

Relaxation of spin $S=3/2$ in the doubly rotating tilted frame

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For spin $S = 3/2$ the time evolution of the density operator under spin-locking is described. It is shown that outside the extreme narrowing limit triple-quantum coherences are excited. An experiment is proposed to monitor these coherences. The corresponding signal evolves according to a simple relaxation function which is suitable for fitting.

INTRODUCTION

In condensed matter, the spin $S = 3/2$ quadrupolar nuclei (e.g., ^7Li , ^{23}Na , ^{87}Rb , ^{35}Cl , and ^{81}Br) occur rather frequently and may experience fluctuating electric field gradients. For instance, in synthetic and biological polymer solutions,^{1,2} and other biological systems,³ the magnetic relaxation behavior is an important probe to study the dynamics and interactions of the small ions. Longitudinal and transverse relaxation rates are sensitive to the spectral densities of the fluctuating field gradient at zero, one, and two times the Larmor frequency, $-\gamma H_0$. The Larmor frequency is usually of the order MHz. In the presence of slowly fluctuating processes, the spectral density function shows a dispersion at relatively low frequencies of the order kHz. Accordingly, transverse relaxation experiments give access to the zero frequency component of this dispersion only. However, the $T_{1\rho}$ experiment is an excellent tool to investigate these slowly fluctuating processes. This is because the spin-lock field strength H_1 can be varied easily to probe the spectral density at frequencies of the order of the precession frequency with respect to the spin-lock field, $-\gamma H_1$. The problem of relaxation during spin-locking has been discussed extensively by Blicharski.⁴ However, the discussion of quadrupolar relaxation has been confined to spin quantum number $S = 1$.

Recently, it has been recognized that due to spin $S \gg 3/2$ relaxation outside the extreme narrowing limit multiple-quantum coherences may be excited.^{5,6} The spin $S = 3/2$ relaxation of zero, single, and multiple quantum coherences in a zero average electric field gradient has extensively been discussed by Jaccard *et al.*⁶ The effect of a static quadrupolar coupling on the relaxation and precession of the spin $S = 3/2$ system has been considered in a previous paper.⁷ In the present contribution, spin $S = 3/2$ $T_{1\rho}$ relaxation will be treated. Expressions are presented which describe the time evolution of the density operator during spin-locking. It is shown that spin-locking excites triple-quantum coherences for $S = 3/2$, provided the relaxation to be outside the extreme narrowing limit.

After spin-locking, the signal may directly be detected. However, outside the extreme narrowing limit, this conventional experiment results in a complicated functional form of the detected signal. Therefore, an experiment involving coherence transfer is designed which allows detection of the excited triple-quantum coherences. In this experiment, after the spin-lock period an additional $\pi/2$ pulse is applied. This

pulse converts the excited triple-quantum coherences into single-quantum coherences. Due to transverse relaxation, the latter coherences are observable during the detection period. The corresponding signal contribution evolves according to a simple relaxation function and is more suitable for fitting.

In this work, the irreducible tensor operators, the relaxation behavior, and coherence transfer are described by the formalism which has extensively been used by Müller *et al.*,⁵ Jaccard *et al.*,⁶ and the present author.⁷ For a description of this formalism the reader is referred to these papers.

PREPARATION AND SPIN LOCKING

To prepare the spin system, an initial $(\pi/2)_y$ pulse is applied. Dropping the factors expressing the number of spins and the temperature, the density operator in the rotating frame is

$$\sigma^*(t=0) = S_x = (5/2)^{1/2}(T_{-1} - T_{+1}). \quad (1)$$

The irreducible tensor operators are normalized according to Ref. 5.

After this initial $(\pi/2)_y$ pulse, a spin-lock pulse with a field strength H_1 along the x axis is applied. To calculate the time evolution of the density operator due to relaxation during the spin-lock period, it is convenient to define an interaction representation where the H_1 field disappears. For this purpose, the density operator in the rotating frame is transformed into the doubly rotating tilted frame.⁴ A possible nonzero average electric field gradient has been ignored. If the general form of the density operator in the rotating frame is

$$\sigma^* = \sum_{l,m} c_{lm} T_{lm} \quad (2)$$

then in the doubly rotating tilted frame the density operator is represented by

$$\sigma^{**} = \sum_{k,l,m} c_{lm} T_{lk} D_{km}^{(l)}(-\omega_1 t, -\beta, 0). \quad (3)$$

In this transformation $\omega_1 = -\gamma H_1$ and on-resonance β is the angle between the direction of the static Zeeman field H_0 and the spin-lock field H_1 . The sign conventions and angle definitions of Rose are adopted.⁸ In the present contribution, the offset of the pulse carrier frequency from exact resonance, $-\gamma H_0$, equals zero. The spin-lock pulse is applied exactly on resonance. Transforming Eq. (1) into the doubly

rotating tilted frame, one obtains, according to Eqs. (2) and (3) with $\beta = \pi/2$,

$$\sigma^{**}(t=0) = 5^{1/2} T_{10}. \quad (4)$$

During the spin-lock period, the density operator evolves due to longitudinal $T_{1\rho}$ relaxation. As shown in the Appendix, the time dependence of the density operator in the doubly rotating tilted frame is analogous to the time dependence in the rotating frame, but with spectral densities $\Sigma_{m=-2}^2 |d_{km}^{(2)}(-\beta)|^2 J_{km}(k\omega_1 + m\omega_0)$ vs $J_k(k\omega_0)$, respectively. The spectral densities are defined in the Appendix. In the rotating frame, the effect of longitudinal relaxation reads with the arrow notation⁶

$$T_{10} \xrightarrow{R^{(0)}} T_{10} f_{11}^{(0)}(t) + T_{30} f_{31}^{(0)}(t). \quad (5)$$

The relaxation functions are given by

$$f_{11}^{(0)}(t) = (1/5)(4 \exp\{R_3^{(0)}t\} + \exp\{R_4^{(0)}t\}), \quad (6)$$

$$f_{31}^{(0)}(t) = (2/5)(-\exp\{R_3^{(0)}t\} + \exp\{R_4^{(0)}t\}), \quad (7)$$

with rates

$$R_3^{(0)} = -2\left(\frac{eQ2\pi}{h}\right)^2 J_2(2\omega_0), \quad (8)$$

$$R_4^{(0)} = -2\left(\frac{eQ2\pi}{h}\right)^2 J_1(\omega_0). \quad (9)$$

The superscript (0) denotes longitudinal relaxation in the rotating frame. In the doubly rotating tilted frame, the time dependence of the spin density operator due to longitudinal $T_{1\rho}$ relaxation is analogous, but with different rates. With Eqs. (5)–(7), and changing the superscript (0) into (ρ) to discern $T_{1\rho}$ relaxation, one obtains the time evolution

$$\sigma^{**}(t_1) = 5^{1/2}\{T_{10}f_{11}^{(\rho)}(t_1) + T_{30}f_{31}^{(\rho)}(t_1)\} \quad (10)$$

with the relaxation functions

$$f_{11}^{(\rho)}(t_1) = (1/5)(4 \exp\{R_3^{(\rho)}t_1\} + \exp\{R_4^{(\rho)}t_1\}), \quad (11)$$

$$f_{31}^{(\rho)}(t_1) = (2/5)(-\exp\{R_3^{(\rho)}t_1\} + \exp\{R_4^{(\rho)}t_1\}). \quad (12)$$

To obtain the relaxation rates $R_3^{(\rho)}$ and $R_4^{(\rho)}$, in Eqs. (8) and (9) the spectral densities $J_k(k\omega_0)$ have to be substituted by $\Sigma_{m=-2}^2 |d_{km}^{(2)}(-\beta)|^2 J_{km}(k\omega_1 + m\omega_0)$. Accordingly, one has

$$R_3^{(\rho)} = -2\left(\frac{eQ2\pi}{h}\right)^2 \left\{ \left(\frac{1-\cos\beta}{2}\right)^4 J_{2-2}(2\omega_1 - 2\omega_0) + \left(\frac{1-\cos\beta}{2} \sin\beta\right)^2 J_{2-1}(2\omega_1 - \omega_0) \right. \\ \left. + \frac{3}{8} \sin^4\beta J_{20}(2\omega_1) + \left(\frac{1+\cos\beta}{2} \sin\beta\right)^2 J_{21}(2\omega_1 + \omega_0) + \left(\frac{1+\cos\beta}{2}\right)^4 J_{22}(2\omega_1 + 2\omega_0) \right\}, \quad (13)$$

$$R_4^{(\rho)} = -2\left(\frac{eQ2\pi}{h}\right)^2 \left\{ \left(\frac{1-\cos\beta}{2} \sin\beta\right)^2 J_{1-2}(\omega_1 - 2\omega_0) + \left(\frac{1+\cos\beta}{2} - \cos^2\beta\right)^2 J_{1-1}(\omega_1 - \omega_0) \right. \\ \left. + \frac{3}{8} \sin^2\beta J_{10}(\omega_1) + \left(\cos^2\beta - \frac{1-\cos\beta}{2}\right)^2 J_{11}(\omega_1 + \omega_0) + \left(\frac{1+\cos\beta}{2} \sin\beta\right)^2 J_{12}(\omega_1 + 2\omega_0) \right\}. \quad (14)$$

In the limit $\omega_1 \ll \omega_0$, for $m \neq 0$ the spectral density function has the property

$$J_{km}(k\omega_1 + m\omega_0) \approx J_{0m}(m\omega_0) = J_{0-m}(-m\omega_0). \quad (15)$$

Accordingly, with $\beta = \pi/2$ and $\omega_1 \ll \omega_0$, the relaxation rates are approximately represented by

$$R_3^{(\rho)} = -\left(\frac{eQ2\pi}{h}\right)^2 \{(3/4)J_{20}(2\omega_1) + J_{01}(\omega_0) + (1/4)J_{02}(2\omega_0)\}, \quad (16)$$

$$R_4^{(\rho)} = -\left(\frac{eQ2\pi}{h}\right)^2 \{J_{01}(\omega_0) + J_{02}(2\omega_0)\}. \quad (17)$$

The $R_3^{(\rho)}$ component contains the spectral density at frequency $2\omega_1$ and, hence, is a probe to study slow motion.

After the spin-lock period, the H_1 field is switched off. Now, the density operator has to be transformed back into the rotating frame. If the general form of the density operator in the doubly rotating tilted frame is

$$\sigma^{**} = \sum_{l,m} b_{lm} T_{lm} \quad (18)$$

then in the rotating frame the density operator is given by

$$\sigma^* = \sum_{k,l,m} b_{lm} T_{lk} D_{km}^{(l)}(0, \beta, \omega_1, t). \quad (19)$$

Backtransforming Eq. (10) into the rotating frame, then yields according to Eqs. (18) and (19) with $\beta = \pi/2$,

$$\sigma^*(t_1) = \sigma^*(t_1, p = \pm 1) + \sigma^*(t_1, p = \pm 3) \quad (20)$$

with

$$\sigma^*(t_1, p = \pm 1) = (5/2)^{1/2} \{(T_{1-1} - T_{1+1})f_{11}^{(\rho)}(t_1) - (3/8)^{1/2}(T_{3-1} - T_{3+1})f_{31}^{(\rho)}(t_1)\}, \quad (21)$$

$$\sigma^*(t_1, p = \pm 3) = (5/4)(T_{3-3} - T_{3+3})f_{31}^{(\rho)}(t_1). \quad (22)$$

Equations (21) and (22) represent order $p = \pm 1$ single- and $p = \pm 3$ triple-quantum coherences, respectively. Hence, due to $T_{1\rho}$ relaxation multiple-quantum coherences are excited. In the extreme narrowing limit, the function $f_{31}^{(\rho)}(t_1)$ vanishes and only single-quantum coherences are excited. This relaxation behavior is similar to longitudinal relaxation without a spin-lock field (but with modified rates).⁶ After the spin-lock period, the signal can directly be detected. Another option is to use the multiple-quantum coherences, which results in a more simple relaxation behav-

ior. For this purpose, an additional $(\pi/2)_x$ pulse has to be applied 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 due to transverse relaxation during the detection period.

DIRECT DETECTION

After switching off the spin-lock field the density operator evolves due to transverse relaxation. Under relaxation, the rank l of the tensor operators may change, but the order p is conserved.⁹ Hence, the multiple-quantum coherences $\sigma^*(t_1, p = \pm 3)$ do not become apparent under direct detection. For order $p = \pm 1$ coherences, the effect of transverse relaxation reads with the arrow notation⁶

$$T_{1\pm 1} \xrightarrow{R^{(1)}} T_{1\pm 1} f_{11}^{(1)}(t_2) + T_{3\pm 1} f_{31}^{(1)}(t_2), \quad (23)$$

$$T_{3\pm 1} \xrightarrow{R^{(1)}} T_{3\pm 1} f_{33}^{(1)}(t_2) + T_{1\pm 1} f_{13}^{(1)}(t_2), \quad (24)$$

with the relaxation functions

$$f_{11}^{(1)}(t_2) = (1/5)(3 \exp\{R_1^{(1)} t_2\} + 2 \exp\{R_2^{(1)} t_2\}), \quad (25)$$

$$f_{13}^{(1)}(t_2) = f_{31}^{(1)}(t_2) = (6^{1/2}/5)(\exp\{R_1^{(1)} t_2\} - \exp\{R_2^{(1)} t_2\}), \quad (26)$$

$$f_{33}^{(1)}(t_2) = (1/5)(2 \exp\{R_1^{(1)} t_2\} + 3 \exp\{R_2^{(1)} t_2\}) \quad (27)$$

with rates

$$R_1^{(1)} = -\left(\frac{eQ2\pi}{h}\right)^2 \{J_0(0) + J_1(\omega_0)\}, \quad (28)$$

$$R_2^{(1)} = -\left(\frac{eQ2\pi}{h}\right)^2 \{J_1(\omega_0) + J_2(2\omega_0)\}. \quad (29)$$

The superscript (1) denotes transverse relaxation. With Eqs. (20), (21), (23), and (24) and focusing on order $p = \pm 1$ coherences during the detection period the density operator is given by

$$\begin{aligned} \sigma^*(t_1, t_2, p = \pm 1) &= (5/2)^{1/2} (T_{1-1} - T_{1+1}) \\ &\times \{f_{11}^{(p)}(t_1) f_{11}^{(1)}(t_2) - (3/8)^{1/2} f_{31}^{(p)}(t_1) f_{13}^{(1)}(t_2)\} \\ &+ (5/2)^{1/2} (T_{3-1} - T_{3+1}) \{f_{11}^{(p)}(t_1) f_{31}^{(1)}(t_2) - (3/8)^{1/2} f_{31}^{(p)}(t_1) f_{33}^{(1)}(t_2)\}. \end{aligned} \quad (30)$$

Under direct detection, only the $T_{1\pm 1}$ coherences become apparent. Hence, the observed signal is represented by

$$s(t_1, t_2) = f_{11}^{(p)}(t_1) f_{11}^{(1)}(t_2) - (3/8)^{1/2} f_{31}^{(p)}(t_1) f_{13}^{(1)}(t_2). \quad (31)$$

Note that the signal under direct detection is a complicated function, which is less suitable for fitting. The second term on the right-hand side of Eq. (31) vanishes in the limit $t_2 \rightarrow 0$. Consequently, the effect of this interference term may be minimized by recording the (extrapolated) amplitude of the detected signal directly after the spin-lock period [i.e., $s(t_1, t_2 \rightarrow 0)$].

COHERENCE TRANSFER

Another strategy is to monitor the excited triple-quantum coherences by applying a pulse with a phase $+x$ after the spin-lock period. The separation of coherences may be obtained by time-proportional phase incrementation (TPPI^{9,10}) of the excitation and spin-lock pulses. The sequence of Fig. 1 is proposed. The phase φ in Fig. 1 is defined

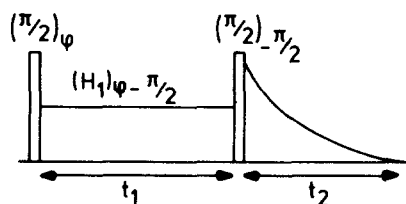


FIG. 1. Pulse sequence to monitor the triple-quantum coherences after spin-locking. The phase φ has to be incremented proportional to the evolution time t_1 (TPPI).

as a positive excursion with respect to the y axis, in accordance with the definitions of the Euler angles.^{5,8}

The effect of pulses is described by a simple transformation. The rank l is conserved, the order m may change.⁹ If the density operator has the general form

$$\sigma^* = \sum_{l,m} c_{lm} T_{lm} \quad (32)$$

then after the pulse with a flip angle β and phase φ' the density operator is represented by⁵

$$\sigma^* = \sum_{k,l,m} c_{lm} T_{lk} d_{km}^{(l)}(\beta) \exp\{-i(k-m)\varphi'\} \quad (33)$$

in which $k-m$ is the change of coherence order induced by the pulse. The reduced matrix elements $d_{km}^{(l)}(\beta)$ are conveniently tabulated in Ref. 5.

With Eqs. (32) and (33), after coherence transfer with a $\pi/2$ pulse and phase $\varphi' = -\pi/2$, the density operator [Eq. (21) and (22)] is represented by

$$\begin{aligned} \sigma^*(t_1, p = \pm 1) &= (5/2)^{1/2} \{ (T_{1-1} - T_{1+1}) f_{11}^{(p)}(t_1) \\ &+ (6^{1/2}/16) (T_{3-1} - T_{3+1}) f_{31}^{(p)}(t_1) \\ &+ (90^{1/2}/16) (T_{3-3} - T_{3+3}) f_{31}^{(p)}(t_1) \}, \end{aligned} \quad (34)$$

$$\begin{aligned} \sigma^*(t_1, p = \pm 3) &= (5/4) \\ &\times \{ - (15^{1/2}/4) (T_{3-1} - T_{3+1}) f_{31}^{(p)}(t_1) \\ &+ (1/4) (T_{3-3} - T_{3+3}) f_{31}^{(p)}(t_1) \}. \end{aligned} \quad (35)$$

Now, during detection the $T_{3\pm 1}$ coherences may evolve into observable $T_{1\pm 1}$ coherences according to Eq. (24).

In the 2D experiment with TPPI, four distinct signal contributions are detected. With Eqs. (23), (24), (34), and (35), and collecting $T_{1\pm 1}$ coherences only, these contributions are

$$s(t_1, t_2, p = \pm 1) = \{ (1/2) f_{11}^{(\rho)}(t_1) f_{11}^{(1)}(t_2) + (6^{1/2}/32) f_{31}^{(\rho)}(t_1) f_{13}^{(1)}(t_2) \} \times \exp(\mp i\varphi), \quad (36)$$

$$s(t_1, t_2, p = \pm 3) = - (5/32) 6^{1/2} f_{31}^{(\rho)}(t_1) f_{13}^{(1)}(t_2) \times \exp(\mp 3i\varphi) \quad (37)$$

in which φ is the phase defined in Fig. 1. The signal originating from the triple-quantum coherences has a relatively simple form and is suitable for fitting. Because the signal has to be detected as a function of t_1 , a true 2D experiment has to be performed. The signals are separated by time-proportional incrementation of the phase $\varphi = n\Delta\varphi^{\text{TPPI}}$, with the counter $n = t_1/\Delta t_1$.^{9,10} The symmetrically disposed signals corresponding to $\pm p$ coherences have equal amplitudes. Therefore, a real cosine Fourier transformation with respect to $\Delta\varphi^{\text{TPPI}}$ results in a pure absorption spectrum after phase correction.

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APPENDIX: ANALOGY OF THE TIME DEPENDENCE OF THE DENSITY OPERATOR IN THE DOUBLY ROTATING TILTED FRAME AND ROTATING FRAME.

A general expression of the time evolution of the density operator due to quadrupolar relaxation in the doubly rotating tilted frame is derived, independent of the spin quantum number S . It is shown how the time dependence of the density operator in the rotating frame has to be modified to include the effect of spin-locking.

In the doubly rotating tilted frame, where no external fields appear explicitly, the time evolution of the density operator σ^{**} is given by¹¹

$$\frac{d\sigma^{**}}{dt} = - \int_0^\infty \langle [H^{**}(t), [H^{**}(t-\tau), \sigma^{**}(t)]] \rangle d\tau. \quad (A1)$$

The conditions for the validity of Eq. (A1) have been discussed by Abragam.¹¹ In the doubly rotating tilted frame, the quadrupolar coupling Hamiltonian H^{**} is given by⁴

$$H^{**} = C \sum_{m,k=-2}^2 (-1)^m A_{2k} D_{km}^{(2)} \times (-\omega_1 t - \beta - \omega_0 t) F_{2-m} \quad (A2)$$

in which $C = (eQ\eta)/S(2S-1)\hbar$, the nuclear spin operator is denoted by A_{2m} , and F_{2m} denotes the field gradient tensor.^{12,13} The field gradient tensor takes the form: $F_{20} = (1/2)V_{zz}$, $F_{2\pm 1} = \mp (6^{-1/2})(V_{xz} \pm iV_{yz})$, and $F_{2\pm 2} = (6^{-1/2}/2)(V_{xx} - V_{yy} \pm 2iV_{xy})$. The transformation from the laboratory frame to the doubly rotating tilted frame is effected by the Wigner matrix $D_{km}^{(2)}(-\omega_1 t - \beta - \omega_0 t)$ as described before. Inserting Eq. (A2) into Eq. (A1), then yields

$$\begin{aligned} \frac{d\sigma^{**}}{dt} = & -C^2 \sum_{\substack{m,k \\ m',k'=-2}}^2 (-1)^{m+m'} \exp\{i[(m+m')\omega_0 \\ & + (k+k')\omega_1]t\} [A_{2k}, [A_{2k'}, \sigma^{**}]] \\ & \times d_{km}^{(2)}(-\beta) d_{k'm'}^{(2)}(-\beta) \\ & \times \int_0^\infty \langle F_{2-m}(t) F_{2-m'}(t-\tau) \rangle \\ & \times \exp\{-i(k'\omega_1 + m'\omega_0)\tau\} d\tau. \end{aligned} \quad (A3)$$

Finally, restricting to the secular terms with $m = -m'$ and $k = -k'$, one obtains the general expression

$$\begin{aligned} \frac{d\sigma^{**}}{dt} = & -C^2 \sum_{k=-2}^2 [A_{2k}, [A_{2k}^\dagger, \sigma^{**}]] \\ & \times \sum_{m=-2}^2 |d_{km}^{(2)}(-\beta)|^2 J_{km}(k\omega_1 + m\omega_0) \end{aligned} \quad (A4)$$

with the spectral densities

$$\begin{aligned} J_{km}(k\omega_1 + m\omega_0) = & (1/2) \int_{-\infty}^\infty \langle F_{2m}^*(t) F_{2m}(t-\tau) \rangle \\ & \times \exp\{i(k\omega_1 + m\omega_0)\tau\} d\tau. \end{aligned} \quad (A5)$$

The imaginary part of the integral in Eq. (A3) has been neglected. This part can be included in the Zeeman Hamiltonian resulting in a very small second-order frequency shift.^{11,14} For comparison, the corresponding equation for the time evolution of the density operator without the presence of a spin-lock field is given by^{11,12,13}

$$\frac{d\sigma^*}{dt} = -C^2 \sum_{k=-2}^2 [A_{2k}, [A_{2k}^\dagger, \sigma^*]] J_k(k\omega_0) \quad (A6)$$

with

$$J_k(k\omega_0) = (1/2) \int_{-\infty}^\infty \langle F_{2k}^*(t) F_{2k}(t-\tau) \rangle \exp\{ik\omega_0\tau\} d\tau. \quad (A7)$$

The spin operator double commutators in Eqs. (A4) and (A6) have the same functional form. Hence, to modify the time dependence of the density operator in the rotating frame [i.e., Eq. (A6)] to include the effect of spin-locking, one has to substitute the spectral densities $J_k(k\omega_0)$ by $\Sigma_m^2 = -2 |d_{km}^{(2)}(-\beta)|^2 J_{km}(k\omega_1 + m\omega_0)$.

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