Exact expression for the spin 7/2 line intensities: application to solid state \( ^{59}\text{Co(III)} \) NMR

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The density matrix of a spin \( I = 7/2 \), excited by a radiofrequency pulse, is calculated in taking into account the first order quadrupolar interaction during the excitation. Therefore, the results are valid for any ratio of the quadrupolar coupling \( \omega_Q \) to the pulse amplitude \( \omega_{RF} \). The behaviour of the central line intensity versus the pulse length is discussed both in time and frequency domains. The quadrupolar coupling constant \( e^2qQ/h = 8.24 \text{ MHz} \) of the \( ^{59}\text{Co(III)} \) nucleus in a polycrystalline sample of \( \text{Na}_3[\text{Co(NO}_2)_6] \) is determined using this one-dimensional nutation method, and the lineshape reveals mainly the presence of chemical shift anisotropy with axial symmetry.

1. Introduction

Quadrupolar nuclei with half-integer spin as solid state nuclear magnetic resonance (NMR) probes are used widely for investigating local environments in inorganic compounds containing, for instance, \( ^{59}\text{Co} \) [1-4], \( ^{51}\text{V} \) [5-8], or \( ^{139}\text{La} \) [9, 10]. The physical parameters (quadrupolar coupling constant \( e^2qQ/h \), asymmetry parameter \( \eta \) and true chemical shift) are obtained mainly from static or spinning powder lineshape analysis [2-7, 10] when the second order quadrupolar interaction dominates. But if it is not the case, a nutation experiment (one-dimensional (1D) or two-dimensional (2D)) is required [1, 11-17]. The 1D nutation experiment consists simply of the acquisition of a series of free induction decays obtained with increasing pulse length \( t \). The fit of the line intensities with an analytical expression allows us to determine the quadrupolar coupling \( \omega_Q \) in a single crystal, or \( e^2qQ/h \) and \( \eta \) in a polycrystalline sample. A systematic study of half-integer spins, up to \( I = 9/2 \), undertaken by Samoson and Lippmaa [11] has given the principal trend. However, the main effects of the first order quadrupolar \( \mathcal{E}_Q^{(1)} \) interaction on the line intensity have been analysed in some detail only for spin \( 3/2 \) [13, 15, 17] and \( 5/2 \) [12, 16] systems.

In this work, we establish the analytical expression for the density matrix by considering explicitly the first order quadrupolar interaction during the excitation of the spin system, and the central and the three satellite line intensities for a spin \( 7/2 \). We apply the 1D nutation method using the \( ^{59}\text{Co(III)} \) in a polycrystalline sample of \( \text{Na}_3[\text{Co(NO}_2)_6] \) for determining the quadrupolar coupling constant, and the lineshape is typical of chemical shift anisotropy with axial symmetry. Moreover, the powder pattern of the satellite transitions is not detected.
2. Theory

The Hamiltonians throughout the paper are defined in angular frequency units. Disregarding relaxation phenomena and second order quadrupolar effects, the dynamics of a spin \( I = 7/2 \) system, excited by an \( x \) pulse (figure 1), is described by the density matrix \( \rho(t) \) expressed in the rotating frame associated with the central transition:

\[
\rho(t) = \exp \left( -i \mathcal{H}^{(a)}(t) \right) \rho(0) \exp \left( i \mathcal{H}^{(a)}(t) \right),
\]

where

\[
\begin{align*}
\rho(0) &= I_z, \\
\mathcal{H}^{(1)}_Q &= \frac{1}{3} \omega_Q (3 I_z^2 - I(I + 1)), \\
\omega_Q &= \frac{3e^2 qQ}{8I(2I-1)\hbar} \left[ 3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\alpha \right], \\
\mathcal{H}^{(a)} &= \mathcal{H}_{RF} + \mathcal{H}^{(1)}_Q, \\
\mathcal{H}_{RF} &= -\omega_{RF} I_x,
\end{align*}
\]

\( \alpha \) and \( \beta \) represent the Euler angles describing the orientation of the strong static magnetic field in the principal axis system of the electric field gradient (EFG) tensor. The eigenstates of \( I_z, |m\rangle \) (figure 2), are redefined as: \( |i\rangle = |i - m + 1\rangle \), so \( i = 1, \ldots, 2I + 1 \). The matrix representation \( M \) (table 1) of \( \mathcal{H}^{(a)} \), expressed in the eigenstates of \( I_z \), is not diagonal. The transformation \( A^t M A \), where the matrix \( A \) is reported in table 1, produces a matrix \( M_1 \) in the form of two \( 4 \times 4 \) diagonal symmetric blocks \([11, 12, 16]\). The superscript letter \( t \) means the transpose of the matrix. When the matrices of eigenvalues \( \Omega \) and eigenvectors \( B \) associated with \( M_1 \) and related by

\[
\Omega = B B^{-1} M_1 B^{-1},
\]

are found, the symbol \(-1\) in the superscript meaning the inverse of the matrix, equation (1) can be rewritten as:

\[
\rho(t) = AB \exp \left( -i \Omega t \right) (AB)^{-1} \rho(0) AB \exp \left( i \Omega t \right) (AB)^{-1}.
\]

To proceed further, the standard method for diagonalizing a \( 4 \times 4 \) symmetric matrix is used \([18]\). The notation used throughout this paper is: the subscripts + and −

Figure 1. The Hamiltonians associated with the one pulse excitation.
The energy levels, their shifts and the two forms of eigenstates of a spin 7/2 ($\mathcal{H}_Z$ means Zeeman interaction).

Figure 2. The energy levels, their shifts and the two forms of eigenstates of a spin 7/2 ($\mathcal{H}_Z$ means Zeeman interaction).

are related to the two $4 \times 4$ submatrices of an $8 \times 8$ matrix as follows:

$$M_1 = \begin{pmatrix} M_{1+} & 0 \\ 0 & M_{1-} \end{pmatrix}, \quad B = \begin{pmatrix} N_+ & 0 \\ 0 & N_- \end{pmatrix},$$

$$\Omega = \begin{pmatrix} \Omega_+ & 0 \\ 0 & \Omega_- \end{pmatrix}, \quad \rho(0) = \begin{pmatrix} \rho(0)_+ & 0 \\ 0 & \rho(0)_- \end{pmatrix}. \quad (5)$$

The $4 \times 4$ submatrices $M_{1\pm}, N_{\pm}, \Omega_{\pm}$ and $\rho(0)_{\pm}$ are defined in table 2. The energy $\omega_{\pm}$ secular equation generated by $M_{1\pm}$ is of fourth degree

$$\omega_{\pm}^4 + b_{1\pm} \omega_{\pm}^3 + b_{2\pm} \omega_{\pm}^2 + b_{3\pm} \omega_{\pm} + b_{4\pm} = 0, \quad (6)$$

with

$$\epsilon = \epsilon_{\omega Q}, \quad (7)$$
Table 1. The $8 \times 8$ matrices involved in this work.

\[
\begin{bmatrix}
14\omega_0 & -(7^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 & 0 & 0 \\
-(7^{1/2})\omega_{RF} & 2\omega_0 & -2(3^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 & 0 \\
0 & -2(3^{1/2})\omega_{RF} & -6\omega_0 & -(15^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 \\
0 & 0 & -(15^{1/2})\omega_{RF} & -10\omega_0 & -4\omega_{RF} & 0 & 0 & 0 \\
0 & 0 & 0 & -4\omega_{RF} & -10\omega_0 & -(15^{1/2})\omega_{RF} & 0 & 0 \\
0 & 0 & 0 & 0 & -(15^{1/2})\omega_{RF} & -6\omega_0 & -2(3^{1/2})\omega_{RF} & 0 \\
0 & 0 & 0 & 0 & 0 & -2(3^{1/2})\omega_{RF} & 2\omega_0 & -(7^{1/2})\omega_{RF} \\
0 & 0 & 0 & 0 & 0 & 0 & -2(3^{1/2})\omega_{RF} & 2\omega_0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -(7^{1/2})\omega_{RF} \\
14\omega_0 & -(7^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 & 0 & 0 \\
-(7^{1/2})\omega_{RF} & 2\omega_0 & -2(3^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 & 0 \\
0 & -2(3^{1/2})\omega_{RF} & -6\omega_0 & -(15^{1/2})\omega_{RF} & 0 & 0 & 0 & 0 \\
0 & 0 & -(15^{1/2})\omega_{RF} & -10\omega_0 & -4\omega_{RF} & 0 & 0 & 0 \\
0 & 0 & 0 & -4\omega_{RF} & -10\omega_0 & -(15^{1/2})\omega_{RF} & 0 & 0 \\
0 & 0 & 0 & 0 & -(15^{1/2})\omega_{RF} & -6\omega_0 & -2(3^{1/2})\omega_{RF} & 0 \\
0 & 0 & 0 & 0 & 0 & -2(3^{1/2})\omega_{RF} & 2\omega_0 & -(7^{1/2})\omega_{RF} \\
0 & 0 & 0 & 0 & 0 & 0 & -2(3^{1/2})\omega_{RF} & 2\omega_0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -(7^{1/2})\omega_{RF} \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

\[
b_1 \pm = \mp 2\omega_{RF}, \\
b_2 \pm = \omega_{RF}^2 (-42\epsilon^2 \pm 10\epsilon - \frac{17}{2}), \\
b_3 \pm = \omega_{RF}^3 (-64\epsilon^3 \pm 34\epsilon^2 + 22\epsilon \pm \frac{19}{2}), \\
b_4 \pm = \omega_{RF}^4 (105\epsilon^4 \mp 42\epsilon^3 \mp 105\epsilon^2 \mp 63\epsilon \mp \frac{105}{16}).
\]

The transformation [19]

\[
\omega_\pm = \zeta_\pm - \frac{b_1 \pm}{4} = \zeta_\pm \pm \frac{\omega_{RF}}{2}
\]

yields

\[
\frac{p_\pm}{4} - \frac{p_\pm r_\pm}{4} - \frac{q_\pm r_\pm}{4} \zeta_\pm + \frac{r_\pm}{16} = 0,
\]
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Table 2. The 4 × 4 submatrices involved in this work.

\[
\begin{bmatrix}
X_1^+ & X_2^+ & X_3^+ & X_4^+ \\
Y_1^+ & Y_2^+ & Y_3^+ & Y_4^+ \\
Z_1^+ & Z_2^+ & Z_3^+ & Z_4^+ \\
V_1^+ & V_2^+ & V_3^+ & V_4^+
\end{bmatrix}
\]

\[
\begin{bmatrix}
X_1^- & X_2^- & X_3^- & X_4^- \\
Y_1^- & Y_2^- & Y_3^- & Y_4^- \\
Z_1^- & Z_2^- & Z_3^- & Z_4^- \\
V_1^- & V_2^- & V_3^- & V_4^{-}
\end{bmatrix}
\]

\[
\begin{bmatrix}
\omega_1^+ & 0 & 0 & 0 \\
0 & \omega_2^+ & 0 & 0 \\
0 & 0 & \omega_3^+ & 0 \\
0 & 0 & 0 & \omega_4^+
\end{bmatrix}
\]

\[
\begin{bmatrix}
\omega_1^- & 0 & 0 & 0 \\
0 & \omega_2^- & 0 & 0 \\
0 & 0 & \omega_3^- & 0 \\
0 & 0 & 0 & \omega_4^-
\end{bmatrix}
\]

\[
\rho(0)^+ = \frac{1}{2}
\begin{bmatrix}
7 & 0 & 0 & 0 \\
0 & 5 & 0 & 0 \\
0 & 0 & 3 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\]

\[
\rho(0)^- = -\frac{1}{2}
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 3 & 0 & 0 \\
0 & 0 & 5 & 0 \\
0 & 0 & 0 & 7
\end{bmatrix}
\]

with

\[
p_\pm = 8\omega_{R\ell}^2(21\epsilon^2 \mp 5\epsilon + 5),
\]

\[
q_\pm = 32\omega_{R\ell}^3\epsilon(8\epsilon^2 \mp \epsilon - 4),
\]

\[
r_\pm = 16\omega_{R\ell}^4(105\epsilon^4 \mp 74\epsilon^3 + 59\epsilon^2 \mp 18\epsilon + 9)
\]

The four roots of equation (9) have the following forms [18]

\[
\zeta_{1 \pm} = (R_{1 \pm} \pm D_\pm)/2,
\]

\[
\zeta_{2 \pm} = (R_{1 \pm} \mp D_\pm)/2,
\]

\[
\zeta_{3 \pm} = -(R_{1 \pm} \mp S_\pm)/2,
\]

\[
\zeta_{4 \pm} = -(R_{1 \pm} \pm S_\pm)/2,
\]

where \(D_\pm\) and \(S_\pm\) are related to \(R_{1 \pm}\) by

\[
D_\pm = \left(\frac{1}{2}\left(p_\pm + \frac{q_\pm}{R_{1 \pm}}\right) - R_{1 \pm}^2\right)^{1/2},
\]

\[
S_\pm = \left(\frac{1}{2}\left(p_\pm - \frac{q_\pm}{R_{1 \pm}}\right) - R_{1 \pm}^2\right)^{1/2},
\]

and \(R_{1 \pm}^2\) is one of the three roots of the cubic equation in \(R_\pm^2\)

\[
R_\pm^6 - \frac{p_\pm}{2}R_\pm^4 + \frac{1}{16}(p_\pm^2 - 4r_\pm)R_\pm^2 - \frac{q_\pm^2}{16} = 0.
\]
The standard trigonometric method \cite{16,19}, applied to equation (13), gives
\[
R_{1\pm} = \frac{p_{\pm} + [p_{\pm}^2 + 12r_{\pm}]^{1/2} \cos (\beta_{\pm}/3)}{6}, \tag{14}
\]
\[
\cos \beta_{\pm} = \frac{-p_{\pm}^3 + 36p_{\pm}r_{\pm} + 54q_{\pm}^2}{(p_{\pm}^2 + 12r_{\pm})^{3/2}}. \tag{15}
\]
The four eigenvalues $\omega_{m\pm}$ of $M_{1\pm}$, expressed in angular frequency units, are
\[
\omega_{m\pm} = \frac{r_{m\pm} \pm \omega_{RF}}{2}. \tag{16}
\]
The components of the normalized eigenvectors associated with the eight eigenvalues $\omega_{m\pm}$ are:
\[
\begin{align*}
X_{m\pm} &= \frac{x_{m\pm}}{Q_{m\pm}}, & Y_{m\pm} &= \frac{y_{m\pm}}{Q_{m\pm}}, & Z_{m\pm} &= \frac{z_{m\pm}}{Q_{m\pm}}, & V_{m\pm} &= \frac{v_{m\pm}}{Q_{m\pm}},
\end{align*}
\tag{17}
\]
with $m = 1, 2, 3$ or 4, and
\[
\begin{align*}
x_{m+} &= \frac{\sqrt{7}}{2} \alpha_{RF}, & x_{m-} &= \frac{-15}{2} \omega_{RF} \frac{v_{m-} - v_{m+}}{2(2\omega_{RF} + 5\omega_Q + \omega_{m-})}, \\
y_{m+} &= 7\omega_Q - \omega_{m+}, & y_{m-} &= \frac{(\omega_Q - \omega_{m-})z_{m-} - v_{m-}^2}{\sqrt{3}\omega_{RF}}, \\
z_{m+} &= \frac{(\omega_Q - \omega_{m+})y_{m+} - x_{m+}^2}{\sqrt{3}\omega_{RF}}, & z_{m-} &= 7\omega_Q - \omega_{m-}, \\
v_{m+} &= \frac{(15)^{1/2} \omega_{RF} z_{m+}}{2(2\omega_{RF} - 5\omega_Q - \omega_{m+})}, & v_{m-} &= \frac{\sqrt{7}}{2} \omega_{RF}, \\
Q_{m\pm} &= (x_{m\pm}^2 + y_{m\pm}^2 + z_{m\pm}^2 + v_{m\pm}^2)^{1/2}.
\end{align*}
\tag{18}
\]
The matrix multiplication in expression (4) were performed using the software 'Mathematica'. The elements of the density matrix (table 3) are written as line intensities
\[
\langle I^{m,n}_k(t) \rangle = \text{Tr} [\rho(t) I^{m,n}_k]. \tag{19}
\]
The symbols $I^{m,n}_k$ are the fictitious spin 1/2 operators \cite{20,21}. A property is worth noting: some line intensities remain unchanged when the $x$ pulse is changed to a $-x$ pulse. This is the case for polarizations, and even quantum coherences. Only the line intensities of odd-quantum coherences change the sign with that of the pulse.

Knowledge of the density matrix $\rho(t)$ allows us to determine the single quantum line intensity $\langle I^{m,n}_k(t) \rangle$ and the relative line intensity $F^{n,n+1}(t)$ related by:
\[
F^{n,n+1}(t) = \frac{\xi \langle I^{n,n+1}_k(t) \rangle}{\text{Tr} [I^{n}_k]}, \tag{20}
\]
with
\[
\xi = (I(I + 1) - (I - n)(I - n + 1))^{1/2}, \tag{21a}
\]
\[
\text{Tr} [I^{n}_k] = \frac{1}{2} l(I + 1)(2I + 1). \tag{21b}
\]
Table 3. Components of the density matrix ρ(τ). For clarity, the symbols $\frac{1}{2} \sum_{m=1}^{4} \sum_{j=1}^{4} K_{mj}$ in front of each term are omitted. For example, $\langle I_1^{1.2} \rangle + i \langle I_1^{2.1} \rangle = \frac{1}{4} \sum_{m=1}^{4} \sum_{j=1}^{4} K_{mj}[(X_m + Z_j - Y_m + V_j) \cos \omega_{mj} + i(X_m + Z_j - Y_m + V_j) \sin \omega_{mj}]$ is written as below with $K_{mj} = 7X_m + Y_j + 5Y_m + Z_j + 3Z_m + Y_j + V_m + X_j$.

\[
\rho(\tau) = \\
\begin{bmatrix}
\langle I_1^{0} \rangle & \langle I_1^{1} \rangle + i\langle I_1^{2} \rangle & \langle I_1^{3} \rangle - i\langle I_1^{4} \rangle & \langle I_1^{5} \rangle - i\langle I_1^{6} \rangle & \langle I_1^{7} \rangle - i\langle I_1^{8} \rangle & -i\langle I_1^{9} \rangle \\
\langle I_2^{1} \rangle + i\langle I_2^{2} \rangle & \langle I_2^{2} \rangle - i\langle I_2^{3} \rangle & \langle I_2^{3} \rangle - i\langle I_2^{4} \rangle & \langle I_2^{4} \rangle - i\langle I_2^{5} \rangle & \langle I_2^{5} \rangle - i\langle I_2^{6} \rangle & \langle I_2^{6} \rangle - i\langle I_2^{7} \rangle \\
\langle I_3^{1} \rangle + i\langle I_3^{2} \rangle & \langle I_3^{2} \rangle - i\langle I_3^{3} \rangle & \langle I_3^{3} \rangle - i\langle I_3^{4} \rangle & \langle I_3^{4} \rangle - i\langle I_3^{5} \rangle & \langle I_3^{5} \rangle - i\langle I_3^{6} \rangle & \langle I_3^{6} \rangle - i\langle I_3^{7} \rangle \\
\langle I_4^{1} \rangle + i\langle I_4^{2} \rangle & \langle I_4^{2} \rangle - i\langle I_4^{3} \rangle & \langle I_4^{3} \rangle - i\langle I_4^{4} \rangle & \langle I_4^{4} \rangle - i\langle I_4^{5} \rangle & \langle I_4^{5} \rangle - i\langle I_4^{6} \rangle & \langle I_4^{6} \rangle - i\langle I_4^{7} \rangle \\
-\langle I_5^{1} \rangle - i\langle I_5^{2} \rangle & -\langle I_5^{2} \rangle - i\langle I_5^{3} \rangle & -\langle I_5^{3} \rangle - i\langle I_5^{4} \rangle & -\langle I_5^{4} \rangle - i\langle I_5^{5} \rangle & -\langle I_5^{5} \rangle - i\langle I_5^{6} \rangle & -\langle I_5^{6} \rangle - i\langle I_5^{7} \rangle \\
\langle I_6^{1} \rangle + i\langle I_6^{2} \rangle & \langle I_6^{2} \rangle - i\langle I_6^{3} \rangle & \langle I_6^{3} \rangle - i\langle I_6^{4} \rangle & \langle I_6^{4} \rangle - i\langle I_6^{5} \rangle & \langle I_6^{5} \rangle - i\langle I_6^{6} \rangle & \langle I_6^{6} \rangle - i\langle I_6^{7} \rangle \\
\langle I_7^{1} \rangle + i\langle I_7^{2} \rangle & \langle I_7^{2} \rangle - i\langle I_7^{3} \rangle & \langle I_7^{3} \rangle - i\langle I_7^{4} \rangle & \langle I_7^{4} \rangle - i\langle I_7^{5} \rangle & \langle I_7^{5} \rangle - i\langle I_7^{6} \rangle & \langle I_7^{6} \rangle - i\langle I_7^{7} \rangle \\
\langle I_8^{1} \rangle + i\langle I_8^{2} \rangle & \langle I_8^{2} \rangle - i\langle I_8^{3} \rangle & \langle I_8^{3} \rangle - i\langle I_8^{4} \rangle & \langle I_8^{4} \rangle - i\langle I_8^{5} \rangle & \langle I_8^{5} \rangle - i\langle I_8^{6} \rangle & \langle I_8^{6} \rangle - i\langle I_8^{7} \rangle \\
\end{bmatrix}
\]
The relative intensity of the central line $F^{4.5}(t)$ is

$$F^{4.5}(t) = \frac{1}{42} \text{Tr} [\rho(t)4I^{4.5}_y] = \frac{2}{21} \langle I^{4.5}_y \rangle$$

$$= \frac{1}{21} \sum_{m=1}^{4} \sum_{j=1}^{4} V_{m+j} X_{j-m} K_{mj} \sin \omega_{mj} t,$$  

(22)

with

$$K_{mj} = 7X_{m+j} + 5Y_{m+j} + 3Z_{m+j} + V_{m+j} X_{j-m}.$$  

(23)

The sixteen angular frequencies $\omega_{mj}$ are formed from the differences of components in $\Omega_+$ and $\Omega_-$

$$\omega_{mj} = \omega_{m+} - \omega_{j-}.$$  

(24)

The relative intensity of an inner line $F^{3.4}(t)$ is

$$F^{3.4}(t) = \frac{1}{42} \text{Tr} [\rho(t)(15)^{1/2}I^{3.4}_y] = \frac{(15)^{1/2}}{42} \langle I^{3.4}_y \rangle$$

$$= \frac{(15)^{1/2}}{168} \sum_{m=1}^{4} \sum_{j=1}^{4} (Z_{m+j} X_{j-m} - V_{m+j} Y_{j-m} ) K_{mj} \sin \omega_{mj} t.$$  

(25)

The relative intensity of a medium line $F^{2.3}(t)$ is

$$F^{2.3}(t) = \frac{1}{42} \text{Tr} [\rho(t)(12)^{1/2}I^{2.3}_y] = \frac{(12)^{1/2}}{42} \langle I^{2.3}_y \rangle$$

$$= \frac{\sqrt{3}}{84} \sum_{m=1}^{4} \sum_{j=1}^{4} (Y_{m+j} + Y_{j-m} - Z_{m+j} + Z_{j-m} ) K_{mj} \sin \omega_{mj} t.$$  

(26)

Finally, the relative intensity of an outer line $F^{1.2}(t)$ is

$$F^{1.2}(t) = \frac{1}{42} \text{Tr} [\rho(t)\sqrt{7}I^{1.2}_y] = \frac{\sqrt{7}}{42} \langle I^{1.2}_y \rangle$$

$$= \frac{\sqrt{7}}{168} \sum_{m=1}^{4} \sum_{j=1}^{4} (X_{m+j} + Z_{j-m} - Y_{m+j} + V_{j-m} ) K_{mj} \sin \omega_{mj} t.$$  

(27)

The four relative line intensities $F^{4.5}(t), F^{3.4}(t), F^{2.3}(t)$ and $F^{1.2}(t)$ are a sum of sixteen sine curves of different amplitudes and frequencies. Figure 3 represents the relative central line intensity $F^{4.5}(\omega_{RF}t)$ versus the pulse flip angle $\omega_{RF}t$; $\epsilon = \omega_{Q}/\omega_{RF}$ is taken as a parameter. The maximum of $F^{4.5}(\omega_{RF}t)$ decreases, as well as the associated pulse flip angle, when $\epsilon$ increases from a small value to a large one, but both reach a limiting value which is one quarter of those when $\omega_{Q} \approx 0$. In other words, when $\epsilon \gg 1$, the magnetization precesses around the RF magnetic field four times faster than in the opposite case ($\epsilon \ll 1$). There is also a loss of relative line intensity by a factor of four. All these properties have been proved already for spins $I = 3/2$ [13] and $5/2$ [12, 16].

There appears also a linear region, defined by $\omega_{RF}t < \pi/20$, where the relative line intensity is proportional to $\omega_{RF}t$ and independent of $\epsilon$. This linear region is therefore available for a distribution of $\omega_{Q}$. This occurs in a powdered sample. This excitation condition must be applied in order to get quantitative determination of spin populations in powdered compounds. This property has been generalized for any integer or half-integer spin [22].
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Figure 3. Relative intensity of the central line $F^{4.5}(\omega_{RF}t)$, equation (22), versus the pulse flip angle $\omega_{RF}t$, for three ratios of $\omega/Q/\omega_{RF}$: $\ldots$, 0; $\ldots$, 1; $\ldots$, 20.

Figure 4. A log–log plot of the $\omega_{m}/\omega_{RF}$ (equation (24)) versus $\omega/Q/\omega_{RF}$: $\nabla$, $\omega_{11}$; $\blacksquare$, $\omega_{12}$; $\triangle$, $\omega_{13}$; $\bigtriangleup$, $\omega_{14}$; $\nabla$, $\omega_{21}$; $\square$, $\omega_{22}$; $\Delta$, $\omega_{23}$; $\diamond$, $\omega_{24}$; $\bigcirc$, $\omega_{31}$; $\bigstar$, $\omega_{32}$; $\bigstar$, $\omega_{33}$; $\bigstar$, $\omega_{34}$; $\times$, $\omega_{41}$; $+$, $\omega_{42}$; $\omega_{43}$; $\omega_{44}$.

The behaviour of equation (22) is analysed better in the frequency domain corresponding to the $F_1$ axis or nutation frequency axis in 2D nutation spectra. Its Fourier transform is a set of sixteen lines located at $\omega_{m}/\omega_{RF}$ whose amplitude are the terms $V_{m}X_{m}K_{m}$. Figure 4 represents $\log_{10}(\omega_{m}/\omega_{RF})$ versus $\log_{10}(\omega/Q/\omega_{RF})$. For simplicity, negative values of $\omega_{m}$ ($\omega_{21}$, $\omega_{31}$, $\omega_{32}$, $\omega_{41}$, $\omega_{42}$, and $\omega_{43}$) are folded as
positive values. For $E < 0.2$, seven lines are located around $\omega_{RF}$, five around $3\omega_{RF}$, three around $5\omega_{RF}$, and one around $7\omega_{RF}$. As $E$ increases, some lines shift towards higher positions and some towards lower positions. Only one line (solid curve without symbol in figure 4) moves from $\omega_{RF}$ to $4\omega_{RF}$. The sixteen amplitudes versus $\log_{10}(\omega_{Q}/\omega_{RF})$ are represented in figure 5 showing: whatever the value of $E$, the amplitudes of the lines located initially at 3, 5 and 7$\omega_{RF}$ are negligible. Mainly, the seven lines located around $\omega_{RF}$ have important amplitudes for $E < 0.2$. As $E$ increases, their amplitudes decrease to zero except that (solid curve within symbol in figure 5) associated with the line moving towards $4\omega_{RF}$ which becomes dominating for $E > 2$. Our results are in perfect agreement with those of Samoson and Lippmaa [11]. Therefore, only seven sine functions instead of sixteen are required to describe the variation of the central line intensity as a function of $\omega_{RF}$ and $\omega_{Q}$.

3. Experimental

We illustrated our theoretical results with a polycrystalline sample of Na$_3$(Co(NO$_2$)$_6$)$_2$. The quadrupolar coupling constant (8.2 MHz) and asymmetry parameter ($\eta$) of $^{59}$Co(III) in this compound were determined previously using lineshape analysis [3, 4].
The static $^{59}$Co NMR spectra were obtained on a Bruker MSL-400 multinuclear spectrometer operating at 95.66 MHz. The high power static probehead was equipped with the standard 10 mm diameter horizontal solenoid coil. The amplitude of the pulse, determined using an aqueous solution of Na$_3$[Co(NO$_2$)$_6$], was $\omega_{RF}/2\pi = 25$ kHz corresponding to a $\pi/2$ pulse of 10 $\mu$s. Each spectrum was obtained with a recycle delay of 1 s (the line intensities did not increase for longer recycle delays), 1000 scans, a spectral width of 125 kHz and a dead time of 6 $\mu$s. The pulse length was incremented from 1 to 10 $\mu$s in steps of 0.5 $\mu$s.

4. Results

$^{59}$Co spectra on the absolute intensity scale, obtained with increasing pulse length, are represented in figure 6. The lineshape is typical of chemical shift anisotropy with axial symmetry, and the powder pattern of the satellite transitions is not detected. Therefore, the quadrupolar parameters cannot be extracted from the lineshape. Previous results [3, 4] were obtained from lineshape analysis of spectra acquired with different strengths of the static magnetic field. In our case (a single static magnetic field measurement), first order quadrupolar interaction is revealed only from the dependency of the integrated line intensity versus the pulse length. In figure 7, the curve corresponds to a fit of the experimental line intensities (full circle) with equation (22). The asymmetry parameter is taken as zero. In fact, using only the seven functions discussed in the previous section yields the same curve. The main contribution to the central line intensity comes from the sine function (dashed curve in figure 7) associated with the line moving from $\omega_{RF}$ to $4\omega_{RF}$. However, this sine...
Figure 7. Experimental (●) central line intensities of $^{59}$Co in a polycrystalline sample of Na$_3$[Co(NO$_2$)$_6$] from figure 6 and calculated powder central line intensities $\langle F^{4.5}(t) \rangle$, equation (22), with the following parameters: $e^2 qQ/h = 8.24$ MHz; $\eta = 0$; $\omega_{RF}/2\pi = 28.36$ kHz. In fact, fitting with seven sine functions (see text) provides the same results. One of them (dashed curve) represents the major contribution.

function alone does not fit the data properly. The fitting method applied to powdered sample was described in a previous paper [23]. Furthermore, a simplex procedure was also used. The results for the quadrupolar coupling constant and the amplitude of the pulse are 8.24 MHz and 28.36 kHz, respectively. The value of the quadrupolar coupling constant is in good agreement with that determined by Chung et al. [4] using lineshape analysis. As already observed [24], the amplitude of the pulse is higher than that of the experimental one: 28.36 kHz instead of 25 kHz. This discrepancy may be due to the real shape of the RF pulse being different from the hypothetical rectangular pulse.

5. Conclusions

In case the lineshape analysis fails to determine the quadrupolar parameters, the 1D nutation method represents an alternative method when a single static magnetic field is available. On the other hand, the theoretical part of this paper is mainly an extension of the previous ones on spin $I = 3/2$ and 5/2 systems. In fact, the results provide the first stage in a study of the spin–echo sequence [22, 25–27], which is required for recovering broad lines lost in the dead time of the receiver.

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References
Spin 7/2 line intensities