2D Quadrupolar-Echo Spectroscopy with Coherence Selection and Optimized Pulse Angle

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The recently developed 2D quadrupolar-echo (QE) method for relaxation studies on \( I > 1 \) nuclei in anisotropic systems is generalized and extended. It is shown that by cycling the phase of the refocusing pulse, so that the conjugate dipolar single-quantum coherences are interchanged rather than mixed, linear as well as quadratic terms in the spin Hamiltonian are refocused. With this extension, the 2D QE method can be used to determine the transverse relaxation rates associated with the different Zeeman transitions even in the simultaneous presence of large quadrupolar and magnetic field inhomogeneities. Further, it is shown that by using an optimized refocusing pulse angle, rather than the conventional \( \pi/2 \) pulse, one can substantially improve the signal-to-noise ratio and, at the same time, reduce or eliminate spectral lines that may otherwise cause overlap problems. For \( I > \frac{3}{2} \) nuclei the refocused intensity can increase with decreasing pulse angle, in contrast to the case of \( I = 1 \) and \( I = \frac{3}{2} \) nuclei, where it decreases as \( \sin^2 \theta \). Thus, small pulse angles can also be profitably used to increase the excitation bandwidth for \( I > \frac{3}{2} \) nuclei in systems with large quadrupole splittings.

In nuclear magnetic relaxation studies of molecular motions one is often faced with the problem of determining the homogeneous widths of spectral lines. Being directly related to motional spectral density functions, the homogeneous linewidths constitute an important source of molecular information. Frequently, however, the spectral lines are also inhomogeneously broadened by spatial inhomogeneities in various static (incompletely motionally averaged) couplings. These couplings may be classified according to the rank of the irreducible spin tensor operators (referring to the resonant nuclear species) appearing in the corresponding term of the spin Hamiltonian (\( \ell - 4 \)). Inhomogeneous line broadening can thus arise from rank-1 (linear) interactions, such as the Zeeman coupling (magnetic field inhomogeneity) and, in anisotropic systems, the static part of the coupling mediated by the anisotropic chemical-shift tensor, as well as from rank-2 (bilinear and quadratic) interactions, such as the static parts of the electric quadrupole and homonuclear dipole–dipole coupling.

The principal method for eliminating or reducing inhomogeneous line broadening is the echo experiment. The classical echo experiment (5, 6), based on the pulse sequence \((\pi/2)_x - \tau - (\pi)_x - \tau - \text{acq}\), produces an echo, usually referred to as a spin echo or a Hahn echo, by refocusing rank-1 interactions, such as the Zeeman coupling (including anisotropic chemical shift) and scalar or dipolar couplings to (weakly cou-
pled) nonresonant nuclei. Another type of echo experiment, variously referred to as the solid echo or the quadrupolar echo (QE), has been designed to refocus rank-2 interactions, such as the static quadrupolar and homonuclear dipolar couplings (7–10). The ability of QE sequences to refocus various couplings has been investigated by numerous authors (11–19). All these studies were primarily concerned with the use of the QE method for investigating the structure of solids, with little or no attention paid to the effects of nuclear spin relaxation.

For spin $I = 1$ nuclei, the QE sequence

$$\left(\frac{\pi}{2}\right)_x - \tau - \left(\frac{\pi}{2}\right)_{xy} - \tau - \text{acq} \quad [1]$$

has been used extensively to eliminate spectral distortion due to acquisition delay and to measure the transverse relaxation rate (20–22). This pulse sequence has also been applied to quadrupolar nuclei with spin $I > 1$ (8–10, 17, 18). In contrast to the $I = 1$ case, where the refocusing is complete, the signal contributions from the various lines in the $I > 1$ spectrum are only partially refocused and, moreover, are modulated in phase and amplitude by the static quadrupole coupling. One consequence of this modulation for $I > 1$ nuclei is that an undistorted (i.e., apart from relaxation effects, identical to the zero-dead-time single-pulse spectrum) powder spectrum cannot, even in principle, be produced by the QE sequence [1], despite claims to the contrary (23).

In partially aligned systems, however, the quadrupolar modulation provides the basis for the 2D QE experiment (24) recently applied in $^{23}$Na relaxation studies of lyotropic liquid crystals (25, 26) and in a $^7$Li relaxation study of oriented DNA (27). The strength of the 2D QE experiment is that the homogeneous linewidth of a satellite can be obtained directly from the central line in the $F_1$ cross-section spectrum taken at the corresponding satellite position in the $F_2$ dimension. ($F_1$ and $F_2$ denote the frequency dimensions created by Fourier transformation with respect to the evolution time $2\tau$ and the acquisition time, respectively.)

On account of its widespread use with spin $I = 1$ nuclei, the pulse sequence [1] has come to be regarded as the QE sequence. However, as suggested by the early work on solids (7–10, 13, 15), a refocusing pulse angle of $\pi/2$ may not be optimal for spin $I > 1$ nuclei. Moreover, it may prove advantageous to cycle the phase of the refocusing pulse. The objective of the present study is therefore to analyze the $F_1$ cross-section spectra obtained in 2D QE experiments based on the more general pulse sequence

$$\left(\frac{\pi}{2}\right)_x - \tau - (\theta)_{xy} - \tau - \text{acq}, \quad [2]$$

with the phase $\phi$ of the refocusing pulse being cycled in various ways. It will be seen that this generalization of the 2D QE experiment improves upon the original version (24) in several important respects. As experimental applications we have in mind, in particular, counterion (e.g., $^7$Li, $^{23}$Na, $^{25}$Mg, $^{35}$Cl, $^{133}$Cs) and water ($^{17}$O) spin-relaxation studies in anisotropic fluids, like lyotropic liquid crystals (25, 26) or ordered biopolymers (27). The reliability of the molecular information that can be derived from such studies is crucially dependent on the accuracy and precision of the relaxation data.

The motivation for using a refocusing pulse angle $\theta$ different from the conventional value of 90° is threefold. First, it is desirable to maximize the signal-to-noise ratio for
the central line in the various $F_1$ spectra. Although $\theta = 90^\circ$ turns out to be optimal for $I = 1$ and $I = \frac{3}{2}$, smaller $\theta$ values can substantially enhance the central line intensity for $I > \frac{3}{2}$. This is a particularly important point since longitudinal relaxation experiments are difficult to analyze for $I = \frac{3}{2}$ nuclei. In contrast, the QE experiment, by providing the various homogeneous linewidths, allows the individual motional spectral densities to be directly determined also for high-spin nuclei. Second, even if spectral line overlap is acceptably small in the $F_2$ dimension, the halving of the quadrupole splitting in the $F_1$ spectra may result in disturbing overlap between the central line and the innermost satellite(s). However, by a judicious choice of the pulse angle $\theta$, the interfering satellite(s) can be suppressed or even eliminated. Third, in systems with large quadrupole splitting $\omega_Q$, it may not be possible to produce a nonselective $\pi/2$ pulse. A pulse of duration of $t_p$ is nonselective if $\omega_Q t_p < 1$, which implies that quadrupolar evolution during the pulse can be neglected, whence the effect of the pulse can be approximated as a pure rotation of the spin density operator. However, if an equilibrium spin system is subjected to an excitation pulse which is not short compared to $1/\omega_Q$, then not only single-quantum coherences, but also coherences of higher quantum order, are generated. The partial refocusing of these multiple-quantum coherences in the QE experiment gives rise to additional so-called forbidden echoes (7, 28, 29). As the theoretical treatment of finite pulse length effects (30–32) is fairly involved even in the $I = 1$ case, it is desirable to avoid these complications. The most direct solution is simply to reduce the pulse length $t_p$ at a given RF field strength $\omega_1 = \gamma B_1$, i.e., to use a pulse angle $\theta$ less than $\pi/2$ for both pulses in the QE sequence. For sufficiently small $\theta$, the inequality $\omega_Q t_p = \theta \omega_Q / \omega_1 \ll 1$ can thus be satisfied. For $I = 1$ nuclei the usefulness of this approach is severely limited by the drastic reduction (proportional to $\sin^3 \theta$) of the refocused signal intensity with decreasing pulse angle (30). This is also true for $I = \frac{3}{2}$ nuclei. For $I > \frac{3}{2}$ nuclei, however, the refocused signal intensity can actually increase for small pulse angles, making this a useful strategy for cases where $\omega_1 \approx \omega_Q$.

The generalization [2] of the basic QE sequence concerns not only the angle $\theta$ of the refocusing pulse, but also its phase $\phi$. We shall analyze $F_1$ cross-section spectra produced by generalized QE experiments with any of the phase cycles

\begin{align}
\text{QECM: } \phi &= 90^\circ, \ 270^\circ, \\
\text{QECI: } \phi &= 90^\circ, \ 180^\circ, \ 270^\circ, \ 360^\circ, \\
\text{QECR: } \phi &= 90^\circ, \ 180^\circ, \ 270^\circ, \ 360^\circ.
\end{align}

where the overbar signifies subtraction of the corresponding signal. The last two letters in the acronyms stand for coherence mixing, coherence interchange, and coherence retention.

The QECM experiment with $\theta = \pi/2$ is the one discussed in our recent reports (24, 25). The $\phi = 90^\circ, \ 270^\circ$ (or $\pm \phi$) phase alternation selects coherence transfers with $\Delta q = 0, \pm 2, \pm 4, \ldots$. Consequently, the (odd-rank) polarizations ($q = 0$) present before the refocusing pulse will not be converted into observable single-quantum coherence. The echo signal thus exclusively reflects the evolution of single-quantum coherences ($q = \pm 1$). However, since the QECM experiment mixes the two conjugate single-quantum coherences—the transfers $q = +1 \rightarrow q = +1$ and $q = +1 \rightarrow q = -1$ are both affected by the refocusing pulse—it does not completely refocus rank-1 cou-
plings. Whereas a small rank-1 inhomogeneous broadening is approximately halved in the $F_1$ dimension, a large rank-1 inhomogeneous broadening may severely distort the $F_1$ spectra (24). Moreover, second-order, static and dynamic, quadrupolar shifts also cause spectral distortion, which often can be approximated as a broadening of the $F_1$ spectral lines (24).

The QECI experiment has the advantage of completely and simultaneously refocusing rank-1 and (quadratic) rank-2 couplings, as well as eliminating the broadening due to second-order quadrupolar shifts. The phase cycle [3b] selects coherence transfers with $\Delta q = \pm 2, \pm 6, \pm 10, \ldots$. The consequent interchange of conjugate single-quantum coherences ($q = +1 \leftrightarrow q = -1$) implies a reversal of the direction of Larmor precession (in the rotating frame) and, hence, leads to complete refocusing of rank-1 couplings. The same coherence interchange and concomitant refocusing is produced by the $\pi$ pulses in the classical spin-echo experiment (6) ($\pi/2$, $\tau$; $-\pi$, $\tau$; acq and in the modified QE experiment (24, 33, 34) ($\pi/2$, $\tau/2$; $-\pi/2$, $\tau/2$; acq. However, because of the relatively narrow excitation bandwidth of the $\pi$ pulses, this modified QE experiment can be applied only on systems with correspondingly small quadrupole splitting (27). Second, pulse-length imprecision in the $\pi$ pulses introduces a signal contribution reflecting the evolution of multiple-quantum coherences. The phase cycle [3b], sometimes referred to as “Exorcycle” (35), has been used in 2D correlation spectroscopy (4), in spin-echo studies on $I = \frac{1}{2}$ nuclei (36), and in 2D QE spectroscopy on $I = 1$ nuclei (37). Here we analyze the effect of this phase cycle on $F_1$ cross-section spectra obtained with the generalized QE sequence (21 applied to arbitrary half-integral $I > 1$ nuclei.

In the QECR experiment, the phase cycle [3c] selects coherence transfers with $\Delta q = 0, \pm 4, \pm 8, \ldots$ and thus does not mix or interconvert the conjugate single-quantum coherences. While eliminating first-order quadrupolar broadening in the $F_1$ spectra, this QE experiment does not affect the shifts. For this reason, and since the refocused signal intensity is strongly reduced for small pulse angles, the QECR experiment is of little practical interest. For the purpose of the following spin-dynamical calculations, however, it is conceptually useful as the QECM phase cycle may be regarded as a superposition of the QECI and the QECR cycles.

The outline of this paper is as follows. First we calculate the response of the spin system to the generalized QE sequence (21 with the phase cycles [3]. The resulting signal following the principal echo is then used to obtain the relevant $F_1$ sections of the 2D frequency spectrum. The emphasis here is on the refocusing effect of the different phase cycles and on the dependence of the $F_1$ spectral line intensities on the pulse angle. We also briefly consider a 2D spin-echo experiment ($\theta = \pi$). In the experimental section $F_1$ spectra from a lyotropic liquid crystal are used to illustrate the theoretical results of this work. The paper is concluded with a summary of the relative merits of the various 2D echo experiments discussed here.
the $I = 1$ case, which can be derived with a slight modification of the treatment for half-integral $I > 1$ nuclei.

The evolution of the single-quantum coherences under a quadrupolar spin Hamiltonian with static and fluctuating parts can be expressed in matrix notation as (24)

$$P_1(t) = T \exp[-(i\Omega + R)t]\tilde{T}P_1(0),$$  \[4\]

where $P_1$ is a column vector with elements $P_1^k$ (rank-$k$ single-quantum coherence) and $T$ is the orthogonal (tilde denotes transposition) matrix that transforms the Zeeman basis into the multipole basis. Further, $\Omega$ and $R$ are the diagonal frequency and relaxation matrices, expressed in the Zeeman basis. (The neglect of the off-diagonal elements in $R$ is justified when the quadrupole splitting is large compared to the homogeneous central linewidth, which we assume to be the case.) All matrices in Eq. [4] are of dimension $2I \times 2I$ and the indexing is such that $n = 1$ and $2I$ refer to the outermost satellites, while $n = I + \frac{1}{2} = J$ refers to the central line. The elements of the frequency matrix are

$$\Omega_n = \hat{\Omega}_n + \delta_n + \delta,$$  \[5\]

$$\hat{\Omega}_n = (J - n)\omega_Q,$$  \[6\]

where $\hat{\Omega}_n$ and $\delta_n$ denote, respectively, the first-order and second-order (static and dynamic) quadrupolar shifts, and $\omega_Q$ is the quadrupole splitting defined as in Ref. (24). In Eq. [5] we also include a term $\delta$, representing a satellite-independent frequency shift due, e.g., magnetic field inhomogeneity.

The RF pulses are taken to be nonselective so that the effect of a $(\theta)_q$ pulse is simply to rotate the multipoles $\bar{P}_q^k$ according to (24, 39)

$$\bar{P}_q^k = \sum_{q'=-k}^{k} D_{qq'}^k(\phi - \frac{\pi}{2}, \theta, \frac{\pi}{2} - \phi)P_q^k,$$  \[7\]

where the bar signifies postpulse conditions.

The excitation pulse in the QE sequence [2] generates dipolar single-quantum coherences $P^k_{\pm 1}$ from the equilibrium polarization (longitudinal magnetization) $P_0$. The nonequilibrium $P_0$ that also is produced can be ignored, since each of the three phase cycles in [3] cancels its contribution to the observed signal. The single-quantum coherences then evolve according to Eq. [4], yielding immediately prior to the refocusing pulse

$$P_{+1}^k(\tau) = -\frac{i}{\sqrt{2}} \sum_{p=1}^{2I} U_{kp}\exp[-(i\Omega_p + R_p)\tau],$$  \[8\]

where the $U$ matrix, with elements $U_{kp} = T_{1p}T_{kp}$, has been given in explicit form elsewhere (41). The conjugate single-quantum coherences $P_{-1}^k$ are trivially obtained from Eq. [8] and the symmetry relation

$$P_{-q}^k = (-1)^q(P_q^k)^*.$$  \[9\]

We also note that the generalization to a first pulse with an arbitrary angle $\theta_1$ is trivial; it merely introduces a factor $\sin \theta_1$ in Eq. [8].
Next we consider the effect of the refocusing pulse in the QE sequence [2], with the phase cycled according to [3]. Using Eq. [7] we find that the single-quantum coherences \( P^1(t) \) and \( P^k_{1}(t) \) have their quantum orders (+1 or -1) mixed, interchanged, or retained depending on the phase cycle; i.e.,

QECI: \( \tilde{P}^1_1(t) = d_{-1}^k(\theta) P^k_{1}(t) \), \[10a\]

QECR: \( \tilde{P}^1_1(t) = d_{11}^k(\theta) P^k_{1}(t) \), \[10b\]

QECM: \( \tilde{P}^1_1(t) = d_{11}^k(\theta) P^k_{1}(t) + d_{-1}^k(\theta) P^k_{1}(t) \). \[10c\]

It is seen that a QECM experiment may be regarded as a superposition of the QECI and QECR experiments. This is also evident from the phase cycles in [3]. The refocusing pulse also produces multiple-quantum coherences, but as these are not observed with conventional NMR spectrometers, they can be ignored.

After the refocusing pulse, the single-quantum coherences again evolve according to Eq. [4], which yields for the observable dipolar single-quantum coherence

\[ P^1_1(t) = \sum_{k=1}^{2l} \sum_{n=1}^{2l} U_{kn} \exp[-(i\Omega_n + R_n)t], \] \[11\]

where \( t \) refers to the time after the refocusing pulse.

The detected complex free-induction signal \( S(t) \) is defined as

\[ S(t) = i\sqrt{2} P^1_1(t). \] \[12\]

[This definition, which differs by a factor of \( i \) from that used earlier by us (24, 41), corresponds to the common experimental convention, where an in-phase pulse, whose phase coincides with the nominal receiver phase (e.g., they are both +\( \pi \)), generates an FID in the “real” (in-phase) channel of the quadrature detector.]

Introducing the evolution time \( t_1 = 2\tau \) and the acquisition time \( t_2 = t - \tau \), we obtain from Eqs. [8]–[12] the complex signal

\[ S(t_1, t_2) = \sum_{n=1}^{2l} \sum_{p=1}^{2l} V_{np}^\pm(\theta) \exp[(i\Omega_n^p - R_n)p] \exp[(i\Omega_n - R_n)t_1] \exp[(i\Omega_n - R_n)t_2]. \] \[13\]

where the upper (lower) signs pertain to the QECR (QECI) experiment. The signal in the QECM experiment is simply the sum of the two versions of Eq. [13]. The new quantities appearing in [13] are defined as

\[ R_n^p = (R_n + R_p)/2, \] \[14\]

\[ \Omega_n^p = (\Omega_n \pm \Omega_p)/2, \] \[15\]

\[ V_{np}^\pm(\theta) = \sum_{k=1}^{2l} d_{\pm1}^k(\theta) U_{kn} U_{kp}. \] \[16\]

For comparison with Eq. [13], the corresponding results for \( I = 1 \) nuclei are, for QECI,

\[ S(t_1, t_2) = \frac{1}{2} \left( \sin^2\theta \cos(\omega_0t_2) - \cos \theta (1 - \cos \theta) \cos[\omega_0(t_1 + t_2)] \right), \] \[17a\]
and, for QECR,

\[ S(t_1, t_2) = \frac{1}{2} \left\{ \sin^2 \theta \cos(\omega_Q t_2) + \cos \theta (1 + \cos \theta) \cos[\omega_Q(t_1 + t_2)] \right\} \]

\[ \times \exp[(i\delta - R)t_1] \exp[(i\delta - R)t_2]. \]  

Again the QECM result is just the sum of [17a] and [17b]. The \( I = 1 \) quadrupole splitting (in the \( F_2 \) dimension) is \( 2\omega_Q \) and the transverse relaxation rate is denoted by \( R \). Since the second-order quadrupolar shifts (static and dynamic) are the same for both spectral lines, they can be incorporated in \( \delta \) for \( I = 1 \) nuclei. The first term within the curly brackets in Eq. [17] exhibits quadrupolar refocusing and decreases in intensity as \( \sin^2 \theta \) (if the excitation and refocusing pulses are of the same angle), as is well-known (30). Due to the second term, the echo peak intensity is in general modulated by the quadrupole coupling. In the conventional QE experiment with \( \theta = \pi/2 \), this term vanishes and the transverse relaxation rate \( R \) can be obtained directly from the exponential decay with \( t_1 = 2\tau \) of the echo amplitude \( (21) \). As seen from Eq. [17a], shift-like inhomogeneities are completely refocused in the QECI experiment on \( I = 1 \) nuclei, whereas they remain unaffected in the QECR experiment. [Thus, for \( \theta = \pi/2 \), only half of the QECM signal exhibits refocusing of rank-1 inhomogeneous broadening (42).] This property of the QECI method has been demonstrated by Vold and Vold (37), who also showed that, as an alternative to using \( \theta = \pi/2 \) in the QECI sequence, a 2D experiment can be performed where the homogeneous satellite linewidth is obtained directly from the central \( (\omega_1 = 0) \) linewidth in the \( F_1 \) cross-section spectrum derived from the \( \omega_Q \)-modulated satellite amplitude at \( \omega_2 = \pm \omega_Q \).

**F\(_1\)** SPECTRA FROM GENERALIZED 2D QE EXPERIMENTS

A complex-valued 2D spectrum is obtained by successively performing two (complex) Fourier transformations on the time-domain signal \( S(t_1, t_2) \) according to

\[ L(\omega_1, \omega_2) = \int_0^\infty dt_1 \exp(-i\omega_1 t_1) \int_0^\infty dt_2 \exp(-i\omega_2 t_2) S(t_1, t_2). \]  

The real-valued spectrum

\[ L_R(\omega_1, \omega_2) = \text{Re}[L(\omega_1, \omega_2)], \]  

observed in the "real" spectrometer channel, contains in general absorption as well as dispersion components. In the following, our attention will be restricted to the \( F_1 \) cross-section spectra \( L_R(\omega_1, \tilde{\Omega}_n) \) taken at the peak positions \( \omega_2 = \tilde{\Omega}_n \) in the \( F_2 \) dimension. [It may be noted that the above definition of the 2D spectrum differs from that in Ref. (24), where cosine Fourier transforms were used. With the present convention, the \( F_1 \) cross-section spectra of Ref. (24) correspond to \( L_R(\omega_1, \tilde{\Omega}_n) + L_R(-\omega_1, \tilde{\Omega}_n) \); i.e., they are symmetric with respect to \( \omega_1 = 0 \). Although the spectra defined by Eq. [19] are asymmetric, we shall refer to the \( \omega_1 = 0 \) peak as the central line.] The time-domain signal \([13] \) gives rise to \( F_1 \) cross-section spectra, defined by Eqs. [18] and [19], of the form

\[ L_R(\omega_1, \tilde{\Omega}_n) = \sum_{m=1}^{2l} \sum_{p=1}^{2l} V_{mp}^+(\theta) \]

\[ \times \text{Re} \left\{ \langle [R_{mp} + i(\omega_1 - \Omega_{mp})]^{-1} [R_{mp} + i(\tilde{\Omega}_n - \Omega_{mp})^{-1}] \rangle \right\}, \]  

\[ [20] \]
where the angular brackets denote averaging over the coupling distributions causing the spread in the frequencies $\Omega_{mp}$ and $\Omega_m$. If there is negligible overlap of spectral lines in the $F_2$ dimension, as is henceforth assumed, then only the $m = n$ term makes a significant contribution and Eq. [20] reduces to

$$L_R(\omega_1, \bar{\Omega}_n) = \sum_{p=1}^{2l} V_{np}(\theta) \times \text{Re} \{ \langle [R_{np} + i(\omega_1 - \omega_{np})]^{-1}[R_n + i(\bar{\Omega}_n - \Omega_n)]^{-1} \rangle \}. \quad [21]$$

The QECI experiment. We consider first the QECI $F_1$ spectra described by Eq. [21] with the lower set of signs. These spectra consist of $2l$ lines, but the relative line intensities are not the conventional ones (see below). More importantly, since $\Omega_{mn} = 0$, the central line (at $\omega_1 = 0$) corresponding to $p = n$, is entirely free from inhomogeneous broadening associated with the quadrupole coupling (to first and second order) and with rank-1 interactions such as the Zeeman coupling (magnetic field inhomogeneity). It should be noted that the inhomogeneous broadening (of either origin) thus eliminated may be much larger than the homogeneous linewidth as long as spectral overlap in the $F_2$ dimension is small.

The central line in a QECI $F_1$ spectrum is given by the $p = n$ term in Eq. [21]; i.e.,

$$L_R(\omega_1, \bar{\Omega}_n) = V_{nn}(\theta) \left[ \frac{R_n}{R_n^2 + \omega_1^2} - \frac{R_n}{R_n^2 + (\bar{\Omega}_n - \Omega_n)^2} \right]. \quad [22]$$

The averaging in Eq. [22] usually refers to spatial inhomogeneities in the magnitude of the residual quadrupole coupling constant, in the orientation of the microcrystallite with respect to laboratory-fixed axes, and in the strength of the static magnetic field experienced by a nucleus. These three parameters generally affect the frequencies $\Omega_n$ as well as the quadrupole relaxation rates $R_n$. Now the averaging in Eq. [22] involves products of two functions referring to the $F_1$ and $F_2$ dimensions. As long as the quadrupole splitting is large compared to $R_n$, as already assumed in deriving Eq. [22], the $F_1$ factors vary much more slowly with the inhomogeneity parameters than the $F_2$ factors, which involve the frequency difference $\bar{\Omega}_n - \Omega_n$. Consequently, the $F_1$ factors can be taken out of the average and [22] can be accurately approximated as

$$L_R(\omega_1, \bar{\Omega}_n) = V_{nn}(\theta) \left[ \alpha_n \frac{R_n}{R_n^2 + \omega_1^2} \right], \quad [23]$$

with the numerical coefficients

$$\alpha_n = \left\langle \frac{R_n}{R_n^2 + (\bar{\Omega}_n - \Omega_n)^2} \right\rangle \quad [24a]$$

$$\beta_n = \left\langle \frac{\bar{\Omega}_n - \Omega_n}{R_n^2 + (\bar{\Omega}_n - \Omega_n)^2} \right\rangle. \quad [24b]$$

According to Eq. [23] the central $F_1$ line does not, in general, have a pure-absorption shape. The dispersion contribution can, however, easily be removed (i.e., transferred
to the other quadrature channel) by a zeroth-order phase correction. (The coefficient \( \beta_n \) also vanishes if the \( \Omega_n \) distribution happens to be symmetric.)

In macroscopically (partially) aligned samples the microcrystallite orientation distribution is usually narrow (25–27). For powder samples, however, the result [21] is not valid since the different satellite lines in the \( F_2 \) dimension overlap even in \( \omega_Q \gg R_n \). This is a problem even in the \( I = \frac{3}{2} \) case, where the overlap involves only the kinetically degenerate companion satellite. Since a satellite powder peak position then corresponds to distinctly different orientations (35.26° and 90°) for the two satellites, the associated relaxation rates may differ substantially. For these reasons, the central line in the \( F_1 \) spectra derived from powder samples is generally multi-Lorentzian and a numerical lineshape fit is required to extract the homogeneous relaxation rates.

The QECR and QECM experiments. The QECR \( F_1 \) spectra are described by Eq. [21] with the upper set of signs. It follows from Eqs. [5] and [6] that the central line in these spectra corresponds to \( p = 2J - n \). In contrast to the QECI case, the central line does not appear precisely at \( \omega_1 = 0 \) but is displaced by the second-order (static and dynamic) quadrupolar shift \( \delta_n \) and the rank-1 shift \( \delta \); i.e.,

\[
\Omega^*_n,2J-n = \delta_n + \delta. \tag{25}
\]

To obtain this result, we made use of the fact (24, 43, 44) that the second-order quadrupolar shift is the same for the companion satellites; i.e., \( \delta_{2J-n} = \delta_n \). Thus, in the QECR experiment, only the first-order quadrupolar broadening is refocused.

By the same reasoning as that in the QECI case, we obtain for the central line

\[
L_k(\omega_1, \tilde{\Omega}_n) = V_{nm}(\pi - \theta) \left[ \left( \alpha_n(\delta) \frac{R_n}{R_n^2 + (\omega_1 - \delta_n - \delta)^2} \right)_{\delta} - \left( \beta_n(\delta) \frac{(\omega_1 - \delta_n - \delta)}{R_n^2 + (\omega_1 - \delta_n - \delta)^2} \right)_{\delta} \right], \tag{26}
\]

where the angular brackets now signify averaging over the \( \delta \) shift distribution, while the quantities \( \alpha_n(\delta) \) and \( \beta_n(\delta) \), given by Eq. [24], are averaged only over the spread in quadrupole coupling constant and microcrystallite orientation. To obtain Eq. [26] we have also used the symmetry relations \( R_{2J-n} = R_n \) (24) and

\[
V_{np}^+(\theta) = V_{n,2J-n}(\pi - \theta). \tag{27}
\]

As already noted, a QECM \( F_1 \) spectrum is simply the sum of the corresponding QECI and QECR spectra. The central line in the QECM \( F_1 \) spectra, given by the sum of [23] and [26], is thus a superposition of a homogeneous component (QECI) and a component (QECR) which is inhomogeneously broadened and displaced by the shifts \( \delta_n \) and \( \delta \) (24).

\( F_1 \) line intensities. We now examine the effect on the \( F_1 \) spectra of varying the refocusing pulse angle \( \theta \). As we are concerned here only with spectral line intensities, we ignore quadrupolar inhomogeneous broadening and shifts. According to Eq. [21], which assumes negligible overlap in the \( F_2 \) dimension, we then obtain pure-absorption spectra in the \( F_1 \) dimension:

\[
L_R(\omega_1, \tilde{\Omega}_n) = \sum_{p=1}^{2J} A_{np}(\theta) \frac{R_{np}}{R_{np}^2 + (\omega_1 - (p - n)\omega_Q/2)^2}. \tag{28}
\]
The line intensities $A_{np}$ depend on the angle $\theta$ and the (cycled) phase of the refocusing pulse. In the QECI and QECM experiments, we have

$$A_{np}^{\text{CI}}(\theta) = V_{np}(\theta),$$  \hspace{1cm} \text{[29a]}$$
$$A_{np}^{\text{CM}}(\theta) = V_{np}(\theta) + V_{np}(\pi - \theta).$$  \hspace{1cm} \text{[29b]}$$

Two comments are in order here. First, in Eq. [28] we have omitted an uninteresting factor $1/R_n$ ($\sigma_n$ in Eq. [24a]). Second, the QECI and QECM intensities given by Eq. [29] are directly comparable; i.e., they refer to the same total acquisition time.

In the special case $\theta = \pi/2$, Eq. [29] shows that the QECI and QECM $F_1$ spectra are identical, except that the latter have twice as large signal-to-noise ratio. This is due to the fact that the $(\pi/2)_n$ pulses in the QECI cycle produce no signal in the absence of shifts. For other pulse angles, however, the $(\theta)_n$ pulses do contribute to the signal (see below). Further, the QECM $F_1$ spectra with $\theta = \pi/2$ are identical to the $F_1$ spectra described in Ref. (24), except that the latter are symmetric with respect to $\omega_1 = 0$ as a result of using cosine Fourier transforms. The matrix $V$ defined in Ref. (24) is related to the present matrix $V$ through $V_{np} = 2V_{n,2J-p}(\pi/2)$.

As discussed above, there are three criteria for choosing the pulse angle: (i) it should maximize the intensity of the central line (which yields the desired transverse relaxation rate), (ii) it should minimize the intensity of the neighboring satellite(s) if the $F_1$ splitting is so small that there is significant overlap with the central line, and (iii) it should be small enough that the pulse can be considered nonselective even if the splitting is large. In most experimental situations, at most two of these criteria are relevant. If the quadrupole splitting is very small or very large it may be necessary to strike a compromise between requirements (i) and (ii) or (i) and (iii), respectively. In the following we discuss these three aspects of the choice of pulse angle. The discussion is restricted to $F_1$ spectra derived from $F_2$ satellites; the $F_1$ spectrum derived from the central $F_2$ line is discussed below in connection with the 2D spin-echo experiment.

The angular functions $V_{np}(\theta)$, which furnish the $F_1$ line intensities according to Eq. [29], may be obtained from the defining relation [16]. This requires reduced Wigner functions of rank $k \leq 2I$ as well as the $U$ matrix which can be obtained explicitly by evaluating certain 3-j symbols (41). An alternative, and sometimes more convenient, expression for the functions $V_{np}(\theta)$ can be obtained by using a contraction formula involving 3-j symbols and Wigner functions (45, 46), with the result

$$V_{np}(\theta) = (-1)^{n+p}(U_{1n}U_{1p})^{1/2}d_{J-n,2J+p}^{J}d_{2J-n,2J-p}^{J}d_{2J}^{J}(\theta).$$  \hspace{1cm} \text{[30]}$$

The reduced Wigner functions for $I \leq \frac{3}{2}$ can be found, for example, in Ref. (46). The quantities $U_{1n}$ are simply the line intensities in the conventional single-pulse spectrum

$$U_{1n} = \frac{3n(2J-n)}{J(4J^2-1)},$$  \hspace{1cm} \text{[31]}$$

normalized according to

$$\sum_{n=1}^{2J} U_{1n} = 1.$$  \hspace{1cm} \text{[32]}$$
The main interest here is in the central $F_1$ line (at $\omega_1 = 0$) with $p = n \neq J$, derived from the $n$th $F_2$ satellite. As demonstrated above, this line is free from first-order quadrupolar broadening (QECM and QECI) and, in QECI spectra, is also unaffected by rank-1 shifts and second-order quadrupolar shifts. The central linewidths in the various $F_1$ spectra thus provide direct access to the transverse relaxation rates $R_\perp$, which involve all three laboratory-frame spectral densities $J_0$, $J_1$, and $J_2$ (24, 44).

It is evident from Eq. [30] that $V_{nm}(\theta) \geq 0$, whence [29] yields, for the central line intensities in QECM and QECI $F_1$ spectra,

$$A_{nm}^{CM}(\theta) \geq A_{nm}^{CI}(\theta) \geq 0. \quad [33]$$

According to Eqs. [28] – [30], the central line intensity in the QECI $F_1$ spectra derived from the outermost $F_2$ satellite ($n = 1$) is given by

$$A_{11}^{CI}(\theta) = \frac{I}{2} U_{11} \sin^2 \theta \left( \cos \frac{\theta}{2} \right)^{4I-4}, \quad [34]$$

which has a maximum at

$$\theta = \arccos \left( 1 - \frac{1}{I} \right), \quad [35]$$

i.e., at $\theta = 70.53^\circ$, $53.13^\circ$, $44.42^\circ$, and $38.94^\circ$ for $I = \frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$, respectively. In Table 1 we give the pulse angles that maximize the central line in all QECI and QECM $F_1$ spectra for $I = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$. The corresponding central line intensities are given relative to the $\theta = 90^\circ$ QECM experiment described in Ref. (24). It is seen that the improvement can be substantial for $I > \frac{3}{2}$ nuclei. Further, comparing the QECM and QECI experiments at their respective optimal pulse angles, we see that the price for elimination of shift-like broadening in QECI $F_1$ spectra is generally less than a factor 2 (as for $\theta = 90^\circ$) in signal-to-noise. In fact, for the outermost $F_2$ satellite ($n = 1$), the two methods yield virtually identical central line intensities for $I > \frac{3}{2}$. In general, the function $V_{nm}(\theta)$ has $n$ maxima in the range $0 \leq \theta \leq 180^\circ$. The entries in Table 1 refer to the global maximum. Except for $I = \frac{3}{2}$ with $n = 2$, the other (local) maxima occur at larger pulse angles.

<table>
<thead>
<tr>
<th>$I$</th>
<th>$n^a$</th>
<th>$\theta$ (degrees)</th>
<th>$\frac{A_{11}^{CI}(\theta)}{A_{nm}^{CM}(90^\circ)}$</th>
<th>$\theta$ (degrees)</th>
<th>$\frac{A_{11}^{CM}(\theta)}{A_{nm}^{CM}(90^\circ)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{3}{2}$</td>
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<td>70.5</td>
<td>0.59</td>
<td>90.0</td>
<td>1.00</td>
</tr>
<tr>
<td>$\frac{5}{2}$</td>
<td>1</td>
<td>53.1</td>
<td>1.31</td>
<td>54.7</td>
<td>1.33</td>
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<tr>
<td></td>
<td>2</td>
<td>38.6</td>
<td>2.93</td>
<td>46.9</td>
<td>4.27</td>
</tr>
<tr>
<td>$\frac{7}{2}$</td>
<td>1</td>
<td>44.4</td>
<td>3.63</td>
<td>44.4</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>31.3</td>
<td>0.85</td>
<td>90.0 (31.6)$^b$</td>
<td>1.00 (0.85)$^b$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>27.7</td>
<td>1.50</td>
<td>33.3</td>
<td>2.13</td>
</tr>
</tbody>
</table>

$^a$ The $F_2$ spectral lines are numbered beginning from the outermost satellite ($n = 1$) and proceeding toward the central line ($n = I + \frac{1}{2}$).

$^b$ Secondary maximum.
Next we consider the satellite intensities in the $F_1$ spectra. It is seen from Eq. [28] that for $n = 1$ all $F_1$ satellites appear on one side of the central line, the innermost satellite, of intensity $A_{12}(\theta)$, appearing at $\omega_1 = \omega_0/2$. For $n > 1$ there are two inner satellites, at $\omega_1 = \pm \omega_0/2$, of intensity $A_{n,n+1}(\theta)$. Unless $\omega_0/2$ is much larger than the (inhomogeneous) satellite linewidth, the central linewidth in $F_1$ may be affected by overlap. This overlap problem can be greatly reduced by choosing a pulse angle that minimizes the satellite intensity. For $n = 1$ it is always possible to choose a pulse angle that cancels the $\omega_1 = \omega_0/2$ satellite. Moreover, it follows from Eq. [30] that, in the QECI experiment, this angle coincides with that which maximizes the central line; i.e., $V_{12}(\theta) = dV_{11}(\theta)/d\theta = 0$ for $\theta = \arccos(1 - I^{-1})$. For $n \geq 2$ only one of the two inner satellites can be cancelled for a given $\theta$ value, but, in the QECI experiment, the remaining inner satellite is small. (In the QECM experiment, the $\omega_1 = +\omega_0/2$ satellite is not cancelled for any $\theta$ if $n = J - 1$.) The optimal pulse angles from the point of view of suppressing the inner satellites are given in Table 2 for the QECI and QECM experiments. Since these angles do not differ greatly from the angles that maximize the central line, satellite suppression only marginally reduces the amplitude of the central line. The considerably reduced spectral crowding accomplished with the optimized pulse angles in Table 2 is illustrated in Fig. 1. As a reference, the top row shows $F_1$ spectra with $\theta = 90^\circ$, while the middle and bottom rows show QECI and QECM spectra, respectively, with optimized pulse angles. The improvement is striking; consider, for example, the case $I = \frac{3}{2}, n = 1$. In most cases, the QECI experiment is most effective in reducing overlap (and, additionally, removes shift-like broadening), although it yields a somewhat lower central line signal-to-noise ratio than the QECM experiment.

As discussed above, the use of short pulses, i.e., small pulse angles at a given RF field, is a simple way to increase the pulse excitation bandwidth for samples with large quadrupole splitting. It is therefore of interest to examine the intensity variation of the central line in the various $F_1$ spectra as the angle $\theta$ of both pulses in the QE sequence $(\theta), -\tau - (\theta), \tau$ is made smaller. The first pulse contributes a factor $\sin \theta$ to the intensity, while the effect of the second pulse in the QECM experiment is given by $A_{mm}^{CM}(\theta)$ according to Eqs. [29b] and [30]. Figure 2 shows the $\theta$ variation of the central line intensity, normalized by its maximum value in each case, in the six QECM $F_1$ spectra derived from $F_2$ satellites for $I = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$. (The difference between the QECI and QECM intensities is small in the $\theta$ range in Fig. 2.) In the $I = \frac{3}{2}$ case, as for $I = 1$, the intensity varies as $\sin^3 \theta$, which severely limits the useful range of pulse angles. For $I > \frac{3}{2}$, however, the loss in signal-to-noise is generally much less prohibitive, as seen in Fig. 2.

The 2D spin-echo experiment. In the classical spin-echo sequence $(\pi/2)\tau - \tau - (\pi), -\tau - \text{acq}$, the $\pi$ pulse refocuses rank-1 interactions but leaves invariant the effective rank-2 quadrupolar Hamiltonian for the $2\tau$ evolution period. While it forms the basis for, e.g., 2D $J$ spectroscopy (4, 35), the spin-echo sequence is of limited value for quadrupolar nuclei, since it does not eliminate quadrupolar inhomogeneous broadening. However, since the central line in the $F_2$ spectrum of half-integral $I > 1$ nuclei is unaffected by the static quadrupole coupling to first order, a 2D spin-echo experiment can yield this linewidth free from inhomogeneous broadening. The associated relaxation rate $(24, 44) R_J \sim 2 j_z(\omega_0) + (J^2 - 2) j_z(2\omega_0)$ generally yields a
TABLE 2
Pulse Angles for Zero Intensity of Inner Satellite in QECI and QECM $F_i$ Spectra

<table>
<thead>
<tr>
<th>$I$</th>
<th>$n$</th>
<th>$\theta$ (degrees)</th>
<th>$\frac{A_{CM}^\theta(\theta)}{A_{CM}^\theta(90^\circ)}$</th>
<th>$\theta$ (degrees)</th>
<th>$\frac{A_{CM}^\theta(\theta)}{A_{CM}^\theta(90^\circ)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{3}{2}$</td>
<td>1</td>
<td>70.5</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{2}$</td>
<td>1</td>
<td>53.1</td>
<td>1.31</td>
<td>49.1</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>46.4</td>
<td>2.66</td>
<td>49.1</td>
<td>4.24</td>
</tr>
<tr>
<td>$\frac{5}{2}$</td>
<td>1</td>
<td>44.4</td>
<td>3.63</td>
<td>44.3</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>37.1</td>
<td>0.78</td>
<td>34.6</td>
<td>0.84</td>
</tr>
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<td></td>
<td>3</td>
<td>34.6</td>
<td>1.29</td>
<td>34.6</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Different linear combination of spectral densities that can be obtained from inversion recovery or even-rank polarization-decay experiments (41).

The 2D spin-echo experiment (27, 47, 48) is contained in the spin-dynamics calculations as the special case $\theta = \pi$. According to Eq. [10], the effect of a $\theta = \pi$ refocusing pulse on the single-quantum coherences is

$$\tilde{P}^k_1(\tau) = (-1)^{k+1} P^k_{-1}(\tau)$$

[36]

for the QECM and QECI phase cycles, whereas the QECR cycle cancels the single-quantum coherences and, hence, produces no signal. With $\theta = \pi$, it is thus not essential

![Fig. 1. Calculated $F_i$ lineshapes for $I = \frac{3}{2}, \frac{5}{2},$ and $\frac{7}{2}$ nuclei in uniformly aligned samples. The top row refers to a refocusing pulse angle $\theta = 90^\circ$, while the middle and bottom rows show QECI and QECM $F_i$ spectra, respectively, with $\theta$ optimized, according to Table 2, for maximal suppression of inner satellites. For simplicity, the effects of inhomogeneous couplings and shifts have been omitted. The reduced spectral parameters are $\omega_0/(2R_j) = 20$, $j_0/j_1 = 3$, and $j_2/j_1 = 1$. The frequency scale is the same in all spectra and the intensities are normalized so that the largest peak has the same amplitude in all spectra. The central line at $\omega_1 = 0$ is marked with an asterisk in all $F_i$ spectra.](image-url)
Fig. 2. Pulse angle dependence of the intensity of the central line in QECM $F_1$ spectra obtained with the pulse sequence $(\theta)_{\text{max}} = \tau - (\theta)_{\text{max}}$. The intensities have been normalized by their maximum values for each case. The various curves labelled $(I; n)$ refer to different spin $I$ and to $F_1$ spectra taken at different $F_2$ satellites $n$.

to cycle the phase of the refocusing pulse (to refocus rank-1 inhomogeneous broadening), though it is advisable because of the ubiquitous RF inhomogeneity (35).

We now consider the $F_1$ spectrum $L_R(\omega_1, \delta)$ derived from the central line ($n = J$) at $\omega_2 = \tilde{\Omega}_J = \tilde{\delta}$ in the $F_2$ dimension. According to Eq. [30], the $F_1$ line intensities are

$$V_{np}(\pi) = \delta_{n,2J-p}U_{1p},$$

whence Eq. [20] yields

$$L_R(\omega_1, \delta) = \sum_{p=1}^{2I} U_{1p} \text{Re} \left\{ \langle [R_p + i(\omega_1 + \tilde{\Omega}_p)]^{-1}[R_p + i(\tilde{\delta} - \Omega_{2J-p})]^{-1} \rangle \right\}. \tag{38}$$

Proceeding as in the derivation of Eq. [23], we obtain for the central line ($p = J$) in the $F_1$ spectrum [38]

$$L_R^*(\omega_1, \delta) = \frac{3J}{4J^2 - 1} \left[ \alpha_J \frac{R_J}{R_J^2 + \omega_1^2} + \beta_J \frac{\omega_1}{R_J^2 + \omega_1^2} \right], \tag{39}$$

with $\alpha_J$ and $\beta_J$ given by Eq. [24]. (Note that $\tilde{\Omega}_J = \tilde{\Omega}_J = \tilde{\delta} = \delta$, where $\tilde{\delta}$ refers to the central peak position in $F_2$. A pure-absorption shape can thus be obtained after a zeroth-order phase correction and the linewidth yields the homogeneous $R_J$.}

- The text is a continuation of the discussion on 2D Quadrupolar-Echo Spectroscopy, focusing on the pulse angle dependence of the intensity of the central line in QECM $F_1$ spectra.
- The mathematical expressions and results are derived from previous equations, providing a deeper understanding of the spectral behavior under different pulse conditions.
- The diagrams illustrate the pulse angle dependence, with various curves labelled $(I; n)$, and highlight the central line of interest at $(7/2;1)$.
- The text emphasizes the importance of phase correction and the role of homogeneous linewidth in the spectral analysis.

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2D QUADRUPOLAR-ECHO SPECTROSCOPY

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In the absence of overlap in the $F_2$ dimension only the $p = J$ term contributes to [38] and the central line [39] is the only one; i.e., there are no satellites in the $F_1$ spectrum. The intensity of the central line is generally given by $V_{JJ}(\theta)$. Since the global maximum of this function is at $\theta = \pi$ it follows, perhaps not surprisingly, that the 2D spin-echo experiment is the best method for determining the homogeneous relaxation rate $R_J$ in the presence of rank-1 inhomogeneous broadening (27, 47).

An additional advantage of the 2D spin-echo experiment for determination of $R_J$ is the absence of satellites that might otherwise overlap with the central line in the $F_1$ dimension (27, 47). As shown in Eq. [38], satellites can appear in the spin-echo $F_1$ spectra only as a result of overlap in the $F_2$ dimension. The inner satellites (in $F_1$) then appear at $\pm \omega_Q$, rather than at $\pm \omega_Q/2$ as in the QE $F_1$ spectra derived from $F_2$ satellites (without overlap). Furthermore, the spin-echo $F_1$ satellites at $\pm \omega_Q$, caused by overlap in $F_2$, are strongly reduced in intensity if the $F_2$ overlap is moderate ($\omega_Q > R_{J-1}$). The main effect of overlap with the central $F_1$ line comes from the dispersion contribution to the $\pm \omega_Q$ satellites. The resulting spectral amplitude at $\omega_1 \approx 0$ is of order $R_{J-1}/\omega_Q$ and, moreover, is constant over the region of the central peak to order $(R_{J-1}/\omega_Q)^3$; i.e., it is easy to correct for.

**EXPERIMENT**

Among the methods discussed here, 2D spin-echo spectroscopy has been used in some recent relaxation studies [$^7$Li and $^{133}$Cs in oriented DNA samples (27, 47) and $^{23}$Na in lyotropic nematic liquid crystals (49)], while 2D QE spectroscopy has been used in several studies of lyotropic liquid crystals (25, 26, 49, 50). The use of the 2D relaxation methods in these applications enabled a separation of the contributions of quadrupolar and CSA relaxation mechanisms (27) and, in the case of pure quadrupolar relaxation, enabled an accurate determination of the three distinct laboratory-frame spectral densities (25, 26, 49, 50). As most of these applications of the 2D QE method employed the original (QECM) version, we present here some experimental illustrations of the optimized QECI and QECM experiments, using the counterion $^{23}$Na ($I = \frac{3}{2}$) and the water $^{17}$O ($I = \frac{3}{2}$) nuclei in a lyotropic nematic liquid crystal.

The nematic sample, in the calamitic ($N_\alpha^+$) phase consisting of prolate-spheroidal aggregates aligned with the magnetic field, was prepared by mixing appropriate amounts of sodium dodecyl sulfate, decanol, and water as described in Ref. (49). The measurements were carried out on a Bruker MSL-100 spectrometer at 26.485 MHz ($^{23}$Na) and 13.571 MHz ($^{17}$O) frequencies using a saddle-coil probe. As the $B_1$ field inhomogeneity is relatively large for this probe (about 20% for the full sample volume) we expect the observed peak intensities to be slightly modified with respect to the theoretical spectra in Fig. 1. The homogeneous linewidths, however, provided by the central lines in the $F_1$ cross-section spectra are not influenced by $B_1$ inhomogeneity. The $90^\circ$ pulse lengths were typically about 7 $\mu$s for $^{23}$Na and 10 $\mu$s for $^{17}$O.

The static magnetic field inhomogeneity can be adjusted to about three or four hertz. As the homogeneous linewidths are much larger than this value, the QECI experiment is not decisively necessary for the $^{23}$Na studies (since there the splitting is much larger than the linewidths) in this particular sample and experimental setup. The primary function of the sodium spectra presented is to demonstrate the refocusing of large magnetic field inhomogeneity, for which purpose the shim currents were...
misadjusted to provide a controlled (~52 Hz) field inhomogeneity of magnitude comparable to the satellite homogeneous linewidth.

The $^{23}$Na spectrum displayed in Fig. 3 was obtained in a QECI experiment. The angle of the second pulse was set to 70.5° (cf. Tables 1 and 2), which theoretically provides maximum intensity for the central line in this $F_1$ cross-section spectrum and zero intensity for the first satellite. The experimental spectrum exhibits a strong suppression of the first satellite. A least-squares fit, using the Levenberg–Marquardt algorithm (51), to the central ($F_1$) line shown in Fig. 4a yielded 116 Hz for the homogeneous ($F_2$) satellite linewidth. The large difference between the central (31 Hz) and the satellite homogeneous linewidths can be ascribed to motional averaging of the long-range disorder by diffusion of the Na$^+$ ion (50). Figure 4b, on the other hand, displays the same central ($F_1$) line obtained by the QECM experiment. As the field inhomogeneity is not refocused there, the linewidth (151 Hz from least-squares fitting) is not the homogeneous one. Since the field inhomogeneity is comparable in magnitude to the homogeneous linewidth, the correction applicable to small inhomogeneous broadening (24, 25) is not quantitatively accurate here.

The satellite suppression in the $^{23}$Na QECI spectrum in Fig. 3 is of little practical interest as the splitting is much larger than the linewidths. Then, in the fitting procedure, a spectral region around the central line can be used with no influence from the other lines. For the $^{17}$O spectra shown in Fig. 5 the situation is different; the splitting is not exceedingly larger than the linewidths. Spectral truncation, as in the $I = \frac{1}{2}$ example, is thus not feasible without introducing a small uncontrolled bias in the deduced linewidths. [We consider here only least-squares fits. While other fitting procedures

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**Fig. 3.** $^{23}$Na $F_1$ cross-section spectrum at the satellite position in $F_2$ obtained with the QECI method on a nematic lyotropic liquid crystal. The 2D experiment included 800 increments; the $t_2$ cross section was zero filled to 4K prior to the Fourier transformation.
are used increasingly in NMR spectroscopy (52), their potential in this experimental situation has yet to be established. Fitting of the full spectrum poses two problems. First, the satellites may not (in the case of significant inhomogeneous broadening) be Lorentzian and fitting to a multi-Lorentzian spectrum may introduce bias in the deduced linewidths. (Inclusion of the full inhomogeneous satellite lineshape in the $F_1$ cross-section fit appears to be impractical.) Second, depending on the signal-to-noise ratio, the error of the obtained linewidth for the central line may be significantly influenced by the other lines in the spectrum: larger adjacent lines yield increased error. Thus, the satellite suppression can enhance accuracy. Consequently, the QECI method is favorable in those cases where it yields suppressed satellites and a central line intensity almost identical to the QECM result ($n = 1$ for $I = \frac{1}{2}$ and $I = \frac{7}{2}$; cf. Table 2). In other cases, the choice between the QECM and QECI methods may
FIG. 5. $^{17}$O $F_1$ cross-section spectra obtained on the outer (left) and inner (right) high-frequency satellites and with the QECI (middle) and QECM (bottom) methods using the optimized pulse angles in Table 2. The top displays the results obtained by a 90° refocusing pulse in the QECM experiment. The central line at $\alpha_1 = 0$ is marked with an asterisk in all spectra. This figure can be directly compared with the $I = \frac{3}{2}$ block in Fig. 1. The 2D experiments consisted of 300 $t_1$ increments; zero filling to 4K was done prior to the Fourier transformation. The line splitting is 850 Hz.

depend on the field inhomogeneity, the quadrupolar inhomogeneous broadening of the satellites, and, possibly, the overall signal-to-noise ratio.

Figure 5 shows the experimental spectra obtained in the same experiments as those considered in Fig. 1. Comparison of the second and third columns of Fig. 1 and Fig. 5 shows good agreement between the theoretical and experimental results; the minor deviations are probably caused by the large $B_1$ inhomogeneity. Least-squares fitting to the QECI spectra yields, for the homogeneous linewidths of the inner and outer $^{17}$O satellites, $177.4 \pm 2$ and $195.8 \pm 3$ Hz, respectively.

SUMMARY

In NMR relaxation studies on $I > 1$ nuclei in anisotropic (partially) aligned systems, one of the main objectives is to determine the distinct relaxation rates $R_n$, $n = 1, 2, \ldots, J = I + \frac{1}{2}$, associated with different single-quantum transitions. This task is best accomplished by means of 2D quadrupolar-echo (or 2D spin-echo) spectroscopy. As the $(\pi/2)_{yz}$ pulse yields optimum refocusing of the first-order quadrupolar inhomogeneous broadening for $I = 1$ nuclei, it is often regarded as the way to refocus quadrupolar inhomogeneity. The present results show, however, that this particular refocusing pulse has no special significance for $I > \frac{3}{2}$ nuclei. By allowing the angle and the phase of the refocusing pulse to differ from the conventional $(\pi/2)_{yz}$, we have
shown that the original version of the 2D QE experiment (24) can be improved in important respects. In particular, the phase-cycled 2D QECI experiment makes it possible to accurately determine the relaxation rates $R_\alpha$ in the simultaneous presence of large quadrupolar and magnetic field inhomogeneities.

The following general guidelines are useful to keep in mind when one is choosing refocusing pulse angle and phase in 2D quadrupolar-echo and spin-echo experiments.

1. For determining the relaxation rate $R_{\alpha}$, associated with the $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition, the 2D spin-echo experiment (with $\theta = \pi$) is the best choice as it refocuses magnetic field inhomogeneity, gives maximum signal-to-noise ratio, and minimizes satellite overlap.

2. For the relaxation rates $R_1, R_2, \ldots, R_{J-1}$, associated with satellite transitions, the 2D QECI experiment is usually a good choice. If there is disturbing overlap between the central line and the neighboring satellite(s) in $F_1$, the pulse angle should be chosen according to Table 2; otherwise it should be chosen according to Table 1. For the relaxation rate $R_{J-1}$, associated with the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transitions, the 2D QECM experiment gives a signal-to-noise ratio 40–60% higher than that of the 2D QECI experiment, but is preferable to the latter only if spectral overlap and magnetic field inhomogeneity are small.

3. In the case of very large quadrupole splittings, both pulse angles in the QE sequence can be substantially reduced to render the pulses nonselective with significant, but often acceptable, loss in signal-to-noise for $I > \frac{3}{2}$ nuclei.

ACKNOWLEDGMENT

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