Relaxation of anisotropically oriented $I=3/2$ nuclei in the multipole basis: Evolution of the second rank tensor in the double quantum filtered nuclear magnetic resonance experiment

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The relaxation of an $I=3/2$ spin system in an anisotropic environment characterized by a finite residual quadrupolar splitting ω_q is modeled by analytically solving for the density operator from Redfield's relaxation theory. The resulting equations are cast into the multipole basis in order to describe the tensorial components of the spin density matrix. Included in the relaxation matrix are off-diagonal elements J_1 and J_2, which account for anisotropic systems with ω_q values less than the width of the resonant line. With the Wigner rotation matrices simulating hard pulses, the response to an arbitrary pulse sequence can be determined. An analytical expression for the response to the double quantum filtered (DQF) pulse sequence $(\pi/2)-(\pi/2)-\pi-(\pi/2)-\theta-\delta-\theta-\mathrm{AQ}$ for $\theta=\pi/2$ is presented, showing explicitly the formation of a second rank tensor owing only to the presence of a finite ω_q. This second rank tensor displays asymptotic behavior when the (reduced) quadrupole splitting is equal to either of the off-diagonal spectral densities J_2 and J_1. Line shape simulations for ω_q values of less than a linewidth reproduce the general features of some recently reported ^{23}Na DQF line shapes from biological systems. Distinct relaxation dynamics govern each of the tensorial components of the resonant signal revealing the influence of the experimental variables on the line shape.

I. INTRODUCTION

The Redfield theory is often sufficient to describe the spin relaxation of quadrupolar nuclei. In the isotropic phase, where the residual quadrupolar interaction is averaged to zero ($\omega_q=0$), Redfield theory applies to all but those systems characterized by very long rotational correlation times τ_c.[1,2] Provided τ_c is not in the extreme narrowing limit, it is possible to induce the formation of multiple quantum (MQ) coherences in a nuclear magnetic resonance (NMR) experiment owing to the presence of multiexponential relaxation.[1] Multiple quantum filtered (MQF) experiments may thus be used to directly distinguish pools in which the nuclei are bound or otherwise associated with slowly rotating macromolecules, since single exponentials describe the relaxation of the free spin concentration. In many cases, the static quadrupolar interaction term of the Hamiltonian contains a contribution from a nonzero quadrupole resulting from an anisotropic distribution of the electric field gradients (EFG) in the sample. In a macroscopically oriented sample with local anisotropy, a static quadrupole splitting results if the diffusion of the spin-bearing particle is slow, i.e., the residence time within each "domain" is much longer than the inverse of the quadrupole splitting. In this context, domain may be a microcrystallite as in some liquid crystal samples,[3] or may be a nomer for the long orientational correlation length of some biomolecular associations. The splitting within one domain is then determined by the orientation with respect to the external magnetic field and the spectrum is the average over many domains.

Observations from some MQF experiments of biological tissue are best interpreted in the context of this latter example.[4–7] Rooney and Springer have produced an exhaustive review of tissue resonances of $I=3/2$ nuclei,[8,9] where the influence of a residual quadrupole is discussed from an experimental perspective. Subsequent efforts describe specific studies of $^{23}Na^+$ in biological systems.[10] More general considerations include chemical exchange between the bound sites and the isotropic surroundings; some theoretical studies examine the modulation of both ω_q and τ_c by chemical exchange by means of a discrete exchange model (DEM).[11–14] This allows a discussion of the intermediate and slow exchange regimes, since in the fast exchange limit, macroscopic parameters are found to be weighted averages of the exchanging sites[12,14] and may therefore be discussed in the context of Redfield's theory. Eliav and Navon have defined the limits of Redfield's theory[15] in terms of the MQF experiment by extending their general treatment of the quantum Liouville equation to describe the line shapes of the higher quantum coherences of a single spin pool over a range of τ_c values for an isotropically oriented system.

The state multipole formalism[16–18] describes the evolution of a spin system in a multipulse NMR experiment. Relaxation under the Redfield operator of an isotropic system has been described in the multipole basis[19] and the evolution of the tensors corresponding to higher quantum coherences for $I\leqslant 9/2$, in the absence of relaxation, has been explored.[18]

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More recently, Furó and Halle have investigated the spin relaxation of nuclei in anisotropic systems in two-dimensional quadrupolar echo[20] and inversion recovery[21] experiments using the multipole formalism. They have also developed a theoretical framework for the use of MQ filters (MQF) for the detection of the evolution of various MQ coherences,[22] again in the multipole basis. While the Redfield superoperator was used to describe spin relaxation, Furó *et al.* assumed a negligible contribution from the off-diagonal elements of the resulting relaxation matrices. The elements of the spin density matrix then diagonalize and relax independently and are solved separately. However, for cases in which ω_q is less than the linewidth of the central line, this approximation will not adequately describe the spin dynamics. For example, we have found that the second rank tensor generated in a MQF experiment, the presence of which is the direct result of an anisotropic environment, displays strikingly rich behavior at small ω_q values that can only be accounted for if the contributions from these off-diagonal matrix elements of the Redfield equation are considered.

Here, we present solutions for the time evolution and relaxation of the eigenvectors of the spin density matrix for $I=3/2$. Cast into the multipole basis, the resulting rate equations may be used conveniently to generate an analytical response function to a general hard pulse sequence. The response to a typical MQF experiment is discussed in the context of the tensorial contributions to the line shape.

II. THEORY

For the system under consideration, in the product operator basis, the Liouville superoperator is diagonal. Assuming the relaxation may be sufficiently described by Redfield's theory, the spin density operator ρ is governed by

$$i\frac{\partial\rho}{\partial t}=\mathbf{L}\rho-i\mathbf{R}\rho. \tag{1}$$

The Redfield relaxation superoperator matrix $\mathbf{R}$ factors into distinct blocks for each of the four possible n-quantum manifolds of the $I=3/2$ spin and has been given elsewhere.[1,23] The spin density operator is expanded in terms of the product basis operators

$$\rho(t)=\sum \rho_{rs}(t)|r\rangle\langle s| \tag{2}$$

with the time dependence being contained exclusively in the coefficients ρ_{rs}. The four eigenstates can be relabeled $|1\rangle=|3/2\rangle$, $|2\rangle=|1/2\rangle$, $|3\rangle=|-1/2\rangle$, and $|4\rangle=|-3/2\rangle$ giving a coupled set of differential equations for the evolution of the n-quantum elements. The single quantum spectrum is characterized by a central line corresponding to the transition between the $m=\pm 1/2$ states flanked by two satellites from the $|1\rangle\leftrightarrow|2\rangle$ and $|3\rangle\leftrightarrow|4\rangle$ transitions. Unlike the Liouville superoperator, the relaxation matrix has off-diagonal terms involving the nonsecular spectral densities J_1 and J_2 which couple the operators governing the relaxation of the satellite lines.[22] If the residual quadrupole splitting is large relative to the width of the central line, then the elements of the equation of motion (1) decouple and may be treated independently.[20] For the quadrupolar spin in an isotropic environment, the spectral degeneracy of the $2I+1-n$, n-quantum coherences is lifted for any $\omega_q\neq 0$. Incorporating the effects of this residual quadrupolar splitting gives for the evolution of the single quantum coefficients

$$-(i\mathbf{L}+\mathbf{R})=C\begin{bmatrix} -i(\omega_0+\omega_q)-(J_0+J_1+J_2) & 0 & J_2 \\ 0 & -i\omega_0-(J_1+J_2) & 0 \\ J_2 & 0 & -i(\omega_0-\omega_q)-(J_0+J_1+J_2) \end{bmatrix}. \tag{3}$$

In the treatment of the isotropic case $\mathbf{L}=\omega_0\mathbf{E}$, where $\mathbf{E}$ is the unit matrix, $i\mathbf{L}$ and $\mathbf{R}$ may then be treated and solved separately as shown elsewhere.[1] To reiterate, the off-diagonal relaxation terms are relevant whenever the detected quadrupolar splitting is comparable to, or less than, the width of the central line. In systems where all spins are homogeneously oriented relative to some external reference axis, as in crystals and oriented liquid crystals, there exists a single valued ω_q. In samples exhibiting local anisotropy,[2] the splitting observed in the laboratory frame is an average over all possible alignments of the local director of the EFG. However, if the splitting shown by the "powder" peaks is large, the relative weight of regions exhibiting a small ω_q is minor. In the development of Eliav *et al.*,[6] it is assumed that the value of ω_q relative to the laboratory reference frame is given in terms of the molecular reference frame by the following:

$$\omega_q=\omega_q^{\mathrm{mol}}(3\cos^2\theta_{\mathrm{LD}}-1)/2,$$

where θ_{LD} specifies the angle between the local director and the lab frame specified by the magnetic field. The heterogeneous orientations are assumed to follow a Gaussian distribution about ω_q^{mol} with a width $\Delta\omega_q^{\mathrm{mol}}$. Furthermore, in the treatment of Ref. 6, chemical exchange of a single spin between anisotropic sites with different θ_{LD} and ω_q^{mol} values is assumed to be slow.

The isotropic spectral densities that determine the evolution of the diagonal terms in Eq. (3) are not strictly real valued and contain a second order dynamic frequency shift term. However, since the evolution of the central line is decoupled from the evolution of the satellites, the dynamic shift effects can be accounted for by adding a relative frequency shift to the central line only and will be neglected in this treatment. The real part of the spectral density is defined as

$$J_n=\frac{2\tau_c}{1+(n\omega_0\tau_c)^2}. \tag{4}$$

In the product operator basis, off-diagonal relaxation terms are strictly real valued.[24] The quadrupolar interaction constant is given by

$$C=\frac{1}{40}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right), \tag{5}$$

in which Q is the nuclear quadrupole moment and e^2q and η are the maximum component and asymmetry parameter of the EFG. For convenience, the resonant frequencies have been reduced by C, i.e.,

$$\omega_q=\frac{\omega_q'}{C}, \quad \omega_0=\frac{\omega_0'}{C}. \tag{6}$$

Solutions to Eq. (1) are found by diagonalizing Eq. (3) and solving the resulting set of uncoupled differential equations

$$\mathbf{T}[-(i\mathbf{L}+\mathbf{R})]\mathbf{T}^{-1}=\mathbf{R}^{(1)}_{\text{diag}}=\begin{pmatrix} R_1^{(1)} & 0 & 0 \\ 0 & R_2^{(1)} & 0 \\ 0 & 0 & R_3^{(1)} \end{pmatrix}. \tag{7}$$

Because Eq. (3) is not Hermitian, the transformation is not unitary and

$$\mathbf{T}=\frac{1}{2^{1/2}J_2}\begin{Bmatrix} -[(J_2^2-\omega_q^2)^{1/2}+i\omega_q] & 0 & J_2 \\ 0 & 2^{1/2}J_2 & 0 \\ J_2 & 0 & (J_2^2-\omega_q^2)^{1/2}+i\omega_q \end{Bmatrix}. \tag{8}$$

Then, for the relaxation eigenvalues and corresponding product basis eigenfunctions, we find the following evolution:

$$\begin{aligned} &R_1^{(1)}=-C[J_0+J_1+J_2+(J_2^2-\omega_q^2)^{1/2}], \quad \rho_1^{(1)}=\frac{1}{2^{1/2}J_2}\{-[(J_2^2-\omega_q^2)^{1/2}+i\omega_q]\rho_{12}+J_2\rho_{34}\}, \\ &R_2^{(1)}=-C(J_1+J_2), \quad \rho_2^{(1)}=\rho_{23}, \\ &R_3^{(1)}=-C[J_0+J_1+J_2-(J_2^2-\omega_q^2)^{1/2}], \quad \rho_3^{(1)}=\frac{1}{2^{1/2}J_2}\{J_2\rho_{12}+[(J_2^2-\omega_q^2)^{1/2}+i\omega_q]\rho_{34}\}. \end{aligned} \tag{9}$$

As solutions to Eq. (1), each eigenvector decays exponentially

$$\rho_n^{(1)}(t)=\rho_n^{(1)}(0)\exp(R_n^{(1)}t). \tag{10}$$

Suitable manipulation of Eq. (9) gives the time dependence of the coefficients of the single element operators

$$\begin{bmatrix}\rho_{12}(t)\\ \rho_{23}(t)\\ \rho_{34}(t)\end{bmatrix}=\mathbf{R}^{(1)}\begin{bmatrix}\rho_{12}(0)\\ \rho_{23}(0)\\ \rho_{34}(0)\end{bmatrix}, \tag{11}$$

where

$$R^{(1)}=K^{(1)}(t)\begin{pmatrix} (J_2^2-\omega_q^2)^{1/2}\cosh[C(J_2^2-\omega_q^2)^{1/2}t] & 0 & J_2\sinh[C(J_2^2-\omega_q^2)^{1/2}t] \\ \quad -i\omega_q\sinh[C(J_2^2-\omega_q^2)^{1/2}t] & & \\ 0 & (J_2^2-\omega_q^2)^{1/2}\exp(CJ_0t) & 0 \\ J_2\sinh[C(J_2^2-\omega_q^2)^{1/2}t] & 0 & (J_2^2-\omega_q^2)^{1/2}\cosh[C(J_2^2-\omega_q^2)^{1/2}t] \\ & & \quad +i\omega_q\sinh[C(J_2^2-\omega_q^2)^{1/2}t] \end{pmatrix} \tag{12}$$

and

$$K^{(1)}(t)=\frac{\exp[-C(J_0+J_1+J_2)t]\exp(-i\omega_0't)}{(J_2^2-\omega_q^2)^{1/2}}\equiv\frac{\exp[-C(J+i\omega_0)t]}{(J_2^2-\omega_q^2)^{1/2}}. \tag{13}$$

Even with the added influence of anisotropy and relaxation coupling via J_2, the satellite and central lines remain uncoupled and relax independently. This result is consistent with previous developments.[25]

Additional physical insight may be gained by transforming the spin dynamics to a spherical tensor basis. In this basis, the spin density of the nucleus is described in contrast to the eigenvectors of the product operator basis that are derived from the lab frame energy levels. In other words, the spin coherences are naturally accounted for. The product operator is related[18] to the spherical tensor operators by a $3-j$ coefficient[26]

TABLE I. $R^{(1)}_{MP}$ evolution matrix elements.

$r^q_{kk'}$	
$r^{\pm1}_{11}$	$:3\left\{\cos[C(\omega_q^2-J_2^2)^{1/2}t]+\frac{J_2}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]\right\}+2\exp(CJ_0t)$
$r^{\pm1}_{12}$	$:\mp15^{1/2}\frac{\omega_q}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]=-r^{\pm1}_{21}$
$r^{\pm1}_{13}$	$:6^{1/2}\left\{\exp(CJ_0t)-\cos[C(\omega_q^2-J_2^2)^{1/2}t]-\frac{J_2}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]\right\}=r^{\pm1}_{31}$
$r^{\pm1}_{22}$	$:5\left\{\cos[C(\omega_q^2-J_2^2)^{1/2}t]-\frac{J_2}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]\right\}$
$r^{\pm1}_{23}$	$:\mp10^{1/2}\frac{\omega_q}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]=-r^{\pm1}_{32}$
$r^{\pm1}_{33}$	$:2\left\{\cos[C(\omega_q^2-J_2^2)^{1/2}t]+\frac{J_2}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}t]\right\}+3\exp(CJ_0t)$

$$|IM\rangle\langle IM'|=(-1)^{I-M}(2I+1)^{-1/2}\sum_{k=0}^{2I}\sum_{q=-k}^{k}(-i)^k \times(2k+I)^{1/2}\begin{pmatrix} I & k & I \\ -M & q & M'\end{pmatrix}\mathscr{G}^{(k)q}(\mathbf{I}). \quad (14)$$

$\mathscr{G}^{(k)q}(\mathbf{I})$ are the operators that span the Liouville space for spin I. In the classical limit when the vector operator $\mathbf{I}$ is replaced by a classical vector $\mathbf{r}$, then the $\mathscr{G}^{(k)q}(\mathbf{r})$'s are related to the spherical harmonics by[25]

$$\mathscr{G}^{(k)q}(\mathbf{r})=(i)^k(4\pi)^{1/2}r^kY_{kq}(\theta,\phi). \quad (15)$$

In the operator basis of $\mathscr{G}^{(k)q}(\mathbf{I})$, the tensor rank k and MQ coherence q are the Liouville space quantum numbers equivalent to the IM quantum numbers in state space. Thus in Dirac notation, the spherical tensor operator may be written $|kq\rangle\rangle$ with the double ket notation indicating an operator in Liouville space in contrast to the state space notation $|IM\rangle$. Since the expectation value of these operators is physically significant, the multipole polarizations are defined

$$\phi^k_q(t)=\mathrm{Tr}[\mathscr{G}^{(k)q}(\mathbf{I})^\dagger\rho(t)]=\langle\mathscr{G}^{(k)q}(\mathbf{I})^\dagger\rangle, \quad (16)$$

where † is the normal operator adjoint. By direct analogy with the $|IM\rangle$ basis, $|kq\rangle\rangle$ can be mixed by coupling interactions. The spin density operator for a single spin can be written as

$$\rho(t)=\sum_{k=0}^{2I}\sum_{q=-k}^{k}\phi^k_q(t)|kq\rangle\rangle, \quad (17)$$

where the ϕ^k_q's are the coefficients that determine the state. Since the product and multipole operator bases span the same space, they are related by a unitary transformation defined by Eq. (14). Applying the appropriate transformation[17] to Eq. (12) gives the evolution matrix in the multipole basis

$$\mathbf{UR}^{(1)}\mathbf{U}^{-1}=-i\left(\frac{2}{5}\right)^{1/2}\begin{pmatrix} 3^{1/2} & 2 & 3^{1/2} \\ i5^{1/2} & 0 & -i5^{1/2} \\ -2^{1/2} & 6^{1/2} & -2^{1/2}\end{pmatrix} \times\mathbf{R}^{(1)}\left(\frac{2}{5}\right)^{1/2} i\frac{1}{4}\begin{pmatrix} 3^{1/2} & -i5^{1/2} & -2^{1/2} \\ 2 & 0 & 6^{1/2} \\ 3^{1/2} & i5^{1/2} & -2^{1/2}\end{pmatrix}$$

$$=\mathbf{R}^{(1)}_{MP}=\frac{\exp(-CJt)\exp(-i\omega_0't)}{5} \times\begin{pmatrix} r^{\pm1}_{11} & r^{\pm1}_{12} & r^{\pm1}_{13} \\ r^{\pm1}_{21} & r^{\pm1}_{22} & r^{\pm1}_{23} \\ r^{\pm1}_{31} & r^{\pm1}_{32} & r^{\pm1}_{33}\end{pmatrix}. \quad (18)$$

The matrix elements for Eq. (18) are given in Table I. Evolution of the $q=1$ multipole coefficients is then given by Eq. (19).

$$\begin{bmatrix}\phi^1_{\pm1}(t)\\ \phi^2_{\pm1}(t)\\ \phi^3_{\pm1}(t)\end{bmatrix}=\mathbf{R}^{(1)}_{MP}\begin{bmatrix}\phi^1_{\pm1}(0)\\ \phi^2_{\pm1}(0)\\ \phi^3_{\pm1}(0)\end{bmatrix}. \quad (19)$$

From the multipole expansion in Eqs. (18) and (19) and the explicit form of the relaxation matrix elements in Table I, it is readily apparent that in anisotropic media, it is possible for a second rank tensor polarization, i.e., $\phi^2_{\pm1}$, to couple to the transverse magnetization $\phi^1_{\pm1}$ produced in a NMR experiment. Moreover, as ω_q approaches zero, the contribution from this vanishes as seen from r^1_{12} in Table I.

The double quantum coherences can be treated in a manner analogous to the SQ coherences above. With the Redfield matrix applicable to the DQ transitions,[1] the DQ eigenvectors evolve according to

$$-(i\mathbf{L}+\mathbf{R})=C\begin{bmatrix}-i(2\omega_0+\omega_q)-(J_0+J_1+J_2) & J_1 \\ J_1 & -i(2\omega_0-\omega_q)-(J_0+J_1+J_2)\end{bmatrix}. \quad (20)$$

As in the single quantum case, the Liouville and Redfield supermatrices cannot be separated. Again, diagonalization of Eq. (20) and subsequent solution of Eq. (1) gives the exponential time dependence of the DQ product basis eigenvectors, from which can be calculated the time dependence of the ρ_{rs} coefficients

$$\begin{bmatrix}\rho_{13}(t)\\ \rho_{24}(t)\end{bmatrix}=K^{(2)}(t)\begin{pmatrix}(J_1^2-\omega_q^2)^{1/2}\cosh[C(J_1^2-\omega_q^2)^{1/2}t] & J_1\sinh[C(J_1^2-\omega_q^2)^{1/2}t]\\ -i\omega_q\sinh[C(J_1^2-\omega_q^2)^{1/2}t] & (J_1^2-\omega_q^2)^{1/2}\cosh[C(J_1^2-\omega_q^2)^{1/2}t]\\ J_1\sinh[C(J_1^2-\omega_q^2)^{1/2}t] & +i\omega_q\sinh[C(J_1^2-\omega_q^2)^{1/2}t]\end{pmatrix}\begin{bmatrix}\rho_{13}(0)\\ \rho_{24}(0)\end{bmatrix}. \quad (21)$$

for which

$$K^{(2)}(t)=\frac{\exp[-C(J+i2\omega_0)t]}{(J_1^2-\omega_q^2)^{1/2}}. \quad (22)$$

Applying Eq. (14) gives the DQ coherences in the multipole expansion[17]

$$\begin{bmatrix}\phi^2_{\pm2}(t)\\ \phi^3_{\pm2}(t)\end{bmatrix}=\exp[-C(J+i2\omega_0)t]\begin{pmatrix}r^{\pm2}_{22} & r^{\pm2}_{23}\\ r^{\pm2}_{32} & r^{\pm2}_{33}\end{pmatrix}\begin{bmatrix}\phi^2_{\pm2}(0)\\ \phi^3_{\pm2}(0)\end{bmatrix}. \quad (23)$$

The matrix elements for the double quantum evolution matrix in the multipole basis $\mathbf{R}^{(2)}_{\mathrm{MP}}$ are given in Table II. Again, in isotropic media, where $\omega_q=0$, there is no coupling between the even and odd rank tensors.

Jaccard *et al.*[1] have treated the longitudinal relaxation processes of the zero quantum polarizations ϕ_0^k, so they are not discussed here, except to say that in the zero quantum manifold, the ϕ_0^k alignments are associated with the $\mathbf{T}_{k,0}$ spherical tensors and the off-diagonal elements of $\mathbf{R}^{(0)}$ reduce to zero in the extreme narrowing limit. The only triple quantum transition is governed by a constant of motion fully given by

$$\rho_{14}(t)=\phi^3_{\pm3}(t)=\phi^3_{\pm3}(0)\exp[-C(J_1+J_2+i3\omega_0)t]. \quad (24)$$

III. RESULTS AND DISCUSSION

For $I=3/2$ nuclei, MQF spectra are typically recorded using the pulse sequence[1,27,28]

$$(\pi/2)-(\tau/2)-\pi-(\tau/2)-\theta-\delta-\theta-\mathrm{AQ} \quad (25)$$

with appropriate phase cycling.[29] For $\theta=\pi/2$, both the contributions from the quadrupolar (second rank) and octapolar (third rank) tensors are maintained. In the context of systems with a finite ω_q, the effect of this pulse sequence may be summarized as follows: The first $\pi/2$ pulse converts the equilibrium magnetization ϕ^1_0 to the transverse plane, where it is described by $\phi^1_{\pm1}$. During the MQ preparation time τ, the relaxation processes governed by the modulation of the quadrupolar interaction produce $\phi^3_{\pm1}$ and $\phi^2_{\pm1}$ as per Eq. (18). The π pulse in the middle of the preparation period serves to refocus the field inhomogeneities and has no effect on the relaxation. The second $\pi/2$ pulse transfers $\phi^3_{\pm1}$ and $\phi^2_{\pm1}$ into the DQ manifold to produce $\phi^3_{\pm2}$ and $\phi^2_{\pm2}$. These evolve according to Eq. (23) during the MQ evolution time δ, and are subsequently converted back to the SQ manifold by the read pulse to contribute to the observable ϕ^1_{-1}, which is monitored during the acquisition period AQ.

In isotropic media, coupling can exist only between tensors differing in rank by an even integer value, a fact borne out by Eqs. (18) and (23). Thus, only odd rank tensors are produced in a NMR experiment on an isotropic system from thermal equilibrium. Conversely, anisotropic ordering permits coupling to $\phi^2_{\pm1}$ for $I=3/2$ nuclei in the preparation period. The DQF phase cycling selects both $\phi^3_{\pm2}$ and $\phi^2_{\pm2}$, while only the contribution from $\phi^3_{\pm3}$ is retained in the triple quantum filtered experiment.

In the DQF experiment, it is necessary to follow only those tensors that contribute to and evolve from the $q=2$ coherences. By using the conventional notation for the reduced Wigner rotation matrix elements $d^{(k)}_{qq'}(\theta)$ (Ref. 26) and the evolution matrix elements $r^{(q)}_{kk'}(t)$ identified from Eqs. (18) and (23)

$$\phi^k_q(t)=\sum_{q'=-k}^{k} d^{(k)}_{qq'}(\theta)\phi^k_{q'}(0), \quad \phi^k_q(t)=\sum_{k'} r^{(q)}_{kk'}(t)\phi^{k'}_q(0) \quad (26)$$

and extracting the relevant terms, one finds for the detectable vector magnetization

$$\begin{aligned}\phi^1_{-1}(\mathrm{FID})=&\frac{\exp[-i\omega_0'(\mathrm{AQ}+\tau+2\delta)]\exp[-CJ(\mathrm{AQ}+\tau+\delta)]}{25}(r^1_{13}(\mathrm{AQ})\{r^2_{32}(\delta)r^1_{21}(\tau)[d^3_{-12}(d^2_{21}-d^2_{2-1})\\ &-d^3_{-1-2}(d^2_{-21}-d^2_{-2-1})]+r^2_{33}(\delta)r^1_{31}(\tau)[d^3_{-12}(d^3_{21}+d^3_{2-1})+d^3_{-1-2}(d^3_{-21}+d^3_{-2-1})]\}\\ &+r^1_{21}(\mathrm{AQ})\{r^2_{22}(\delta)r^1_{21}(\tau)[d^2_{-12}(d^2_{21}-d^2_{2-1})+d^2_{-1-2}(d^2_{-21}-d^2_{-2-1})]\\ &+r^2_{23}(\delta)r^1_{31}(\tau)[d^2_{-1-2}(d^3_{-21}+d^3_{-2-1})-d^2_{-12}(d^3_{21}+d^3_{2-1})]\})d^1_{10}\phi^1_0(0). \quad (27)\end{aligned}$$

TABLE II. $R^{(2)}_{kk'}$ evolution matrix elements.

$r^q_{kk'}$
$r^{\pm 2}_{22}$: $\cos[C(\omega_q^2-J_1^2)^{1/2}t]+\frac{J_1}{(\omega_q^2-J_1^2)^{1/2}}\sin[C(\omega_q^2-J_1^2)^{1/2}t]=r^{\pm 2}_{33}$
$r^{\pm 2}_{23}$: $\mp\frac{\omega_q}{(\omega_q^2-J_1^2)^{1/2}}\sin[C(\omega_q^2-J_1^2)^{1/2}t]=-r^{\pm 2}_{32}$

Assuming hard, delta function pulses, evolution and relaxation are ignored during the pulse interval. All relaxation matrix elements are positive. The relevant signs for the elements coupling the even and odd rank tensors have been extracted and appear in the pulse terms.

The FID given by Eq. (27) is exact and incorporates the effects of evolution of the DQ, $q=2$, multipoles in the short δ period. Simulation of the DQF experiment setting $\omega_q=0$ gives results identical to those obtained by Jaccard *et al.*[1] after Fourier transforming a suitably partitioned FID, as expected for an isotropic system [Fig. 1(a)]. Since we are interested in the analytical behavior of the frequency domain line shape function, we will restrict the discussion to the case of oriented systems. In the anisotropic case, all nuclei experience the same value of ω_q in a uniformly oriented sample. Consequently, there is no broadening due to (numerical) averaging over the heterogeneous sites. Increased values of the quadrupole splitting generate a contribution from the second rank alignment tensor. For splittings less than the resonant linewidth, the more complex shape of the signal is due to the overlap of the quadrupolar and octapolar contributions [Figs. 1(c) and 1(d)]. As ω_q is increased beyond the magnitude of the resonant linewidth, the satellite lines become resolved [Fig. 1(e)].

Figure 2 shows the relative amplitudes of the real parts of the second and third rank tensors at the end of the read pulse {i.e., $\phi^k_{-1}[(\pi/2)-\tau-(\pi/2)-\delta-(\pi/2)]$} with varying ω_q. As expected, the third rank tensor oscillates through a range of positive values maintaining the DQF signal through all conditions. In contrast, ϕ^2_{-1} is zero for $\omega_q=0$ and subsequently oscillates through positive and negative values as ω_q increases. Moreover, ϕ^2_{-1} goes through two cusps at small ω_q values. The first is at $\omega_q=J_2$, where the second rank tensor completely dominates the spectrum as shown in Fig. 1(b) and 2(b). The contribution of ϕ^2_{-1} to the FID may be further elucidated by the form of the analytical expressions of the relaxation elements in Eq. (18) governing the development of ϕ^2_{-1} and the value of the expression $r^2_{22}(\delta)r^1_{21}(\tau)D1+r^2_{23}(\delta)r^1_{31}(\tau)D2$ (D's represent pulse terms) from Eq. (27). As ω_q approaches J_2, the sine term in r^1_{21} rapidly approaches a finite value

$$\lim_{\omega_q\to J_2} r^1_{21}(\tau)=\lim_{\omega_q\to J_2}\left\{(15)^{1/2}C\tau J_2\,\frac{\sin[C(\omega_q^2-J_2^2)^{1/2}\tau]}{C(\omega_q^2-J_2^2)^{1/2}\tau}\right\}$$
$$=(15)^{1/2}C\tau J_2. \tag{27}$$

The contribution from the sine term in $r^1_{31}(\tau)$ is also maintained, although it is much less significant for small values of δ. Simulation of the line shape with this splitting value accordingly gives a line out of phase [Fig. 1(b)] with respect to that produced by the third rank tensor. In addition, as ω_q approaches J_1, the amplitude of the contribution from ϕ^2_{-1} follows:

$$\phi^2_{-1}(\omega_q=J_1)\propto(1+J_1C\delta)\,\frac{5^{1/2}\omega_q}{(\omega_q^2-J_2^2)^{1/2}}$$
$$\times\sin[C(\omega_q^2-J_2^2)^{1/2}\tau]D1+2^{1/2}J_1C\delta$$
$$\times\left\{\exp(CJ_0\tau)-\cos[C(\omega_q^2-J_2^2)^{1/2}\tau]\right.$$
$$\left.-\frac{J_2}{(\omega_q^2-J_2^2)^{1/2}}\sin[C(\omega_q^2-J_2^2)^{1/2}\tau]\right\}D2, \tag{28}$$

in which ϕ^2_{-1} is rapidly minimized for finite values of δ. It should be noted that while the intensities of each of these tensorial components is modulated by τ and δ, the positions of these cusps are determined by the nonsecular spectral densities J_1 and J_2. While such asymptotic terms exist in the evolution of ϕ^3_{-1}, they are mitigated by the preponderance of other exponential terms that dominate the evolution of the odd rank tensor components.

By setting $\theta=54.73°$ in the DQF pulse sequence,[30] it is possible to isolate the contribution of the second rank tensor. That is, the explicit form of the Wigner rotation matrix selectively filters out any third rank tensor components.[1,5] Simulation of this modified pulse sequence produces results nearly identical to those shown in Fig. 1(b) showing that this line is indeed dominated by the presence of a second rank tensor. Notice is made here of the line shape of the isolated contribution from the second rank tensor, which may be thought of a powder distribution of antiphase doublets. It is antiphase in the sense that this signal is 90° out of phase with respect to the third rank tensor contribution to the observable. Consequently, the ϕ^2_{-1} contribution to the signal appears to be in a dispersive mode when plotted so that the contribution from ϕ^3_{-1} is in an absorptive mode, as is the custom. When properly shown in an absorptive mode, the poorly resolved antiphase doublet appears with an apparent dispersive line shape, from which the experimentally observed ω_q' can be measured. For clarity, in Fig. 1(b) the isolated ϕ^2_{-1} portion of the signal is presented as it would appear in a dispersive mode so that its contribution to the reported experimental results is more obvious.

Using this multipole approach, it is not difficult to show the dependence of the line shape on the preparation time as recently observed in biological tissues.[4,5,7] In Fig. 3, the relative amplitudes of the real parts of ϕ^3_{-1} and ϕ^2_{-1} at the end of the read pulse are plotted as a function of τ, showing that under the conditions used to generate the line reported in Fig. 1(c), ϕ^2_{-1} has a significant contribution only up to about 20 ms, after which it quickly decays ϕ^3_{-1} maintains a significant contribution to approximately 40 ms. This underscores the fact that each of the tensorial components of the observed signal, including the higher quantum coherences, are gov-

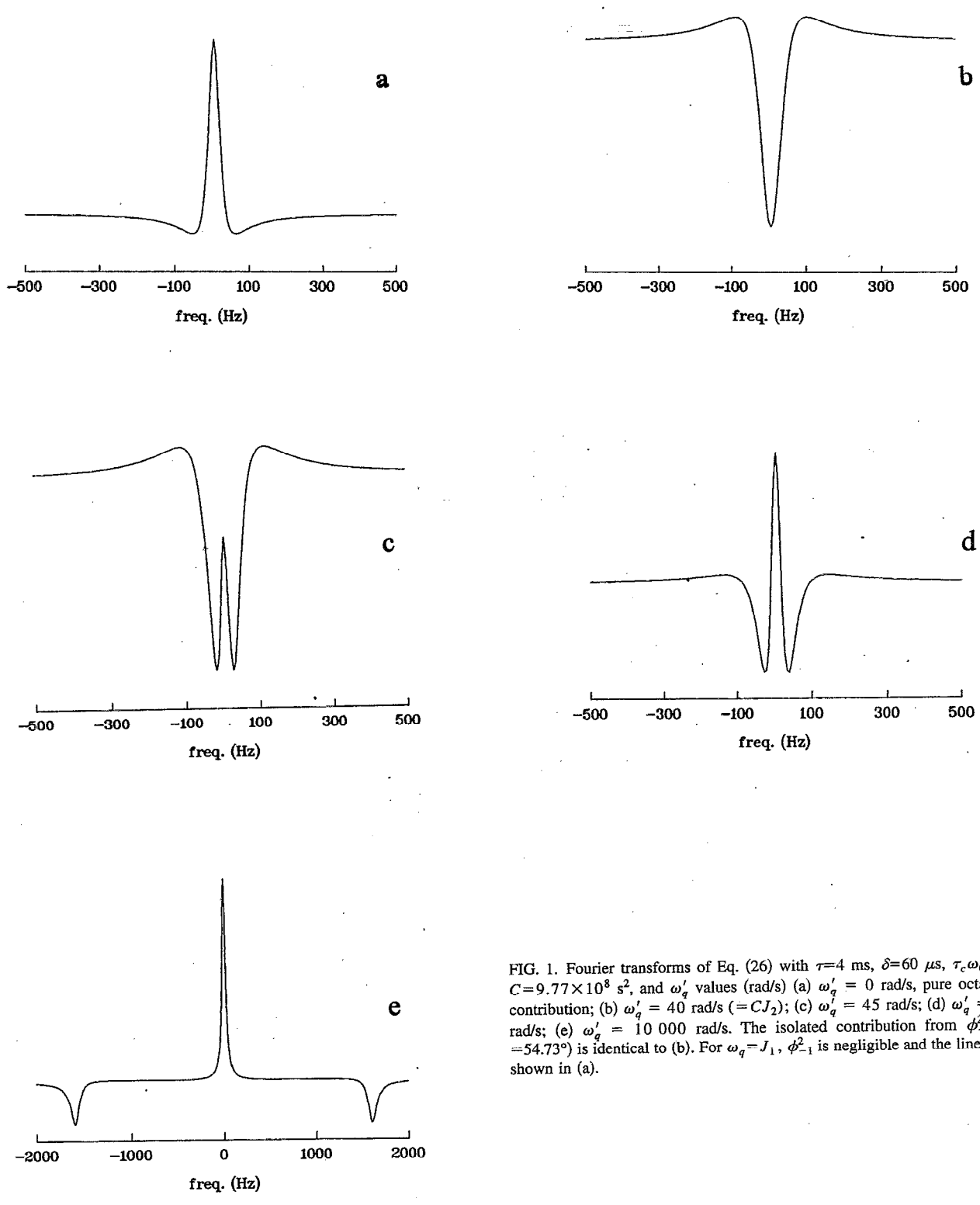

FIG. 1. Fourier transforms of Eq. (26) with τ=4 ms, δ=60 μs, $\tau_c\omega_0=1$, $C=9.77\times10^8$ s^2, and ω_q' values (rad/s) (a) ω_q' = 0 rad/s, pure octapole contribution; (b) ω_q' = 40 rad/s ($=CJ_2$); (c) ω_q' = 45 rad/s; (d) ω_q' = 50 rad/s; (e) ω_q' = 10 000 rad/s. The isolated contribution from ϕ^2_{-1} (θ =54.73°) is identical to (b). For $\omega_q=J_1$, ϕ^2_{-1} is negligible and the line is as shown in (a).

erned by distinct relaxation behavior. The fact that the lines in a resonant signal may be the result of several tensorial contributions may complicate the interpretation of relaxation data inferred from analysis using a product operator basis. Use of spherical tensors gives an alternative way of treating these contributions to the more commonly used concepts of the customary "slow" relaxation of the central line and "fast" relaxation of the satellites.

IV. CONCLUSION

The formation of even-rank tensors in a MQF experiment on a half-integer spin system initially at thermal equilibrium is a direct result of the existence of a finite residual quadrupole splitting. When ω_q is less than the resonant linewidth of the $|-1/2\rangle\rightarrow|1/2\rangle$ transition, it is necessary to account for the off-diagonal terms in the Redfield perturbation

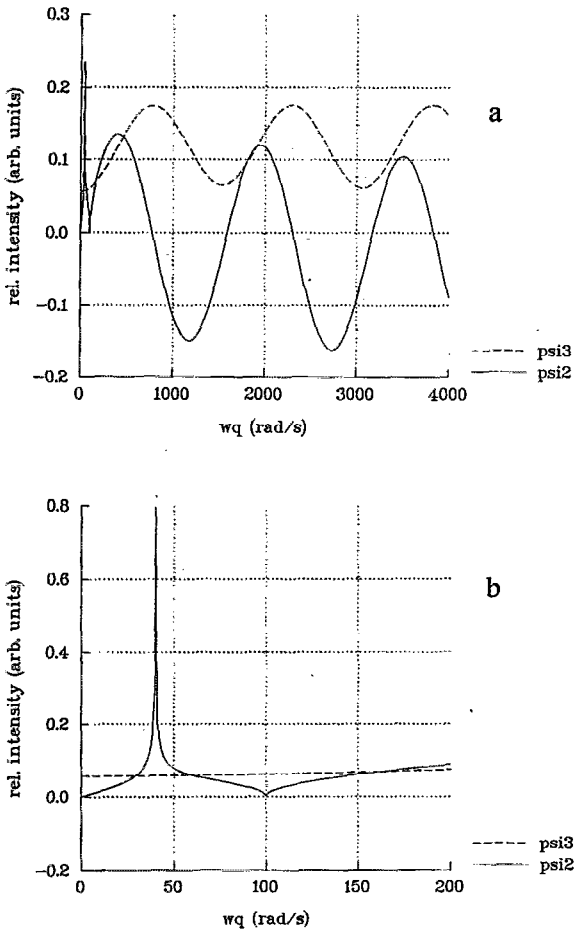

FIG. 2. The dependence on the quadrupolar splitting of the relative amplitudes of ϕ^2_{-1} (solid line) and ϕ^3_{-1} (dashed line) at the end of the read pulse in the DQF experiment (a) large splittings showing the oscillation in both tensors (b) small splittings showing the dominance of ϕ^2_{-1} near $\omega'_q = 40$ rad/s ($=CJ_2$). Parameters are the same as in Fig. 1.

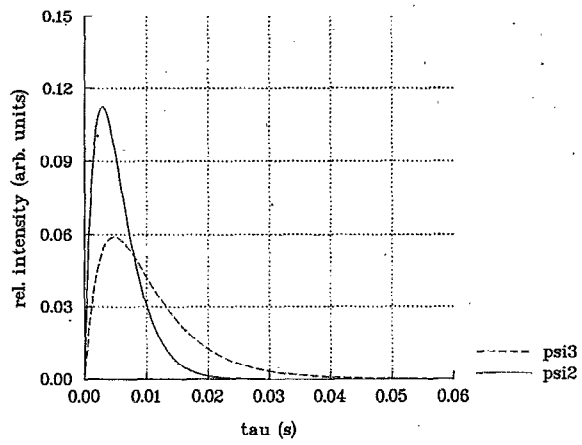

FIG. 3. The dependence of the relative amplitudes of ϕ^2_{-1} (solid line) and ϕ^3_{-1} (dashed line) at the end of the read pulse in the DQF experiment on the preparation time. At short times, the contribution of ϕ^2_{-1} can be observed, but quickly dies beyond about 15 ms. $\omega'_q = 45$ rad/s. Other parameters are the same as in Fig. 1.

treatment of the relaxation. Even though relaxation does not couple the central line to the innermost satellites for half-integer spins, inclusion of these nonsecular terms is required to generate the asymptotic behavior of the even rank tensor and, thus, the full contribution to the line shape in a MQF experiment.

The use of Redfield's theory to describe the evolution of the tensorial components of the spin density matrix has been shown to provide a convenient method for the analysis of the dynamics of a spin system in a MQF pulse sequence; with the multipole evolution matrices presented here, it is easy to recognize the response to a general hard pulse sequence and the origins of each of the tensor components. Since there is a relatively small number of characteristics of the quadrupolar nucleus that avail themselves to interpretation by relaxation studies, the problem is to try to directly relate this nuclear dynamic behavior to well-established attributes of the anisotropic system in question. The analytical solutions offered here not only describe the relaxation behavior of each of the tensor components, but have reproduced some of the general features observed in experiment and in more fundamental analyses.

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