Measurement of the Quadrupolar Coupling with Two Pulses of Opposite Phase

P. P. MAN

Laboratoire de Chimie des Surfaces, C.N.R.S. U.R.A. 14:28, Université Pierre et Marie Curie,
4 Place Jussieu, Tour 55, 75252 Paris, Cedex 05, France

Received September 21, 1990; revised January 22, 1991

The central line intensity of a spin-½ system following excitation by two RF pulses of opposite phase is calculated using the fictitious spin-4 operator formalism. Measurement of this line intensity as a function of the duration of the second pulse enables the quadrupolar coupling ωQ to be determined. Moreover, alternating the phase of the second pulse will filter the polarizations and the double-quantum coherences; only the single- and the triple-quantum coherences are detected. The opposite case happens when the receiver phase is also alternated. These methods are illustrated in a study of 7Li nuclei in a single crystal of LiTaO₃. In the particular case of the rotary-echo sequence, signals having small or large ωQ values compared to the amplitude of the pulse are filtered.

Much progress has been made in relating NMR data to structural information in inorganic solids (1–5). Recently Lippmaa et al. (6) have shown that there is a linear dependence of 27Al chemical shifts on the mean [Al–O–Si] bond angles in framework aluminosilicates. But a precise determination of true 27Al chemical shift (δCS) is necessary (7) and this requires accurate values of the quadrupolar coupling constant (e²qQ/h), the asymmetry parameter (η), and the chemical shift (δCG) of the center of gravity of the lineshape. Several methods are available for this purpose. For a non-symmetrical lineshape, magic-angle spinning or variable-angle spinning (8, 9) gives a better spectrum from which e²qQ/h, η, and δCG can be obtained by comparison with simulated spectra. Another way of obtaining these parameters is to examine the spinning sideband intensities over a wide spectral width (10, 11). With double-rotor spinning (12–14), δCG can be directly measured. If the lineshape is symmetrical, other methods based on two-dimensional NMR are available for determining e²qQ/h and η; quadrupolar nutation (15–19), rotary-echo nutation (20, 21), or two-pulse sequence (22–24). With modern high-power pulsed spectrometers, these 2D experiments are easy to perform. As shown by Janssen et al. (20), the extension of the quadrupolar nutation is rotary-echo nutation, where two consecutive radiofrequency pulses of equal length and opposite phase are applied.

In this paper a generalization of rotary-echo nutation is presented, where a delay τ₂ is introduced between the two pulses. The time-domain response F(t₁, τ₂, t₃, τ₄) of a spin I = ½ system excited by the {X}—τ₂—{−X}—τ₄ sequence is studied for any ratio of ωQ/ωRF, where ωQ is the quadrupolar coupling and ωRF the amplitude of the pulse. In the particular case of rotary-echo nutation, this sequence applied to a
FIG. 1. A sequence of two x pulses of opposite phase; \( t_1 \) and \( t_3 \) are the lengths, \( \tau_2 \) is the delay between them, and \( \tau_4 \) is the signal acquisition delay.

A single crystal behaves like a bandpass filter which eliminates signals having very strong or very weak \( \omega_Q \) values compared to \( \omega_{RF} \). The fictitious spin-1/2 operator formalism is used for this computation (25–27). An experimental study of \(^7\)Li nuclei in a single crystal of LiTaO\(_3\) has been carried out to illustrate the application of these calculations.

**THEORY**

As in previous papers (22, 23), only the first-order quadrupolar interaction \( H_Q^{(1)} \) is considered during the experiment,

\[
H_Q^{(1)} = \frac{1}{2} \omega_Q [3 J_z^2 - J(J+1)],
\]

with

\[
\omega_Q = \left[ 3 e^2 q Q / 8 I (2I - 1) \right] \{ 3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2 \alpha \}.
\]

The Euler angles \( \alpha \) and \( \beta \) describe the orientation of the strong static magnetic field \( B_0 \) in the principal-axis system of the electric-field-gradient (efg) tensor. In Fig. 1 are shown the Hamiltonians during the four periods. The dynamics of the spin system is described by the density matrix expressed in the rotating frame,

\[
\rho(t_1, \tau_2, t_3, \tau_4) = \exp(-i \mathcal{H}_Q^{(1)} \tau_4) \exp(-i \mathcal{H}^{(b)} t_3) \exp(-i \mathcal{H}_Q^{(1)} \tau_2) \exp(-i \mathcal{H}^{(a)} t_1) \rho(0) \exp(i \mathcal{H}^{(a)} t_1) \exp(i \mathcal{H}_Q^{(1)} \tau_2) \exp(i \mathcal{H}^{(b)} t_3) \exp(i \mathcal{H}_Q^{(1)} \tau_4),
\]

where

\[
\mathcal{H}^{(a)} = -\omega_{RF} I_x + H_Q^{(1)},
\]

\[
\mathcal{H}^{(b)} = +\omega_{RF} I_x + H_Q^{(1)},
\]

\[
\rho(0) = I_z.
\]

\( \mathcal{H}^{(a)} \) and \( \mathcal{H}^{(b)} \) were diagonalized with the same procedure (16, 27). \( \mathcal{T} \) and \( T \) and \( \mathcal{U} \) and \( U \) are the diagonalized form and the transformation operator of \( \mathcal{H}^{(a)} \) and \( \mathcal{H}^{(b)} \), respectively,
TABLE 1

Matrices Belonging to the Matrices \( n_1, n_2, \) and \( n_3 \)

\[
\begin{align*}
a_1 &= \begin{bmatrix}
\cos \theta \cos \omega_{14,13} \\
\cos \theta \cos \omega_{23,13} \\
-\cos \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{14,13} \\
\sin \theta \cos \omega_{12,13} \\
-\sin \theta \cos \omega_{24,13} \\
-\sin \theta \sin \omega_{24,13} \\
\sin \theta \cos \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
\cos \theta \cos \omega_{14,13} \\
-\cos \theta \cos \omega_{23,13} \\
\cos \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{14,13} \\
\sin \theta \sin \omega_{12,13} \\
\sin \theta \cos \omega_{24,13} \\
\sin \theta \sin \omega_{24,13} \\
-\sin \theta \cos \omega_{12,13}
\end{bmatrix},
\end{align*}
\]

\[
\begin{align*}
h_1 &= \begin{bmatrix}
-\sin \theta \cos \omega_{14,13} \\
-\sin \theta \cos \omega_{23,13} \\
\sin \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{14,13} \\
\cos \theta \cos \omega_{24,13} \\
\cos \theta \cos \omega_{24,13} \\
\sin \theta \cos \omega_{12,13} \\
\cos \theta \cos \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
\sin \theta \cos \omega_{14,13} \\
\sin \theta \cos \omega_{23,13} \\
-\sin \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{14,13} \\
\cos \theta \cos \omega_{24,13} \\
\cos \theta \cos \omega_{24,13} \\
-\sin \theta \cos \omega_{12,13} \\
-\sin \theta \cos \omega_{12,13}
\end{bmatrix},
\end{align*}
\]

\[
\begin{align*}
c_1 &= \begin{bmatrix}
\cos \theta \sin \omega_{14,13} \\
\cos \theta \sin \omega_{23,13} \\
-\cos \theta \cos \omega_{23,13} \\
\sin \theta \sin \omega_{14,13} \\
\sin \theta \sin \omega_{34,13} \\
\sin \theta \sin \omega_{34,13} \\
\cos \theta \sin \omega_{12,13} \\
\cos \theta \sin \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
\sin \theta \sin \omega_{14,13} \\
\sin \theta \sin \omega_{23,13} \\
-\cos \theta \cos \omega_{23,13} \\
\sin \theta \sin \omega_{14,13} \\
-\sin \theta \cos \omega_{34,13} \\
-\sin \theta \cos \omega_{34,13} \\
\cos \theta \sin \omega_{12,13} \\
-\cos \theta \sin \omega_{12,13}
\end{bmatrix},
\end{align*}
\]

\[
\begin{align*}
d_1 &= \begin{bmatrix}
\cos \theta \sin \omega_{14,13} \\
\cos \theta \sin \omega_{23,13} \\
-\cos \theta \cos \omega_{23,13} \\
\sin \theta \sin \omega_{14,13} \\
\sin \theta \sin \omega_{34,13} \\
\sin \theta \sin \omega_{34,13} \\
\cos \theta \sin \omega_{12,13} \\
-\cos \theta \sin \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
\sin \theta \sin \omega_{14,13} \\
\sin \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{23,13} \\
\sin \theta \sin \omega_{14,13} \\
\sin \theta \cos \omega_{34,13} \\
\sin \theta \cos \omega_{34,13} \\
\cos \theta \sin \omega_{12,13} \\
\cos \theta \sin \omega_{12,13}
\end{bmatrix},
\end{align*}
\]

\[
\begin{align*}
f_1 &= \begin{bmatrix}
-\sin \theta \sin \omega_{14,13} \\
-\sin \theta \sin \omega_{23,13} \\
\sin \theta \cos \omega_{24,13} \\
\sin \theta \sin \omega_{24,13} \\
\sin \theta \cos \omega_{34,13} \\
\sin \theta \cos \omega_{34,13} \\
-\cos \theta \sin \omega_{12,13} \\
\cos \theta \cos \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
-\sin \theta \sin \omega_{14,13} \\
-\sin \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{24,13} \\
-\sin \theta \cos \omega_{24,13} \\
\sin \theta \cos \omega_{34,13} \\
\sin \theta \cos \omega_{34,13} \\
-\cos \theta \sin \omega_{12,13} \\
-\cos \theta \sin \omega_{12,13}
\end{bmatrix},
\end{align*}
\]

\[
\begin{align*}
g_1 &= \begin{bmatrix}
-\sin \theta \sin \omega_{14,13} \\
-\sin \theta \sin \omega_{23,13} \\
\sin \theta \cos \omega_{24,13} \\
\sin \theta \sin \omega_{24,13} \\
\sin \theta \cos \omega_{34,13} \\
\sin \theta \cos \omega_{34,13} \\
-\cos \theta \sin \omega_{12,13} \\
\cos \theta \cos \omega_{12,13}
\end{bmatrix}
&= \begin{bmatrix}
-\sin \theta \sin \omega_{14,13} \\
-\sin \theta \sin \omega_{23,13} \\
\cos \theta \cos \omega_{24,13} \\
-\sin \theta \cos \omega_{24,13} \\
\sin \theta \cos \omega_{34,13} \\
\sin \theta \cos \omega_{34,13} \\
-\cos \theta \sin \omega_{12,13} \\
\cos \theta \cos \omega_{12,13}
\end{bmatrix}.
\end{align*}
\]

\[
\mathcal{H}_U = U^+ \mathcal{H}_T^T U.
\]  \[6\]

with

\[
\mathcal{H}_U = -\omega_{24} I_{2,3} - \omega_{13} I_{2,4}^2 - \omega_{RF}(I_{1,2}^1 + I_{2,4}^3),
\]  \[7a\]

\[
U = \exp \left( \frac{i \pi}{2} (I_{1,4}^1 - I_{2,3}^2) \right) \exp(i2\theta_2 I_{1,3}^2) \exp(i2\theta_1 I_{1,4}^2).
\]  \[7b\]

\( \mathcal{H}_T \) and \( T \) were obtained previously (22). Thus Eq. [2] can be rewritten as

\[
\rho(t_1, t_2, t_3, t_4) = \exp(-i \mathcal{H}_T^{(1)} t_4) U \exp(-i \mathcal{H}_U t_3) U^+ \exp(-i \mathcal{H}_T^{(1)} t_2) T
\]

\times \exp(-i \mathcal{H}_T^T t_1) T^+ \rho(0) T \exp(i \mathcal{H}_T^T t_1) T^+ \exp(i \mathcal{H}_T^{(1)} t_2) U
\]

\times \exp(i \mathcal{H}_U t_3) U^+ \exp(i \mathcal{H}_T^{(1)} t_4).  \[8\]
TABLE 2
Relationships between Results Concerning the \( \{X\} \rightarrow \tau_2 \rightarrow \{-X\} \rightarrow \tau_4 \) Sequence (this Work) and the \( \{X\} \rightarrow \tau_2 \rightarrow \{X\} \rightarrow \tau_4 \) Sequence (Ref. (22))

<table>
<thead>
<tr>
<th>( \Psi \Delta A )</th>
<th>( \Psi \Gamma A )</th>
<th>( \Psi \Omega A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\xi \Delta a )</td>
<td>( -\xi \Gamma a )</td>
<td>( -\xi \Omega a )</td>
</tr>
<tr>
<td>( -\xi \Delta h )</td>
<td>( -\xi \Gamma h )</td>
<td>( -\xi \Omega h )</td>
</tr>
<tr>
<td>( +\xi \Delta b )</td>
<td>( +\xi \Gamma b )</td>
<td>( +\xi \Omega b )</td>
</tr>
<tr>
<td>( -\xi \Delta c )</td>
<td>( -\xi \Gamma c )</td>
<td>( -\xi \Omega c )</td>
</tr>
<tr>
<td>( +\xi \Delta d )</td>
<td>( -\xi \Gamma d )</td>
<td>( +\xi \Omega d )</td>
</tr>
<tr>
<td>( +\xi \Delta e )</td>
<td>( +\xi \Gamma e )</td>
<td>( +\xi \Omega e )</td>
</tr>
<tr>
<td>( -\xi \Delta f )</td>
<td>( -\xi \Gamma f )</td>
<td>( -\xi \Omega f )</td>
</tr>
<tr>
<td>( +\xi \Delta g )</td>
<td>( +\xi \Gamma g )</td>
<td>( +\xi \Omega g )</td>
</tr>
</tbody>
</table>

Now the expressions of the density matrix during the four periods of time are detailed. The quantities \( \rho(t_1) \) and \( \rho(t_1, \tau_2) \), describing the spin system at the end of the first pulse and before the application of the second, respectively, are similar to those obtained previously (22). During the second pulse, the evolution of the spin system is described by the Hamiltonian \( \mathcal{H}^{(b)} \). So the density matrix becomes

\[
\rho(t_1, \tau_2, t_3) = U \exp(-i\mathcal{H} U t_3) U^+ \rho(t_1, \tau_2) U \exp(i\mathcal{H} U t_3) U^+ \\
= \frac{1}{2} \xi \{ U \exp(-i\mathcal{H} U t_3) U^+ (M_1 + M_2 \cos 2\omega Q \tau_2 + M_3 \sin 2\omega Q \tau_2) U \\
\times \exp(i\mathcal{H} U t_3) U^+ \} K. \quad [9]
\]

Application of the operator \( U \exp(-i\mathcal{H} U t_3) U^+ \) and its adjoint to the eight spin operators \( A, \ldots, H \) composing the matrices \( M_i \), then yields

\[
\rho(t_1, \tau_2, t_3) = \frac{1}{2} \xi \{ \frac{1}{2} (\Psi[M_1 + M_2]) \cap (n_1 + n_2 \cos 2\omega Q \tau_2 + n_3 \sin 2\omega Q \tau_2) \} K, \quad [10]
\]

with

\[
\Psi = (\cos \theta_+, \cos \theta_-, \sin \theta_+, -\sin \theta_-). \quad [11]
\]

The matrices \( n_1, n_2, \) and \( n_3 \) have the same form as the matrices \( m_1, m_2, \) and \( m_3 \) except that their elements are column matrices \( (a_1, \ldots, h_1) \) given in Table 1 instead of \( (a, \ldots, h) \). The symbol \( \cap \) means matrix multiplication of \( \Psi M_i \) by each column matrix \( (a_1, \ldots, h_1) \) inside \( n_1, n_2, \) and \( n_3 \). Finally, the density matrix after the second pulse is described by

\[
\rho(t_1, \tau_2, t_3, \tau_4) = \exp(-i\mathcal{H}'^{(1)}(\tau_4) \rho(t_1, \tau_2, t_3) \exp(i\mathcal{H}'^{(1)}(\tau_4)) = \frac{1}{2} \xi \{ \frac{1}{2} (\Psi[M_1 \\
\quad + M_2 \cos 2\omega Q \tau_4 + M_3 \sin 2\omega Q \tau_4]) \cap (n_1 + n_2 \cos 2\omega Q \tau_2 + n_3 \sin 2\omega Q \tau_2) \} K. \quad [12]
\]

Knowledge of the density matrix allows the determination of experimentally accessible data, \( F^c(t_1, \tau_2, t_3, \tau_4) \) and \( F^s(t_1, \tau_2, t_3, \tau_4), \) the intensity of the central and a satellite line, respectively,

\[1\] The notation employed is defined in Refs. (22) and (23). For consistency with the material in these references, many matrices are represented here by italic, rather than boldface characters.
Fig. 2. Theoretical central line intensity $F_3(t_1, t_2 \neq 0, t_3 = t_1)$ (Eq. [19]) of a spin $I = \frac{3}{2}$ excited by the rotary-echo sequence versus the pulse length $t_3$ for $\omega_{RF}/2\pi = 50$ kHz and several values of the quadrupolar coupling $\omega_Q/2\pi$. Upper figure: $\bullet$ (1 kHz), $\bigcirc$ (10 kHz), $\blacksquare$ (15 kHz), $\square$ (24 kHz); lower figure: $\bullet$ (26 kHz), $\bigcirc$ (50 kHz), $\blacksquare$ (200 kHz), $\square$ (1 MHz).

\[
F^c(t_1, t_2, t_3, t_4) = \text{Tr}[\rho(t_1, t_2, t_3, t_4)2I^{23}_y] \\
= \frac{1}{2} \xi\left\{ (\Psi \Delta) \otimes (n_1 + n_2 \cos 2\omega_Q \tau_2 + n_3 \sin 2\omega_Q \tau_2) \right\} \mathcal{K} \tag{13}
\]

\[
F^s(t_1, t_2, t_3, t_4) = \text{Tr}[\rho(t_1, t_2, t_3, t_4)\sqrt{3}I^{12}_y] = \frac{1}{2} \xi\left\{ \left( \frac{\sqrt{3}}{2} \Psi \Omega \cos 2\omega_Q \tau_4 \\
+ \Gamma \sin 2\omega_Q \tau_4 \right) \otimes (n_1 + n_2 \cos 2\omega_Q \tau_2 + n_3 \sin 2\omega_Q \tau_2) \right\} \mathcal{K} \tag{14}
\]

with

\[
\Delta = \text{TR}[M_1I^{23}_y], \quad \Omega = \text{TR}[M_2I^{12}_y], \quad \Gamma = \text{TR}[M_3I^{12}_y]. \tag{15}
\]

$\text{TR}$ means the trace of each element of the matrix $M_jI^{jk}_y$. The final expression for $F^c(t_1, t_2, t_3, t_4)$ is
\[ F^c(t_1, \tau_2, t_3, \tau_4) = \Psi \Delta e_{12} \text{Tr}[\rho(t_{12})(I_{y}^{2,3} + I_{y}^{1,4})] + \Psi \Delta d_{12} \text{Tr}[\rho(t_{12})(I_{y}^{2,3} - I_{y}^{1,4})] \]

\[ + \Psi \Delta a_{12} \text{Tr}[\rho(t_{12})(I_{y}^{1,4} - I_{y}^{2,3})] + \Psi \Delta b_{12} \text{Tr}[\rho(t_{12})(I_{y}^{1,4} + I_{y}^{2,3})] \]

\[ + \{ \Psi \Delta b_{12} \cos 2\omega_{Q}\tau_2 - \Psi \Delta c_{12} \sin 2\omega_{Q}\tau_2 \} \text{Tr}[\rho(t_{12})(I_{y}^{1,4} - I_{y}^{1,2})] \]

\[ + \{ \Psi \Delta c_{12} \cos 2\omega_{Q}\tau_2 + \Psi \Delta b_{12} \sin 2\omega_{Q}\tau_2 \} \text{Tr}[\rho(t_{12})(I_{y}^{1,4} + I_{y}^{1,2})] \]

\[ + \{ \Psi \Delta c_{12} \cos 2\omega_{Q}\tau_2 - \Psi \Delta a_{12} \sin 2\omega_{Q}\tau_2 \} \text{Tr}[\rho(t_{12})(I_{y}^{1,3} + I_{y}^{2,4})] \]

\[ + \{ \Psi \Delta a_{12} \cos 2\omega_{Q}\tau_2 + \Psi \Delta c_{12} \sin 2\omega_{Q}\tau_2 \} \text{Tr}[\rho(t_{12})(I_{y}^{1,3} - I_{y}^{2,4})]. \] [16]

In fact, \( F^c \) does not depend on \( \tau_4 \). This is not surprising because, when relaxation phenomena are disregarded, the line intensity of the on-resonance transition depends

FIG. 4. Experimental central line intensity of \(^7\)Li from Fig. 3 (squares) and theoretical central line intensity \( F^c(t_1, \tau_2, t_3) \) of Eq. [16] (solid line), plotted versus \( t_3 \).
FIG. 5. $^7$Li NMR spectra of a single crystal of LiTaO$_3$, obtained with the sequence $\{ X \} - \tau_2 - \{ -X \} - \tau_4[\text{acquisition}(y)] - \text{recycle delay} - \{ X \} - \tau_2 - \{ X \} - \tau_4[\text{acquisition}(-y)] - \text{recycle delay}$ for increasing $\tau_1$, $\tau_3 = 20$ $\mu$s, and $\tau_4 = 10$ $\mu$s.

on the pulse length. From now on, $\tau_4$ is dropped in the parentheses of $F^c$. The expression for a satellite line intensity is similar to Eq. [16], where $\Delta$ must be replaced by $\sqrt{3}[\Omega \cos 2\omega_Q\tau_4 + \Gamma \sin 2\omega_Q\tau_4]/2$. The $\text{Tr}[\rho(t_f)T_i]$ terms were defined previously (22). By comparing the results with the previous ones concerning two pulses of the same phase (22), the relationships given in Table 2 can be established. Two applications are now considered.

Alternate phase sequences. Consider the experimental condition $\tau_2 \ll T_{\text{FID}}$, where $T_{\text{FID}}$ is the duration of the free induction decay (FID) following the first pulse. The spin–spin and spin–lattice relaxations can be neglected. If the phase of the second pulse alternates, e.g., $\{ X \} - \tau_2 - \{ -X \} - \tau_4[\text{acquisition}(y)] - \text{recycle delay} - \{ X \} - \tau_2 - \{ X \} - \tau_4[\text{acquisition}(y)] - \text{recycle delay}$, where $y$ is the receiver phase, the central line intensity becomes

![Graph](image-url)

FIG. 6. Experimental central line intensity of $^7$Li from Fig. 5 (squares) and theoretical central line intensity $F^c_i(t_\ell, \tau_2, \tau_3)$ of Eq. [18] (solid line), plotted versus $\tau_3$. 

Fig. 5. $^7$Li NMR spectra of a single crystal of LiTaO$_3$, obtained with the sequence $\{ X \} - \tau_2 - \{ -X \} - \tau_4[\text{acquisition}(y)] - \text{recycle delay} - \{ X \} - \tau_2 - \{ X \} - \tau_4[\text{acquisition}(-y)] - \text{recycle delay}$ for increasing $\tau_1$, $\tau_3 = 20$ $\mu$s, and $\tau_4 = 10$ $\mu$s.
QUADRUPOLE COUPLING FROM OPPOSITE-PHASE PULSES

Fig. 7. $^7$Li NMR spectra of a single crystal of LiTaO$_3$, obtained with the rotary-echo sequence, for increasing $t_3$ ($=t_1$) and $\tau_4 = 10$ $\mu$s.

\begin{equation}
F^z(t_1, \tau_2, t_3) = \Psi \Delta e_i \text{Tr}[\rho(t_1)(I^{13}_z + I^{14}_z)] + \Psi \Delta d_i \text{Tr}[\rho(t_1)(I^{13}_z - I^{14}_z)]
\end{equation}

\begin{equation}
+ \{ \Psi \Delta b_1 \cos 2\omega Q \tau_2 - \Psi \Delta g_1 \sin 2\omega Q \tau_2 \} \text{Tr}[\rho(t_1)(I^{14}_z - I^{13}_z)]
\end{equation}

\begin{equation}
+ \{ \Psi \Delta g_1 \cos 2\omega Q \tau_2 + \Psi \Delta b_1 \sin 2\omega Q \tau_2 \} \text{Tr}[\rho(t_1)(I^{13}_z + I^{14}_z)].
\end{equation}

The polarizations and the double-quantum coherences present in Eq. [16] are canceled.

If the receiver phase also alternates during the sequence, e.g., \{ X \} $\rightarrow$ $\tau_2$ $\rightarrow$ $\{ -X \} $ $\rightarrow$ $\tau_4$ [acquisition(+) $\rightarrow$ recycle delay $\rightarrow$ { X } $\rightarrow$ $\tau_2$ $\rightarrow$ { X } $\rightarrow$ $\tau_4$ [acquisition(-) $\rightarrow$ recycle delay, the central line intensity is now given by the polarizations and the double-quantum coherences:

\begin{equation}
F^z(t_1, \tau_2, t_3) = \Psi \Delta e_i \text{Tr}[\rho(t_1)(I^{13}_z + I^{23}_z)] + \Psi \Delta d_i \text{Tr}[\rho(t_1)(I^{14}_z + I^{24}_z)]
\end{equation}

\begin{equation}
+ \{ \Psi \Delta b_1 \cos 2\omega Q \tau_2 - \Psi \Delta g_1 \sin 2\omega Q \tau_2 \} \text{Tr}[\rho(t_1)(I^{14}_z + I^{23}_z)]
\end{equation}

\begin{equation}
+ \{ \Psi \Delta g_1 \cos 2\omega Q \tau_2 + \Psi \Delta b_1 \sin 2\omega Q \tau_2 \} \text{Tr}[\rho(t_1)(I^{13}_z - I^{23}_z)].
\end{equation}

Fig. 8. Experimental central line intensity of $^7$Li from Fig. 7 (squares) and theoretical central line intensity $F^z(t_1, \tau_2 = 0, t_3 = t_1)$ from Eq. [19] (solid line).
The single- and triple-quantum coherences are canceled. 

**Spin-rotary-echo experiment.** Recently Janssen et al. (20) extended the quadrupolar nutation to rotary-echo nutation. In this method the delay \( \tau_2 \) is zero and \( t_1 = t_3 \). From Eq. [16] the central line intensity can be calculated:

\[
F_4(t_1, \tau_2 = 0, t_3 = t_1) = -6 \sin 2\theta_+ \left\{ -\sin \theta_+ \cos \theta_+ \sin (\omega_{13} + \omega_{24})t_1 \\
+ \cos \theta_+ \sin \theta_+ \sin (\omega_{13} - \omega_{24})t_1 + \sin 2\theta_1 \sin \omega_{24}t_1 + \sin 2\theta_2 \sin \omega_{13}t_1 \right\}/4. \tag{19}
\]

In Fig. 2 is represented the central line intensity \( F_4(t_1, \tau_2 = 0, t_3 = t_1) \) versus the pulse length \( t_3 \) for \( \omega_{RF}/2\pi = 50 \text{ kHz} \) and several \( \omega_Q \) values. The graph clearly shows that the line intensities of small and strong \( \omega_Q \) compared to \( \omega_{RF} \) are canceled by this sequence. The rotary-echo sequence behaves as a bandpass filter for medium \( \omega_Q \). Moreover, for short \( t_3 \) the line intensity is negative. This is an unexpected result.

**EXPERIMENTAL VERIFICATIONS**

LiTaO₃ crystallizes in the space group \( R\bar{3}c \) (28), with two molecules per rhombohedral unit cell. The lithium atoms have a trigonal symmetry environment and the efg tensor at these sites is axially symmetric. Consequently \( \eta \) is zero; \( e^2qQ/h = 85 \text{ kHz} \) for lithium \(^7\text{Li} \) atoms (28).

\(^7\text{Li} \) spectra were recorded at room temperature with a Bruker MSL 400 multinuclear high-power pulsed NMR spectrometer. The high-power static probehead was equipped with a 5 mm diameter horizontal solenoid coil. The different sequences were composed of two pulses; \( \omega_{RF}/2\pi = 36 \text{ kHz} \) and the associated \( \pi/2 \) pulse length \( t_{90} = 7 \mu\text{s} \) were determined using a lithium chloride solution. The acquisition parameters were \( t_1 = 7 \mu\text{s} \), an acquisition delay \( \tau_4 \) of 10 \mu\text{s}, a recycle time of 300 s, and a spectral width of 125 kHz.

For lithium nuclei in a single crystal of LiTaO₃, \( T_{\text{FID}} \approx 400 \mu\text{s} \). The central linewidth is about 5 kHz. The experimental value of \( \omega_Q/2\pi \) is 19 kHz. In the time range of \( \tau_2 = 20 \mu\text{s} \) and \( \tau_4 = 10 \mu\text{s} \) the spin–spin and spin–lattice relaxations are negligible. Now the \{X\}→\tau_2→{-X}→\tau_4 sequence is illustrated. The \(^7\text{Li} \) spectra (absolute intensity) are represented in Fig. 3 for \( t_3 = 1 \) to 15 \mu\text{s} \). The central line intensity versus \( t_3 \) was fitted with Eq. [16] and the following parameters: \( t_1 = 7 \mu\text{s} \), \( \omega_{RF}/2\pi = 36 \text{ kHz} \), and \( \omega_Q/2\pi = 19 \text{ kHz} \) (Fig. 4).

\(^7\text{Li} \) NMR spectra (absolute intensity) for increasing \( t_3 \) obtained with the alternate phase sequence \{X\}→\tau_2→{-X}→\tau_4[acquisition(y)]—recycle delay—{X}→\tau_2→{-X}→\tau_4[acquisition(−y)]—recycle delay are represented in Fig. 5. In Fig. 6 is represented the experimental \(^7\text{Li} \) central line intensity as a function of \( t_3 \). The solid line corresponds to a fit of the experimental points with Eq. [18] and the following parameters: \( t_1 = 7 \mu\text{s} \), \( \omega_{RF}/2\pi = 37 \text{ kHz} \) (instead of 36 kHz), and \( \omega_Q/2\pi = 20 \text{ kHz} \) (instead of 19 kHz).

Finally, \(^7\text{Li} \) NMR spectra (absolute intensity) for increasing \( t_3 \) obtained with the rotary-echo sequence are represented in Fig. 7. In Fig. 8 is represented the experimental \(^7\text{Li} \) central line intensity as a function of \( t_3 \). The full line corresponds to a fit of the experimental points with Eq. [19] and the following parameters: \( \omega_{RF}/2\pi = 36 \text{ kHz} \) and \( \omega_Q/2\pi = 19 \text{ kHz} \). There is good agreement between theory and experiment in the three measurements.
QUADRUF'OLE COUPLING FROM OPPOSITE-PHASE PULSES

CONCLUSION

Several sequences presented in this paper are useful for determining the quadrupolar coupling of a spin \( I = \frac{3}{2} \) system in a single crystal. For powdered samples, a high-speed computer is needed to average the two Euler angles (Eq. [1b]) in order to determine the values of \( e^2\zeta Q/h \) and \( \eta \). These parameters are very important for an accurate calculation of the true chemical shift. Moreover, the rotary-echo sequence behaves like a bandpass filter for a signal having medium \( \omega_0 \) values.

ACKNOWLEDGMENTS

I thank Technic de Bouregas for providing the NMR simulation program ANTIPOE. I also thank Dr. A. Trokiner, Dr. P. Tougne, and Dr. B. Lomas for valuable discussions.

REFERENCES