretical angle dependence for two pulse sequence $(\pi/2)_0$–τ_1–$(\beta)_{90}$–τ_2 on (a) $\tau_2 = \tau_1$ echo from [10] and (b) $\tau_2 = \tau_1/2$ and $\tau_2 = 2\tau_1$ echoes from [11]. Circles correspond to data from Ref. (7).

where

$$A(\beta) = 2\cos^2\beta - 1 \qquad [9a]$$

$$B(\beta) = 1 + 3\cos^2\beta - 2\sin^2\beta \qquad [9b]$$

$$C(\beta) = \cos^4\beta + 30\sin^4\beta + 6\cos^2\beta - 25\sin^2\beta(1 + \cos^2\beta) + 1 \qquad [9c]$$

$$D(\beta) = 5\cos^4\beta + 10\cos^2\beta + 10\sin^4\beta - 9\sin^2\beta(1 + 3\cos^2\beta) + 1. \qquad [9d]$$

Weisman and Bennett present experimental results for ^{127}I echoes in KI crystals, in Figs. 10 and 11 of Ref. (7). When $\beta = \pi/2$ and $\phi_2 = 90$, the ratio of the $\tau_2 = \tau_1$

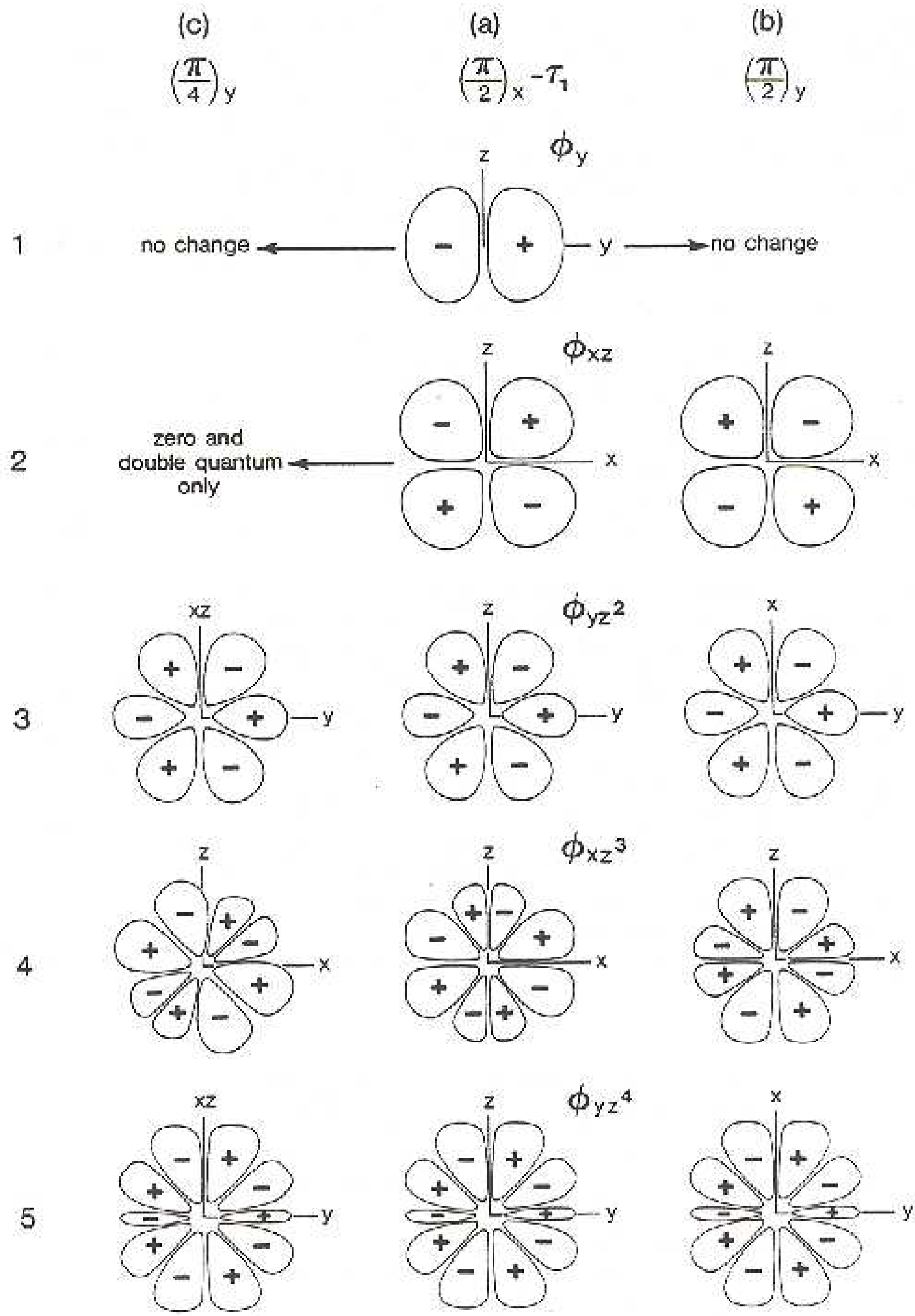

FIG. 2. Orbital shapes of the various polarizations. (a) only single-quantum coherences we produced in τ_1 but these are rotated anticlockwise about the y axis by $\pi/2$ in (b) and $\pi/4$ in (c). Generally the new orientation of the lobes leads to other multiquantum coherences. (See Table 2). The axis xz lies at 45° between the x and z axes.

echo amplitude to that of $\tau_2 = \tau_1/2$ is 0.68. From Eq. [8] is is found that the $\tau_2 = \tau_1$ echo amplitude is $41/280\sqrt{2}$ and that of the $\tau_2 = \tau_1/2$ and $\tau_2 = 2\tau_1$ echo is $3/14\sqrt{2}$. this gives a ratio of 0.68 in agreement with experiment.

To study the β dependence of the echo amplitudes, Eq. [8] is used to collect all terms involving $\cos(\chi_1 - \chi_2)$, $\cos(\chi_1 - 2\chi_2)$, and $\cos(2\chi_1 - \chi_2)$ which give the echo positions. The resulting β dependence for the $\tau_2 = \tau_1$ echo is given by

$$\epsilon_{\rm I}(\beta) = \frac{178}{1225\sqrt{2}} - \frac{41 \cdot A(\beta)}{245\sqrt{2}} + \frac{29 \cdot B(\beta)}{1050\sqrt{2}} - \frac{5 \cdot C(\beta)}{196\sqrt{2}} + \frac{17 \cdot D(\beta)}{2352\sqrt{2}} \qquad [10]$$

while for the $\tau_2 = \tau_1/2$ and $\tau_2 = 2\tau_1$ echoes it is given by

$$\epsilon_{\rm II}(\beta) = \frac{16}{245\sqrt{2}} - \frac{4A(\beta)}{49\sqrt{2}} - \frac{B(\beta)}{105\sqrt{2}} + \frac{C(\beta)}{98\sqrt{2}} - \frac{D(\beta)}{588\sqrt{2}}. \qquad [11]$$

The β dependence of the $\tau_2 = \tau_1/2$ and $\tau_2 = 2\tau_1$ echoes are identical. The β dependence of these echo amplitudes is plotted in Figs. 1a and b. The constant contribution $178/1225\sqrt{2}$ is subtracted out in Fig. 10b of Ref. (*7*). The circles in Fig. 1 correspond to the experimental points from Fig. 10 of Ref. (*7*) and are in excellent agreement.

It is possible to visualize the formation of these echoes by means of polar graph representations (*8*). Since each multipole polarization can be given an orbital shape, one can follow the evolution of the multipole polarizations graphically. Figure 4 of (*8*) shows the quadrupole echo formation for a spin 1. For a spin 5/2, the same description is applicable but with modifications resulting from the existence of higher multipoles. Figure 2a shows the orbitals produced from ϕ_y due to quadrupole coupling. The second pulse rotates these and introduces sign changes. (Figs. 2b and 2c).

Consider a $(\pi/2)_{90}$ second pulse which rotates about the y axis. It leaves ϕ_y unchanged, but rotates $\phi_{yz^2} \equiv \phi_y(5z^2 - r^2)$, and $\phi_{yz^4} = \phi_y(21z^4 - 14z^2r^2 + r^4)$ out of the zy plane into the xy plane. This reduces their relative magnitudes. On the other hand the polarizations ϕ_{xz} and $\phi_{xz^3} \equiv \phi_x(7z^3 - 3zr^2)$ remain in the xz plane but with reoriented lobes. The associated sign changes caused by the pulse leads to constructive or destructive interference between the polarizations as they evolve. The calculations

TABLE 1

Summary of Dominant Contributions to the Echo Amplitudes A from Quadrupole Q or Hexadecapole H Polarizations for Second Pulse Angles β

$I = 5/2$	Echo position	
β	$\tau_2 = \tau_1/2,\ 2\tau_1$	$\tau_2 = \tau_1$
90°	Maximized $A \approx Q - H$	Minimized
69°, 111°	Quadrupole echo $A \approx Q$	—
45°	Minimized	Hexadecapole echo $A \approx H$

TABLE 2

Parallel Description to Fig. 2 Which Shows the Nonzero Multiquantum Coherences (MQ) into Which the Reoriented Lobes Can Be Decomposed

(2^N) N	(c) $(\pi/4)_y$	(a) $(\pi/2)_x - \tau_1$	(b) $(\pi/2)_y$
1	ϕ_y	ϕ_y	ϕ_y
2	0Q, 2Q	ϕ_{xz}	$-\phi_{xz}$
3	ϕ_{yz^2}, 2Q, 3Q	ϕ_{yz^2}	$-\phi_{yz^2}$, 3Q
4	ϕ_{xz^3}, 2Q, 3Q, 4Q	ϕ_{xz^3}	ϕ_{xz^3}, 3Q
5	$-\phi_{yz^4}$, 2Q, 3Q, 4Q, 5Q	ϕ_{yz^4}	ϕ_{yz^4}, 3Q, 5Q

given here (see also (*13*)) show that for the $\tau_2 = \tau_1/2$ and $\tau_2 = 2\tau_1$ echoes, the quadrupole ϕ_{xz} and hexadecapole ϕ_{xz^3} properties add to maximize the amplitudes; while for the $\tau_2 = \tau_1$ echo, the two polarizations have opposite signs and almost cancel. Hence we denote the $\tau_2 = \tau_1/2$, $2\tau_1$ echoes as quadrupole in character for $(\beta)_{\phi_2} = (\pi/2)_{90}$.

It is possible to suppress virtually all contributions to this echo by choosing the second out-of-phase pulse angle as either 69 or 111°. Under these conditions the amplitudes of the three echoes are about equal and arise from almost pure quadrupole polarization, the ratio of the amplitudes being, from [10] and [11],

$$\frac{A_{\tau_2=\tau_1}}{A_{\tau_2=\tau_1/2}} = \frac{41\cdot 49}{8\cdot 245} = 1\cdot 025 \qquad [12]$$

—"almost pure" quadrupole means that the $\tau_2 = \tau_1$ echo in 87% quadrupole while the $\tau_2 = \tau_1/2$, $2\tau_1$ are 97% quadrupole. It is the latter two which are denoted as quadrupole echoes.

It is possible to suppress completely the quadrupole parts by using a $(\pi/2)_0$–τ_1–$(\pi/4)_{90}$–τ_2 pulse sequence. This case corresponds to the first part of a Jeener–Broekaert sequence which produces no ϕ_{xz}. On the other hand the remaining three single-quantum coherences ϕ_{yz^2}, ϕ_{xz^3}, and ϕ_{yz^4} occur but are dominated by the hexadecapole which accounts for 71% of the intensity of the $\tau_2 = \tau_1$ echo. The reason for more ϕ_{yz} (23%) and ϕ_{yz^4} (6%) contribution to this echo than to the pure quadrupole echoes described above is that the $\pi/4$ pulse only rotates ϕ_{yz} and ϕ_{yz^4} to 45° between the z and x axis, while the $\pi/2$ pulse puts ϕ_{yz} and ϕ_{yz^4} completely in the xy plane (see Fig. 2). These arguments show that the $(\beta)_{\phi_2} = (\pi/4)_{90}$ pulse produce a predominantly hexadecapole echo at $\tau_2 = \tau_1$. Table 1 summarizes the results.

The composition of the echoes in terms of polarizations depends critically upon the pulse angles. In general each echo reflects the development of all the single-quantum coherences in the τ_1 period, but certain second-pulse angles and phases can be made to maximize or suppress various contributions. A systematic analysis, using different angles, should make it possible to extract the relaxation properties of individual multipole polarizations.

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