

RELAXATION OF SPIN 3/2 IN A NONZERO AVERAGE ELECTRIC FIELD GRADIENT

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The time dependence of the density operator under relaxation and precession for spin $S=3/2$ in a nonzero average electric field gradient has been evaluated. Transverse relaxation, nonselective inversion recovery and multiple-quantum relaxation experiments are discussed.

1. Introduction

The magnetic relaxation of quadrupolar nuclei may provide information about the structure and dynamics around small ions in solution [1]. A great deal of experimental work has been concerned with complex macromolecular systems such as, e.g. silica [2], synthetic polymers [3], DNA [4], and other biological systems [5]. Spin $S=3/2$ nuclei (e.g. ${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{87}\text{Rb}$, ${}^{35}\text{Cl}$, and ${}^{81}\text{Br}$) constitute an important class, for which the time evolution of the density operator under precession and relaxation can be solved analytically. For isotropic systems, i.e. with a zero average electric field gradient, this has recently been reconsidered by Jaccard et al. [6]. Using an irreducible tensor representation, it was shown that due to relaxation outside the extreme narrowing limit multiple-quantum coherences may be excited.

In anisotropically ordered media, the quadrupolar nuclei may experience a nonzero average electric field gradient. The static quadrupolar coupling induces a shift in the energy levels of the spin system. A well known result of this shift is the splitting of the magnetic resonance. The time evolution of the density operator under relaxation and precession is modified due to the nonzero average field gradient. In the case of spin $S=1$, this has well been documented by Vold [7]. In the present contribution, explicit expressions are derived for spin $S=3/2$. First the relaxation of zero- and nonzero-quantum coherences is discussed. Using this formalism, transverse relaxation and inversion recovery experiments are described. Finally, multiple-quantum relaxation experiments are discussed. Extensive use will be made of irreducible tensor operators. For a description of the formalism in the context of relaxation and coherence transfer, the reader is referred to refs. [6,8].

2. Relaxation of zero-quantum coherences

In the Zeeman eigenbasis of the unperturbed Hamiltonian [9,10]

$$H = -\omega_0 S_z + \frac{1}{6} \omega_Q (3S_z^2 - \mathbf{S} \cdot \mathbf{S}), \quad (1)$$

with eigenstates $|\alpha\rangle$, $|\beta\rangle$, the time dependence of the density matrix is given by the Redfield equation [9,10]

$$d\sigma_{\alpha\alpha'}^*/dt = \sum_{\beta\beta'} \exp\{i[(\alpha - \alpha') - (\beta - \beta')]t\} R_{\alpha\alpha'\beta\beta'} \sigma_{\beta\beta'}^*. \quad (2)$$

The energy level diagram is depicted in fig. 1. Second-order effects have been neglected. Relaxation of zero-

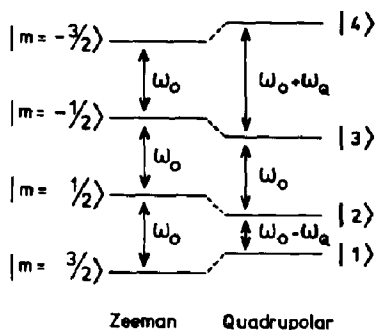


Fig. 1. The energy level diagram of spin $S=3/2$ in a nonzero average electric field gradient.

quantum coherences involves the dynamics of the eigenstate populations corresponding to the diagonal elements $\sigma_{\alpha\alpha}^*$. Hence, for zero-quantum coherences $\alpha=\alpha'$, $\beta=\beta'$, and, accordingly, the exponential part in eq. (2) equals unity. In consequence, the time evolution of the density matrix is described by a set of coupled differential equations, similar to the situation with a zero average electric field gradient,

$$d\sigma_{\alpha\alpha}^*/dt = \sum_{\beta} R_{\alpha\alpha\beta\beta} \sigma_{\beta\beta}^* . \quad (3)$$

By solving this set, the time evolution of the irreducible tensor operators under longitudinal relaxation has been extensively discussed by Jaccard et al. [6]. For ease of reference, the relaxation of the irreducible tensor operator T_{10} reads with the arrow notation [6]

$$T_{10} \xrightarrow{R^{(0)}} T_{10} f_{11}^{(0)}(t) + T_{30} f_{31}^{(0)}(t) , \quad (4)$$

with the relaxation functions

$$f_{11}^{(0)}(t) = \frac{1}{5} [4 \exp(R_3^{(0)} t) + \exp(R_4^{(0)} t)] , \quad (5)$$

$$f_{31}^{(0)}(t) = \frac{2}{5} [-\exp(R_3^{(0)} t) + \exp(R_4^{(0)} t)] \quad (6)$$

and rates

$$R_3^{(0)} = -2(eQ2\pi/h)^2 J(2\omega_0) , \quad (7)$$

$$R_4^{(0)} = -2(eQ2\pi/h)^2 J(\omega_0) . \quad (8)$$

The superscript (0) denotes relaxation of zero-quantum coherences. The irreducible tensor operators are normalized according to ref. [8]. The spectral density function is defined according to

$$J(k\omega_0) = \frac{1}{2} \int_{-\infty}^{\infty} [\langle F_{2k}^*(t) F_{2k}(t-\tau) \rangle - \langle F_{2k}^* F_{2k} \rangle] \exp(ik\omega_0 \tau) d\tau , \quad (9)$$

in which F_{2k} denotes the field gradient tensor. The field gradient tensor components are: $F_{20} = \frac{1}{2} V_{zz}$, $F_{2\pm 1} = \mp \sqrt{\frac{1}{6}} (V_{xz} \pm iV_{yz})$, and $F_{2\pm 2} = \frac{1}{2} \sqrt{\frac{1}{6}} (V_{xx} - V_{yy} \pm 2iV_{xy})$.

3. Relaxation and precession of nonzero-quantum coherences

With a nonzero average electric field gradient, the energy levels are shifted compared to the situation with a vanishing average quadrupolar coupling (fig. 1). If the resulting line splitting is much larger than the line-

widths the non-secular terms in eq. (2) may be neglected. Accordingly, for nonzero-quantum coherences, the corresponding matrix elements relax independently and exponentially

$$d\sigma_{\alpha\beta}^*/dt = R_{\alpha\beta\alpha\beta}\sigma_{\alpha\beta}^*, \quad \text{with } \alpha \neq \beta. \quad (10)$$

This is in contrast to the situation with a zero average electric field gradient, where a coupled set of differential equations has to be solved [6]. Using eq. (10), the time evolution of the relevant irreducible tensor operators representing nonzero-quantum coherences may be evaluated.

To start with, the relevant tensor operators are expressed in terms of transition-shift operators $|\alpha\rangle\langle\beta|$. The eigenstates $|\alpha\rangle$ are defined in fig. 1. Matrix representations of the irreducible tensor operators are conveniently tabulated in ref. [8]^{#1}. For positive single-quantum coherence, one has

$$\begin{aligned} T_{1+1} &= -\sqrt{\frac{3}{10}}|1\rangle\langle 2| - \sqrt{\frac{2}{3}}|2\rangle\langle 3| - \sqrt{\frac{3}{10}}|3\rangle\langle 4|, \\ T_{2+1} &= -\sqrt{\frac{1}{2}}|1\rangle\langle 2| + \sqrt{\frac{1}{2}}|3\rangle\langle 4|, \\ T_{3+1} &= -\sqrt{\frac{1}{5}}|1\rangle\langle 2| + \sqrt{\frac{2}{5}}|2\rangle\langle 3| - \sqrt{\frac{1}{5}}|3\rangle\langle 4|. \end{aligned} \quad (11)$$

The positive double-quantum coherences are given by

$$\begin{aligned} T_{2+2} &= \sqrt{\frac{1}{2}}|1\rangle\langle 3| + \sqrt{\frac{1}{2}}|2\rangle\langle 4|, \\ T_{3+2} &= \sqrt{\frac{1}{2}}|1\rangle\langle 3| - \sqrt{\frac{1}{2}}|2\rangle\langle 4| \end{aligned} \quad (12)$$

and the positive triple-quantum coherence by

$$T_{3+3} = -|1\rangle\langle 4|. \quad (13)$$

According to eq. (10) and the corresponding Redfield matrix elements (see ref. [6]^{#2}), the time evolution of the transition-shift operators takes the form

$$\begin{aligned} |1\rangle\langle 2| &\xrightarrow{R^{(1)}} \exp[(-i\omega_Q + R_s^{(1)})t]|1\rangle\langle 2|, \\ |2\rangle\langle 3| &\xrightarrow{R^{(1)}} \exp(R_c^{(1)}t)|2\rangle\langle 3|, \\ |3\rangle\langle 4| &\xrightarrow{R^{(1)}} \exp[(i\omega_Q + R_s^{(1)})t]|3\rangle\langle 4| \end{aligned} \quad (14)$$

for the single-quantum transitions. For the double-quantum transitions one has

$$\begin{aligned} |1\rangle\langle 3| &\xrightarrow{R^{(2)}} \exp[(-i\omega_Q + R^{(2)})t]|1\rangle\langle 3|, \\ |2\rangle\langle 4| &\xrightarrow{R^{(2)}} \exp[(i\omega_Q + R^{(2)})t]|2\rangle\langle 4| \end{aligned} \quad (15)$$

and for the triple-quantum transition the time evolution is given by

$$|1\rangle\langle 4| \xrightarrow{R^{(3)}} \exp(R^{(3)}t)|1\rangle\langle 4|. \quad (16)$$

The rates are obtained from the corresponding Redfield relaxation matrix elements:

$$R_s^{(1)} = -(eQ2\pi/\hbar)^2[J(0) + J(\omega_0) + J(2\omega_0)], \quad (17)$$

^{#1} Please note the following printing errors; In table 1, $T_{32}^2 = \lambda_3^2(3/2)^{1/2}S^+S_zS^+$ and table 3, $d_{22}^2 = d_{2-2}^2 = \cos^4\beta/2$ should read $T_{32}^2 = \lambda_3^2(3^{1/2}/2)S^+S_zS^+$ and $d_{22}^2 = d_{2-2}^2 = \cos^4\beta/2$, respectively.

^{#2} In eq. (65) the off-diagonal elements J_1 should read $-J_1$. This results in an interchange of the expressions for $R^{(2)}$ and $R^{(3)}$, in eq. (67).

$$R_c^{(1)} = -(eQ2\pi/h)^2 [J(\omega_0) + J(2\omega_0)] , \quad (18)$$

for the single-quantum transition-shift operators,

$$R^{(2)} = R_s^{(1)} , \quad (19)$$

for the double-quantum transition-shift operators and

$$R^{(3)} = R_c^{(1)} , \quad (20)$$

for the triple-quantum transition-shift operator. The superscripts (1), (2) and (3) denote relaxation of single-, double-, and triple-quantum coherences, respectively. These expressions refer to an interaction representation in which the Zeeman field disappears. For negative coherences similar expressions can be derived, but with different signs. Subsequently, the transition-shift operators have to be expressed in terms of irreducible tensor operators. Finally, the time dependence of the tensor operators takes the form

$$\begin{aligned} T_{1\pm 1} &\xrightarrow{R^{(1)}} T_{1\pm 1} q_{11}^{(1)}(t) \mp T_{2\pm 1} q_{21}^{(1)}(t) + T_{3\pm 1} q_{31}^{(1)}(t) , \\ T_{2\pm 1} &\xrightarrow{R^{(1)}} \mp T_{1\pm 1} q_{12}^{(1)}(t) + T_{2\pm 1} q_{22}^{(1)}(t) \mp T_{3\pm 1} q_{32}^{(1)}(t) , \\ T_{3\pm 1} &\xrightarrow{R^{(1)}} T_{1\pm 1} q_{13}^{(1)}(t) \mp T_{2\pm 1} q_{23}^{(1)}(t) + T_{3\pm 1} q_{33}^{(1)}(t) \end{aligned} \quad (21)$$

for the single-quantum coherences,

$$\begin{aligned} T_{2\pm 2} &\xrightarrow{R^{(2)}} T_{2\pm 2} q_{22}^{(2)}(t) \mp T_{3\pm 2} q_{32}^{(2)}(t) , \\ T_{3\pm 2} &\xrightarrow{R^{(2)}} \mp T_{2\pm 2} q_{23}^{(2)}(t) + T_{3\pm 2} q_{33}^{(2)}(t) \end{aligned} \quad (22)$$

for the double-quantum coherences, and

$$T_{3\pm 3} \xrightarrow{R^{(3)}} T_{3\pm 3} q_{33}^{(3)}(t) \quad (23)$$

for the triple-quantum coherence. The relaxation and precession functions are given by

$$\begin{aligned} q_{11}^{(1)}(t) &= \frac{1}{3} [3 \exp(R_s^{(1)} t) \cos(\omega_Q t) + 2 \exp(R_c^{(1)} t)] , \\ q_{12}^{(1)}(t) &= q_{21}^{(1)}(t) = \sqrt{\frac{3}{2}} \exp(R_s^{(1)} t) i \sin(\omega_Q t) , \\ q_{13}^{(1)}(t) &= q_{31}^{(1)}(t) = \frac{1}{3} \sqrt{6} [\exp(R_s^{(1)} t) \cos(\omega_Q t) - \exp(R_c^{(1)} t)] , \\ q_{22}^{(1)}(t) &= \exp(R_s^{(1)} t) \cos(\omega_Q t) , \\ q_{23}^{(1)}(t) &= q_{32}^{(1)}(t) = \sqrt{\frac{2}{3}} \exp(R_s^{(1)} t) i \sin(\omega_Q t) , \\ q_{33}^{(1)}(t) &= \frac{1}{3} [2 \exp(R_s^{(1)} t) \cos(\omega_Q t) + 3 \exp(R_c^{(1)} t)] \end{aligned} \quad (24)$$

for the single-quantum coherences,

$$\begin{aligned} q_{22}^{(2)}(t) &= q_{33}^{(2)}(t) = \exp(R^{(2)} t) \cos(\omega_Q t) , \\ q_{23}^{(2)}(t) &= q_{32}^{(2)}(t) = \exp(R^{(2)} t) i \sin(\omega_Q t) \end{aligned} \quad (25)$$

for the double-quantum coherences, and

$$q_{33}^{(3)}(t) = \exp(R^{(3)} t) \quad (26)$$

for the triple-quantum coherence.

In contrast to multiexponential relaxation only, precession under a nonvanishing quadrupolar coupling generates second-rank tensors in the density operator expansion. This has already been discussed by Jaccard et al., although their analysis was confined to the time-evolution of single-quantum coherences [6]. In the present contribution, free precession under the static Zeeman Hamiltonian is ignored. This is allowed if the offset of the pulse carrier frequency from exact resonance equals zero or if the signals are properly refocused in the evolution period. When these conditions are not fulfilled, the resulting signal contributions have to be multiplied by an additional phase factor depending on the offset and coherence orders involved. With eqs. (21)–(26) it is possible to estimate the destiny of the density operator under a series of rf pulses and evolution periods. In the following the transverse relaxation experiment, the inversion recovery experiment, and determination of the multiple-quantum relaxation rates will be discussed.

4. Transverse relaxation experiment

After an initial $(\pi/2)_y$ pulse, the density operator in the rotating frame is given by

$$\sigma^*(t=0) = S_x = \sqrt{\frac{3}{2}}(T_{1-1} - T_{1+1}). \quad (27)$$

Factors representing the temperature and number of spins have been dropped. During transverse relaxation, the density operator evolves according to eq. (21)

$$\sigma^*(t) = \sqrt{\frac{5}{2}}[(T_{1-1} - T_{1+1})q_{11}^{(1)}(t) + (T_{2-1} + T_{2+1})q_{21}^{(1)}(t) + (T_{3-1} - T_{3+1})q_{31}^{(1)}(t)]. \quad (28)$$

A similar expression has been reported by Jaccard et al. [6]. Under detection only the $T_{1\pm 1}$ coherences become apparent. Hence, according to eq. (28), the detected signal is represented by the well known expression

$$s(t) = q_{11}^{(1)}(t). \quad (29)$$

The Fourier transform of eq. (29) consists of two satellites and a central line with widths $\pi^{-1}R_s^{(1)}$ and $\pi^{-1}R_c^{(1)}$, respectively, and relative intensities 3:4:3.

To overcome spectrometer dead time and/or field inhomogeneity effects it may be convenient to measure the transverse relaxation by a spin-echo experiment. It should be noted that the echos are modulated due to interference effects of the satellites and the central transition. This is because the quadrupolar interaction is quadratic in S_z (see eq. (1)) and does not change sign under the action of a refocusing π pulse. However, analogous to a homonuclear J -resolved experiment [11], a 2D experiment with Fourier transformation with respect to the evolution time may be used to separate the satellites and the central transition in the F_1 dimension.

5. Inversion recovery experiment

In an inversion recovery experiment, a nonselective initial $(\pi)_y$ pulse is applied to invert the magnetization. After this pulse, the deviation of the density operator with respect to thermal equilibrium is given by

$$\Delta\sigma^*(t=0) = -2S_z = -2\sqrt{5}T_{10}. \quad (30)$$

After this preparation pulse, the density operator evolves towards equilibrium due to longitudinal relaxation. According to eq. (4), one obtains the time evolution

$$\Delta\sigma^*(t_1) = -2\sqrt{5}[T_{10}f_{11}^{(0)}(t_1) + T_{30}f_{31}^{(0)}(t_1)]. \quad (31)$$

To obtain the density operator as a function of the evolution time t_1 , the equilibrium value of the density operator, S_z , has to be added

$$\sigma^*(t_1) = \sqrt{5}T_{10} + \Delta\sigma^*(t_1) = \sqrt{5}\{T_{10}[1 - 2f_{11}^{(0)}(t_1)] - 2T_{30}f_{31}^{(0)}(t_1)\}. \quad (32)$$

After partial recovery, a $(\pi/2)_y$ pulse is applied. It has been shown that this pulse creates single- and triple-quantum coherences, provided the relaxation is outside the extreme narrowing limit [6].

The effect of pulses is described by a simple transformation. The rank l of the irreducible tensor operators is conserved, the order m may change [11]. If the density operator has the general form

$$\sigma^* = \sum_{l,m} c_{lm} T_{lm} \quad (33)$$

then after the pulse with a flip angle β and phase φ' the density operator is represented by [8]

$$\sigma^* = \sum_{k,l,m} c_{lm} T_{lk} d_{km}^{(l)}(\beta) \exp[-i(k-m)\varphi'], \quad (34)$$

in which $k-m$ is the change of coherence order induced by the pulse. The phase φ' is defined as a positive excursion with respect to the y axis, in accordance with the definitions of the Euler angles [12]. The reduced matrix elements $d_{km}^{(l)}(\beta)$ are tabulated in ref. [8].

With eqs. (33) and (34), after the $\pi/2$ pulse with phase $\varphi' = 0$, the density operator (eq. (32)) is represented by

$$\sigma^*(t_1) = \sigma^*(t_1, p = \pm 1) + \sigma^*(t_1, p = \pm 3), \quad (35)$$

$$\sigma^*(t_1, p = \pm 1) = \sqrt{\frac{5}{2}}\{(T_{1-1} - T_{1+1})[1 - 2f_{11}^{(0)}(t_1)] + \sqrt{\frac{2}{5}}(T_{3-1} - T_{3+1})f_{31}^{(0)}(t_1)\}, \quad (36)$$

$$\sigma^*(t_1, p = \pm 3) = -\sqrt{\frac{5}{2}}(T_{3-3} - T_{3+3})f_{31}^{(0)}(t_1). \quad (37)$$

Eqs. (36) and (37) represent $p = \pm 1$ single- and $p = \pm 3$ triple-quantum coherences, respectively. Due to multiexponential longitudinal relaxation, multiple-quantum coherences are generated. In the extreme narrowing limit, the function $f_{31}^{(0)}(t_1)$ vanishes and only single-quantum coherences are created.

After this $(\pi/2)_0$ pulse the signal can be directly detected. Another possibility is to use triple-quantum coherences, which results in a different relaxation behavior. This can be done by applying an additional $(\pi/2)_{-\pi/2}$ pulse to convert the $T_{3\pm 3}$ coherences into $T_{3\pm 1}$ coherences. The latter coherences may evolve into observable $T_{1\pm 1}$ coherences during the detection period.

5.1. Direct detection

After the $(\pi/2)_0$ pulse the density operator evolves due to relaxation and precession. In this period, the rank l of the tensor operators may change, while the order m is conserved (eq. (21)). Hence, the multiple-quantum coherences $\sigma^*(t_1, p = \pm 3)$ (eq. (37)) do not become apparent under direct detection. Under direct detection, with eqs. (21) and (36) and collecting terms proportional to $T_{1\pm 1}$ coherences only, the signal is represented by

$$s(t_1, t_2) = [1 - 2f_{11}^{(0)}(t_1)]q_{11}^{(1)}(t_2) + \sqrt{\frac{3}{2}}f_{31}^{(0)}(t_1)q_{13}^{(1)}(t_2). \quad (38)$$

To identify the longitudinal relaxation of the satellites and the central line, the relaxation functions are expanded

$$s(t_1, t_2) = \frac{1}{5}\{3[1 - 2\exp(R_3^{(0)}t_1)]\exp(R_3^{(1)}t_2)\cos(\omega_Q t_2) + 2\{1 - [\exp(R_3^{(0)}t_1) + \exp(R_4^{(0)}t_1)]\}\exp(R_4^{(1)}t_2)\}. \quad (39)$$

Hence, in the conventional inversion recovery experiment, the satellites relax monoexponentially with rate $R_3^{(0)}$. The central line relaxes biexponentially with equal fractions $R_3^{(0)}$ and $R_4^{(0)}$, respectively.

5.2. Detection of the triple-quantum coherences

The created triple-quantum coherences, eq. (37), can be monitored by applying an additional $\pi/2$ pulse with phase $\varphi' = -\pi/2$. For a zero average electric field gradient, Jaccard et al. proposed the pulse sequence:

$$(\pi)_0\text{-evolution, } t_1 - (\pi/2)_\varphi\text{-mixing, } \tau_m - (\pi/2)_{-\pi/2}\text{-detection, } t_2, \quad (40)$$

in which τ_m denotes a mixing period [6]. If τ_m is small compared to $1/\omega_Q$ and the relaxation times $-1/R_s^{(1)}$, $-1/R_c^{(1)}$ and $-1/R^{(3)}$, relaxation and precession during the mixing period can be neglected. Separation of coherences may be achieved by time-proportional phase incrementation of the second, $(\pi/2)_\varphi$, pulse (TPPI [11]). Neglecting the time evolution in the mixing period, after coherence transfer with a $(\pi/2)_{\varphi' = -\pi/2}$ pulse, the density operator (eqs. (36) and (37)) is given by

$$\begin{aligned} \sigma^*(t_1, p = \pm 1) = & \sqrt{\frac{5}{2}} \{ (T_{1-1} - T_{1+1}) [1 - 2f_{11}^{(0)}(t_1)] - \frac{1}{8}\sqrt{6}(T_{3-1} - T_{3+1})f_{31}^{(0)}(t_1) \} \\ & + \text{order } \pm 3 \text{ coherences,} \end{aligned} \quad (41)$$

$$\sigma^*(t_1, p = \pm 3) = \frac{5}{8}\sqrt{15}(T_{3-1} - T_{3+1})f_{31}^{(0)}(t_1) + \text{order } \pm 3 \text{ coherences.} \quad (42)$$

Now, during detection the $T_{3\pm 1}$ coherences evolve into detectable $T_{1\pm 1}$ coherences.

In the 2D experiment with TPPI, four distinct signal contributions are detected. With eqs. (21), (41), and (42) and collecting $T_{1\pm 1}$ coherences only, these contributions are

$$s(t_1, t_2, p = \pm 1) = \frac{1}{2} \{ [1 - 2f_{11}^{(0)}(t_1)] q_{11}^{(1)}(t_2) - \frac{1}{8}\sqrt{6}f_{31}^{(0)}(t_1) q_{13}^{(1)}(t_2) \} \exp(\mp i\varphi), \quad (43)$$

$$s(t_1, t_2, p = \pm 3) = \frac{5}{16}\sqrt{6}f_{31}^{(0)}(t_1) q_{13}^{(1)}(t_2) \exp(\mp 3i\varphi), \quad (44)$$

in which φ is the phase of the second pulse in eq. (40).

The Fourier transform of the single- as well as the triple-quantum signal with respect to t_2 consists of two satellites and a central line. In the case of the single-quantum contribution it may be clarifying to expand the relaxation functions

$$\begin{aligned} s(t_1, t_2, p = \pm 1) = & \frac{1}{10} \{ 3[1 - \frac{1}{2} \{ 3 \exp(R_3^{(0)} t_1) + \exp(R_4^{(0)} t_1) \}] \exp(R_s^{(1)} t_2) \cos(\omega_Q t_2) \\ & + 2[1 - \frac{1}{4} \{ 7 \exp(R_3^{(0)} t_1) + \exp(R_4^{(0)} t_1) \}] \exp(R_c^{(1)} t_2) \} \exp(\mp i\varphi). \end{aligned} \quad (45)$$

The satellites as well as the central line of the single-quantum signal show biexponential longitudinal relaxation.

For the sake of completeness, expressions for the signal contributions including relaxation and precession during the mixing period are presented. Analogous to the preceding derivation, but specifying the time evolution in the mixing period, one has

$$\begin{aligned} s(t_1, \tau_m, t_2, p = \pm 1) = & \frac{1}{2} \{ [1 - 2f_{11}^{(0)}(t_1)] [q_{11}^{(1)}(\tau_m) q_{11}^{(1)}(t_2) - q_{21}^{(1)}(\tau_m) q_{12}^{(1)}(t_2) - \frac{1}{4} q_{31}^{(1)}(\tau_m) q_{13}^{(1)}(t_2)] \\ & + \sqrt{\frac{3}{2}} f_{31}^{(0)}(t_1) [q_{13}^{(1)}(\tau_m) q_{11}^{(1)}(t_2) - q_{23}^{(1)}(\tau_m) q_{12}^{(1)}(t_2) - \frac{1}{4} q_{33}^{(1)}(\tau_m) q_{13}^{(1)}(t_2)] \} \exp(\mp i\varphi), \end{aligned} \quad (46)$$

$$s(t_1, t_2, p = \pm 3) = \frac{5}{16}\sqrt{6}f_{31}^{(0)}(t_1) q_{33}^{(1)}(\tau_m) q_{13}^{(1)}(t_2) \exp(\mp 3i\varphi). \quad (47)$$

The single-quantum contribution is complicated and less suitable for fitting. The triple-quantum signal is only modulated due to relaxation in the mixing period and is therefore still tractable.

In inversion recovery experiments, the time evolution in the evolution and detection period is unequal. Therefore, true 2D experiments have to be performed. Signals of different coherence order can be separated by time-proportional incrementation of the phase $\varphi = n\Delta\varphi^{\text{TPPI}}$, with the counter $n = t_1/\Delta t_1$ [11]. A real cosine Fourier transformation with respect to $\Delta\varphi^{\text{TPPI}}$ should result in a pure absorption spectrum, because signals corresponding to $\pm p$ coherences have equal amplitudes.

6. Multiple-quantum relaxation

In section 5 it was shown that due to longitudinal relaxation single- and triple-quantum coherences may be excited. However, using transverse relaxation during the preparation period, multiple-quantum coherences may be created with higher efficiency. An additional advantage of the latter preparation scheme is the possibility of generating double-quantum coherences as well. However, an important drawback of the multiple-quantum relaxation experiments is the fact that the double- and triple-quantum relaxation rates, $R^{(2)}$ and $R^{(3)}$, are equal to the single-quantum rates, $R_s^{(1)}$ and $R_c^{(1)}$, respectively (eqs. (16) and (17)). The latter values can be measured with high accuracy using conventional transverse relaxation schemes, while the multiple-quantum relaxation experiments are rather cumbersome.

The multiple-quantum relaxation rates may be obtained using the pulse sequences:

$$(\pi/2)_{\varphi}\text{-preparation}, \tau - (\pi/2)_{\varphi+\varphi'}\text{-evolution}, t_1 - (\pi/2)_{\varphi'}\text{-detection}, t_2, \quad (48)$$

with $\varphi' = 0$ for the double-quantum excitation, and $\varphi' = -\pi/2$ for the triple-quantum excitation. Separation of coherence order can be achieved by time-proportional phase incrementation of the excitation sandwich, i.e. the phase φ . To eliminate magnetic inhomogeneity, one or more refocusing pulses may be included. Longitudinal relaxation effects during the preparation may be suppressed by a $(\pi)_{\varphi-\pi/2}$ pulse in the middle of this period. The former pulse sequence has been used by Rooney et al. to obtain the ^{23}Na double-quantum spectrum in a liquid crystal [13].

During the preparation period, the density operator is represented by eq. (28). After this period, multiple-quantum coherences can be excited. In the double-quantum experiment, according to eqs. (28), (33) and (34) with a $(\pi/2)_{\varphi'=0}$ pulse, one has

$$\sigma^*(\tau, p = \pm 2) = \sqrt{\frac{5}{2}} [(T_{2-2} - T_{2+2}) q_{21}^{(1)}(\tau) - \frac{1}{4}\sqrt{10}(T_{3-2} + T_{3+2}) q_{31}^{(1)}(\tau)], \quad (49)$$

and for the triple-quantum experiment, with a $(\pi/2)_{\varphi'=-\pi/2}$ pulse, one has

$$\sigma^*(\tau, p = \pm 3) = -\frac{5}{4}\sqrt{\frac{3}{2}}(T_{3-3} - T_{3+3}) q_{31}^{(1)}(\tau). \quad (50)$$

It should be noted that in the double- and triple-quantum experiment zero- and single-quantum coherences, respectively, are also excited. These contributions are not explicitly specified.

In the evolution period the density operator evolves due to relaxation and precession. According to eqs. (22) and (23), the time evolution can be represented by

$$\begin{aligned} \sigma^*(\tau, t_1, p = \pm 2) = & \sqrt{\frac{5}{2}} \{ (T_{2-2} - T_{2+2}) [q_{21}^{(1)}(\tau) q_{22}^{(2)}(t_1) - \frac{1}{4}\sqrt{10} q_{31}^{(1)}(\tau) q_{23}^{(2)}(t_1)] \\ & + (T_{3-2} + T_{3+2}) [q_{21}^{(1)}(\tau) q_{32}^{(2)}(t_1) - \frac{1}{4}\sqrt{10} q_{31}^{(1)}(\tau) q_{33}^{(2)}(t_1)] \} \end{aligned} \quad (51)$$

for the double-quantum excitation experiment, and

$$\sigma^*(\tau, t_1, p = \pm 3) = -\frac{5}{4}\sqrt{\frac{3}{2}}(T_{3-3} - T_{3+3}) q_{31}^{(1)}(\tau) q_{33}^{(3)}(t_1) \quad (52)$$

for the triple-quantum excitation.

After the evolution period a detection pulse is applied. In the 2D experiment with TPPI the signal contributions are

$$\begin{aligned} s(\tau, t_1, t_2, p = \pm 2) = & \frac{1}{2} \{ -q_{21}^{(1)}(\tau) [q_{22}^{(2)}(t_1) q_{12}^{(1)}(t_2) - \frac{1}{4}\sqrt{10} q_{32}^{(2)}(t_1) q_{13}^{(1)}(t_2)] \\ & + q_{31}^{(1)}(\tau) [\frac{1}{4}\sqrt{10} q_{23}^{(2)}(t_1) q_{12}^{(1)}(t_2) - \frac{5}{8} q_{33}^{(2)}(t_1) q_{13}^{(1)}(t_2)] \} \exp(\mp 2i\varphi) \end{aligned} \quad (53)$$

for the double-quantum excitation experiment, and

$$s(\tau, t_1, t_2, p = \pm 3) = \frac{15}{32} q_{31}^{(1)}(\tau) q_{33}^{(3)}(t_1) q_{13}^{(1)}(t_2) \exp(\mp 3i\varphi) \quad (54)$$

for the triple-quantum excitation.

The double-quantum signal is rather complicated, but has been measured by Rooney et al. [13]. To the author's knowledge, the triple-quantum spectrum has not been reported.

7. Conclusions

In the presence of a nonvanishing average quadrupolar coupling, the formalism in terms of irreducible tensor operators and relaxation functions conveniently describes the density operator under a series of rf pulses and evolution periods. With this framework, it is relatively easy to design experiments to investigate the spectral densities of the fluctuating electric field gradients experienced by the relaxing nucleus. A number of examples are presented. Longitudinal relaxation of the satellites and central transition conveniently provides the spectral density at one and two times the Larmor frequency. The spectral density at zero frequency can be evaluated from the linewidths. This is an important probe for investigating low frequency dynamics in, e.g. liquid crystals and ordered heterogeneous systems. The multiple-quantum experiment provide no additional information, but may be used as a consistency check.

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