

Nearly Exponential Quadrupolar Relaxation. A Perturbation Treatment

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Quadrupolar nuclear spin relaxation is treated by a perturbation method, which shows that the relaxation is nearly exponential provided that the effective spectral density is only weakly frequency dependent. Approximate analytical expressions for the relaxation rates are derived and tested against the experimentally accessible apparent relaxation rates, for a fast-exchange two-state model. The results for spin $I = 5/2$ and $7/2$ indicate that the analytical expressions are accurate to within a few percent in most experimental situations.

INTRODUCTION

The magnetic relaxation of a nucleus with spin $I \geq 1$ is usually due mainly to the interaction of the nuclear electric quadrupole moment with fluctuating electric field gradients present at the position of the nucleus. It was shown 25 years ago (1) that, except for the case $I = 1$, which will not concern us here, quadrupolar relaxation is, in general, not a simple exponential decay. For nuclei with half-integral spin, such as ${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{35}\text{Cl}$, ${}^{39}\text{K}$ ($I = 3/2$), ${}^{17}\text{O}$, ${}^{25}\text{Mg}$ ($I = 5/2$), ${}^{43}\text{Ca}$, ${}^{133}\text{Cs}$, and ${}^{139}\text{La}$ ($I = 7/2$), the magnetization decays as a weighted sum of $I + 1/2$ exponentials. For $I = 3/2$ there exist analytical expressions (1, 2) for the two relaxation rates, whereas for $I = 5/2$ and $7/2$ the relaxation matrix has to be diagonalized numerically. This has been done in a series of papers (3–6) dealing with the completely analogous case of electron spin relaxation by modulation of the quadratic zero-field splitting, which, like the quadrupole coupling, is a second-rank interaction, and, more recently, also in connection with nuclear quadrupole relaxation (7, 8).

In recent years, nuclear magnetic relaxation of quadrupolar nuclei has been used extensively to obtain information on the interaction of ions and small molecules with macromolecules and large molecular aggregates (9–12). In many cases, the observed nuclei are involved in rapid chemical exchange between a "bound" state, where there is significant interaction with the macromolecule or aggregate, and a "free" state, where fast reorientation makes the "extreme narrowing" approximation (the spectral density of the fluctuating field gradient is constant up to twice the resonance frequency) valid. In the bound state, however, extreme narrowing conditions do not usually obtain, with the result that the relaxation becomes multiexponential.

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Pronounced deviations from simple exponential decay and Lorentzian absorption lineshape, a prerequisite for a full nonexponential analysis, have, to our knowledge, been observed only for ^{23}Na (13–18). More commonly, the relaxation appears exponential, even when the contribution from the bound state is considerable and when the longitudinal and transverse relaxation rates are unequal and frequency dependent. Clearly, approximate analytical expressions for the apparent longitudinal and transverse relaxation rates in this regime of “nearly exponential” relaxation would be very useful. This is particularly so for $I = 5/2$ and $7/2$, where, otherwise, the relaxation matrix must be diagonalized numerically for each set of values for the spectral densities, and apparent relaxation rates then calculated from a fit to a simple exponential decay or from the linewidth of the actual superposition of Lorentzians.

We approach the problem of obtaining approximate analytical expressions for the relaxation rates through a perturbation treatment, in which we regard the extreme narrowing situation as being “perturbed” by allowing for a frequency dependence in the spectral density. In order to assess the validity of the resulting equations, we present numerical results for $I = 3/2, 5/2$, and $7/2$.

MULTIEXPONENTIAL SPIN RELAXATION IN MATRIX FORMALISM (19, 20)

In the basis of eigenvectors of the Zeeman Hamiltonian, the longitudinal ($\alpha = 1$) and transverse ($\alpha = 2$) components of the macroscopic magnetization may be written

$$M_{\alpha}(t) = N\gamma\hbar \tilde{\mathbf{I}}_{\alpha}\chi_{\alpha}(t), \quad [1]$$

where $M_1(t) \equiv M_z(t) - M_{\text{eq}}$ and $M_2(t) \equiv M'_+(t)$. The \mathbf{I}_{α} are column vectors (tilde denotes transposition) representing spin operators and have components $I_{1,m} = m$ and $I_{2,m} = [I(I+1) - m(m+1)]^{1/2}$, respectively. The χ_{α} are column vectors composed of matrix elements of the reduced density operator according to $\chi_{1,m} = \chi_{mm} - \chi_{-m-m}$ and $\chi_{2,m} = \chi'_{mm+1}$, the superscript referring to the interaction representation.

The time evolution of the vectors $\chi_{\alpha}(t)$ is, under certain conditions, given by Redfield's equation of motion in the Zeeman basis,

$$\frac{d}{dt}\chi_{\alpha}(t) = -\mathbf{R}_{\alpha}\chi_{\alpha}(t), \quad [2]$$

with the formal solution

$$\chi_{\alpha}(t) = \exp[-\mathbf{R}_{\alpha}t]\chi_{\alpha}(0). \quad [3]$$

The elements of the square matrices \mathbf{R}_{α} are related to the elements of the conventional relaxation matrix through $R_{1,mn} = R_{mm-n-n} - R_{mnmn}$ and $R_{2,mn} = -R_{mm+1nn+1}$. For half-integral spin, the dimension of the vector space is $I + 1/2$ ($m = 1/2, 3/2, \dots, I$) for $\alpha = 1$ and $2I$ ($m = -I, -I + 1, \dots, I - 1$) for $\alpha = 2$.

The symmetric relaxation matrices \mathbf{R}_{α} are diagonalized by orthogonal transformation matrices \mathbf{S}_{α} ,

$$\mathbf{R}_{\alpha}^S = \mathbf{S}_{\alpha}\mathbf{R}_{\alpha}\tilde{\mathbf{S}}_{\alpha}. \quad [4]$$

The columns of $\tilde{\mathbf{S}}_\alpha$ constitute the eigenvectors $\mathbf{S}_{\alpha k}$ of \mathbf{R}_α with eigenvalues $R_{\alpha k}$,

$$\mathbf{R}_\alpha \mathbf{S}_{\alpha k} = R_{\alpha k} \mathbf{S}_{\alpha k}. \quad [5]$$

Equations [1], [3], and [4] yield the solution

$$M_\alpha(t) = M_\alpha(0) [\tilde{\mathbf{I}}_\alpha \mathbf{I}_\alpha]^{-1} \tilde{\mathbf{I}}_\alpha^S \exp[-\mathbf{R}_\alpha^S t] \mathbf{I}_\alpha^S, \quad [6]$$

where use has been made of the proportionality $\chi_\alpha(0) \propto \mathbf{I}_\alpha$ and where $\mathbf{I}_\alpha^S = \mathbf{S}_\alpha \mathbf{I}_\alpha$ is the spin vector transformed to the eigenbasis of \mathbf{R}_α . Equation [6] may be rewritten as

$$M_\alpha(t) = M_\alpha(0) \sum_{k=1}^{I+1/2} c_{\alpha k} e^{-R_{\alpha k} t}, \quad [7]$$

where the normalized amplitudes are defined by

$$c_{\alpha k} \equiv [\tilde{\mathbf{I}}_\alpha \mathbf{I}_\alpha]^{-1} [\tilde{\mathbf{S}}_{\alpha k} \mathbf{I}_\alpha]^2. \quad [8]$$

Equation [7] shows that the magnetization decays as a weighted sum of $I + 1/2$ exponentials. This is true also in the transverse case, since the $2I$ -dimensional \mathbf{R}_2 matrix can be transformed to block-diagonal form by exploiting the invariance of \mathbf{I}_2 and \mathbf{R}_2 with respect to the replacement $m \rightarrow -m - 1$. The transverse relaxation is then described by the largest block, of dimension $I + 1/2$.

The simple exponential decay obtained for extreme narrowing emerges since, in that case, \mathbf{I}_α is proportional to an eigenvector of \mathbf{R}_α . According to Eq. [8], only one of the amplitudes $c_{\alpha k}$ is then nonzero. For nonextreme narrowing this is no longer true and it becomes necessary to determine the eigenvalues and eigenvectors of the relaxation matrices. For $I = 3/2$ this can be accomplished analytically ($I, 2$), whereas for $I = 5/2$ and $7/2$ one must, in the general case, rely on numerical methods. However, for practical purposes it is desirable to have approximate analytical expressions for the relaxation behavior.

PERTURBATION TREATMENT

As a first step in determining approximate eigenvalues and eigenvectors of the relaxation matrices, we make the transformation

$$\mathbf{R}_\alpha^{S_0} = \mathbf{S}_\alpha^{(0)} \mathbf{R}_\alpha \tilde{\mathbf{S}}_\alpha^{(0)}. \quad [9]$$

where $\mathbf{S}_\alpha^{(0)}$ defines the transformation that diagonalizes \mathbf{R}_α for extreme narrowing conditions; $\mathbf{S}_\alpha^{(0)}$ depends only on α and I and can be obtained in analytical form. There are two points worth noting about the transformation [9]. First, if the deviation from extreme narrowing is small, then $\mathbf{R}_\alpha^{S_0}$ will be "nearly diagonal." Second, one of the columns of $\tilde{\mathbf{S}}_\alpha^{(0)}$ is proportional to \mathbf{I}_α .

From Tables 1 and 2, which show the transformed relaxation matrices $\mathbf{R}_\alpha^{S_0}$ for $I = 5/2$ and $7/2$, respectively, it is seen that the off-diagonal elements are determined by differences between spectral densities at frequencies 0, ω_0 , and $2\omega_0$. Thus, for extreme narrowing, i.e., when $J(\omega)$ is independent of ω , the matrices correctly reduce to diagonal form (with elements that are independent of α). Here, and in the following, we assume that the Hamiltonian describing the mo-

TABLE 1
TRANSFORMED RELAXATION MATRICES FOR $I = 5/2$

$$\mathbf{R}_\alpha^{S_0} = K \begin{bmatrix} A & E & 0 \\ E & B & F \\ 0 & F & C \end{bmatrix}, \quad K = \frac{3}{125} \left[\frac{eQ}{\hbar} \right]^2$$

| | $\alpha = 1$ | $\alpha = 2$ |
|---|--|---|
| A | $2J_1 + 8J_2$ | $3J_0 + 5J_1 + 2J_2$ |
| B | $\frac{1}{4} (82J_1 + 83J_2)$ | $\frac{1}{24} (123J_0 + 370J_1 + 497J_2)$ |
| C | $\frac{25}{4} (2J_1 + J_2)$ | $\frac{5}{12} (3J_0 + 26J_1 + 16J_2)$ |
| E | $-\frac{18}{(14)^{1/2}} (J_1 - J_2)$ | $\frac{27}{2(21)^{1/2}} (J_0 - J_2)$ |
| F | $-\frac{125}{2(35)^{1/2}} (J_1 - J_2)$ | $-\frac{25}{12(14)^{1/2}} (3J_0 + 14J_1 - 17J_2)$ |

lecular motion is invariant under rotations. The relaxation matrix elements then contain spectral densities of the form (19)

$$J_q \equiv J_{00}(q\omega_0) = \frac{1}{4} \int_{-\infty}^{\infty} d\tau e^{-iq\omega_0\tau} \langle V_{zz}^L(0) V_{zz}^L(\tau) \rangle, \quad [10]$$

where V_{zz}^L is the second partial derivative, with respect to the laboratory-fixed z coordinate, of the electric potential at the position of the nucleus.

If all off-diagonal elements $R_{\alpha,lk}^{S_0}$ are small relative to the difference between the diagonal elements which they connect, then approximate eigenvalues and eigenvectors of \mathbf{R}_α can be obtained through a perturbation expansion. To first order, the eigenvalues are simply the diagonal elements of $\mathbf{R}_\alpha^{S_0}$ with corresponding eigenvectors (21),

$$S_{\alpha k}^{(1)} = S_{\alpha k}^{(0)} + \sum_{l \neq k} \frac{R_{\alpha,lk}^{S_0}}{R_k^{(0)} - R_l^{(0)}} S_{\alpha l}^{(0)}, \quad [11]$$

where the $R_k^{(0)}$ denote the zeroth-order eigenvalues, i.e., $R_{\alpha,kk}^{S_0}$ for $J(\omega)$ independent of ω and where the $S_{\alpha,k}^{(0)}$ are the columns of $\tilde{\mathbf{S}}_\alpha^{(0)}$. On inserting this expression into Eq. [8] one obtains for the (unnormalized) amplitudes

$$c_{\alpha k}^{(1)} = [\tilde{\mathbf{I}}_\alpha \mathbf{I}_\alpha]^{-1} \left[\tilde{\mathbf{S}}_{\alpha k}^{(0)} \mathbf{I}_\alpha + \sum_{l \neq k} \frac{R_{\alpha,lk}^{S_0}}{R_k^{(0)} - R_l^{(0)}} \tilde{\mathbf{S}}_{\alpha l}^{(0)} \mathbf{I}_\alpha \right]^2. \quad [12]$$

Since \mathbf{I}_α is proportional to the first column of $\tilde{\mathbf{S}}_\alpha^{(0)}$ we have $\tilde{\mathbf{S}}_{\alpha k}^{(0)} \mathbf{I}_\alpha = \delta_{k1} [\tilde{\mathbf{I}}_\alpha \mathbf{I}_\alpha]^{1/2}$

and consequently

$$\begin{aligned} c_{\alpha 1}^{(1)} &= 1, \\ c_{\alpha 2}^{(1)} &= \left[\frac{R_{\alpha,12}^{S_0}}{R_2^{(0)} - R_1^{(0)}} \right]^2, \\ c_{\alpha k}^{(1)} &= 0, \quad k > 2, \end{aligned} \quad [13]$$

where use has been made of the fact that only one-off-diagonal elements of $\mathbf{R}_{\alpha}^{S_0}$ are nonzero (see tables).

Thus, to first order the relaxation is biexponential and the relaxation rate of the major component, corresponding to element A in the tables, is

$$R_{11}^{(1)} = \frac{3}{40} \left[\frac{eQ}{\hbar} \right]^2 \frac{2I + 3}{I^2(2I - 1)} [2J_1 + 8J_2], \quad [14a]$$

$$R_{21}^{(1)} = \frac{3}{40} \left[\frac{eQ}{\hbar} \right]^2 \frac{2I + 3}{I^2(2I - 1)} [3J_0 + 5J_1 + 2J_2], \quad [14b]$$

where eQ is the nuclear electric quadrupole moment. It is interesting to note that

TABLE 2
TRANSFORMED RELAXATION MATRICES FOR $I = 7/2$

| $\mathbf{R}_{\alpha}^{S_0} = K \begin{bmatrix} A & E & 0 & 0 \\ E & B & F & 0 \\ 0 & F & C & G \\ 0 & 0 & G & D \end{bmatrix}, \quad K = \frac{1}{98} \left[\frac{eQ}{\hbar} \right]^2$ | | $\alpha = 1$ | $\alpha = 2$ |
|--|--|--|--------------|
| A | $2J_1 + 8J_2$ | $3J_0 + 5J_1 + 2J_2$ | |
| B | $2(12J_1 + 13J_2)$ | $\frac{11}{3} \left(\frac{18}{11} J_0 + 5J_1 + 7J_2 \right)$ | |
| C | $\frac{10}{13} (53J_1 + 51J_2)$ | $\frac{1}{39} (159J_0 + 1427J_1 + 1534J_2)$ | |
| D | $\frac{28}{13} (8J_1 + 5J_2)$ | $\frac{11}{13} \left(\frac{12}{11} J_0 + 19J_1 + 13J_2 \right)$ | |
| E | $-\frac{44}{(77)^{1/2}} (J_1 - J_2)$ | $\frac{3(22)^{1/2}}{(21)^{1/2}} (J_0 - J_2)$ | |
| F | $-\frac{40(13)^{1/2}}{(77)^{1/2}} (J_1 - J_2)$ | $-\frac{52(5)^{1/2}}{3(2002)^{1/2}} (3J_0 + 14J_1 - 17J_2)$ | |
| G | $-\frac{1960}{13(77)^{1/2}} (J_1 - J_2)$ | $\frac{42(35)^{1/2}}{(39,039)^{1/2}} (J_0 + 12J_1 - 13J_2)$ | |

the same expressions are valid for the initial relaxation rates, defined by

$$R_{\alpha}(0) \equiv - \left. \frac{1}{M_{\alpha}(0)} \frac{dM_{\alpha}(t)}{dt} \right|_{t=0}. \quad [15]$$

This is most directly shown by evaluating the operator equations [130] and [131] of Chap. VIII in Abragam's treatise (19). The analogous equations, for the case of electron spin relaxation, have previously been derived by McLachlan (22), who also noted that the initial rates, $R_{\alpha}(0)$, may be regarded as average relaxation rates in the sense

$$\langle R_{\alpha} \rangle = \sum_{k=1}^{I+1/2} c_{\alpha k} R_{\alpha k}. \quad [16]$$

The equality of $R_{\alpha}(0)$ and $\langle R_{\alpha} \rangle$ follows directly from Eqs. [7] and [15]. Expressions [14] have been obtained, for the special case of $I = 3/2$, in yet another way by Bull (23), who linearized the analytic expressions for $I = 3/2$ in the time variable.

According to the perturbation treatment, the initial rates actually apply over the entire decay, provided that the spectral density is only weakly frequency dependent. The rate of convergence of the perturbation expansion and thus the accuracy of a description of the relaxation behavior as a simple exponential decay with a rate given by Eq. [14] may be investigated by proceeding to higher orders and making an assumption about the functional form of the frequency dependence of $J(\omega)$. However, experimentally one does not measure the rates, $R_{\alpha 1}$, to which Eq. [14] is an approximation, but rather apparent relaxation rates R_{α}^* obtained from the absorption line width or from an exponential least-squares fit to the decay following certain pulse sequences. It is therefore more useful to assess the validity of expressions [14] in relation to the apparent rates R_{α}^* .

CALCULATIONS

We consider a nucleus which is part of a species that exchanges rapidly, relative to the relaxation rates, between a "bound" state (B) and a "free" state (F). The effective spectral density is then a weighted average of the individual spectral densities,

$$J_q = P_F J_q^F + P_B J_q^B, \quad [17]$$

where P_F and P_B are the relative populations of the two states. In most cases of interest, the observed nucleus resides in an ion or in a water molecule (^{17}O) in an aqueous solution containing macromolecules or large molecular aggregates. The F state then corresponds to the bulk of the solution, where it is reasonable to assume that $J_q^F = J_0^F$. In the B state, however, the probe experiences the slower motion of the macromolecule so that the spectral density may become frequency dependent. If we assume that the correlation function in Eq. [10] decays exponentially, corresponding to isotropic motion, with a correlation time τ_{cB} , then

$$J_q^B = \frac{1}{10} (V_{zz}^M)^2 \left[1 + \frac{\eta^2}{3} \right] \frac{\tau_{\text{cB}}}{1 + (q\omega_0\tau_{\text{cB}})^2}, \quad [18]$$

where V_{zz}^M and η have their usual meanings (19). Due to the frequency-independent term in [17], the relative variation of the spectral density with frequency will be smaller and the first-order result [14] is expected to be valid over a fairly wide range of conditions.

On inserting [17] and [18] into Eq. [14] we obtain

$$\frac{\langle R_1 \rangle}{P_F R_F} = 1 + Q[0.2\bar{J}_1^B + 0.8\bar{J}_2^B], \quad [19a]$$

$$\frac{\langle R_2 \rangle}{P_F R_F} = 1 + Q[0.3 + 0.5\bar{J}_1^B + 0.2\bar{J}_2^B]. \quad [19b]$$

Here, and in the following, we use the symbol $\langle R_\alpha \rangle$ to denote the rates given by Eq. [14]. In [19] we have introduced two dimensionless quantities

$$\bar{J}_q^B \equiv \frac{J_q^B}{J_0^B} = [1 + (q\omega_0\tau_{cB})^2]^{-1}, \quad [20]$$

$$Q \equiv \frac{P_B \chi_{eB}^2 \tau_{cB}}{P_F \chi_{eF}^2 \tau_{cF}}, \quad [21]$$

where the effective quadrupole coupling constant is defined by

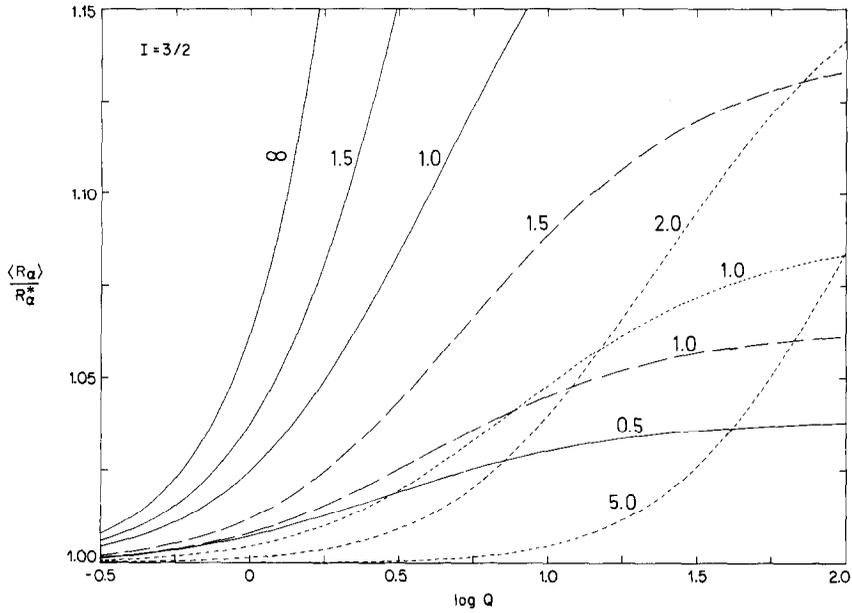
$$\chi_e \equiv \frac{|eQV_{zz}^M|}{h} \left[1 + \frac{\eta^2}{3} \right]^{1/2}. \quad [22]$$

Thus, $\langle R_\alpha \rangle / P_F R_F$, as well as the "reduced" relaxation matrix $\mathbf{R}_\alpha / P_F R_F$, are completely determined by the system parameter Q and the instrumental (for fixed τ_{cB}) parameter $\omega_0\tau_{cB}$. The slow-exchange limit (B state observed) obtains when Q becomes so large that unity is negligible compared to the second term in Eq. [19].

Reduced apparent relaxation rates $R_\alpha^* / P_F R_F$ were obtained, for given values of Q and $\omega_0\tau_{cB}$, through numerical diagonalization of the full relaxation matrices. With the resulting $c_{\alpha k}$ and $R_{\alpha k} / P_F R_F$ we then calculated apparent rates from the linewidth of the $I + 1/2$ superposed Lorentzians (R_2^{*a}) or from a least-squares fit of a simple exponential decay to ten points, equally spaced in magnetization from $0.95 M_\alpha(0)$ to $0.05 M_\alpha(0)$, taken from the $(I + 1/2)$ -exponential decay (R_α^{*e}).

Figures 1–3 illustrate the error made by equating the various apparent relaxation rates, R_1^{*e} , R_2^{*e} , or R_2^{*a} , to the corresponding first-order relaxation rate $\langle R_\alpha \rangle$ as given by Eq. [14]. First we may note that the approximation improves considerably in going from $I = 3/2$ to $5/2$. Increasing I to $7/2$ results in a further slight improvement. The error in the longitudinal rate (dotted curves) goes through a maximum for $\omega_0\tau_{cB}$ of the order unity. In a ^{139}La ($I = 7/2$) relaxation study of albumin solutions (7) the expression for the first-order longitudinal relaxation rate $\langle R_1 \rangle$ was used. For this case, with $\omega_0\tau_{cB} \approx 2$ and an estimated $Q \geq 100$, Figure 3 shows that the error is not less than 8%. Although, for given Q and $\omega_0\tau_{cB}$, the longitudinal decay is more nearly exponential (the dominating amplitude is closer to unity) than the transverse decay, it is seen that the first-order expressions may be less accurate in the longitudinal (dotted curves) than in the transverse (dashed curves) case. This is because the minor components are associated with larger relaxation rates in the longitudinal case.

When the apparent transverse relaxation rate is obtained from the linewidth



FIGS. 1-3. The ratio of the first-order relaxation rate $\langle R_\alpha \rangle$, given by Eq. [19], and the apparent rates R_1^{*e} (dotted curves), R_2^{*e} (dashed curves), or R_2^{*a} (solid curves), for indicated spin I . The dimensionless parameters are Q , which is defined by Eq. [21], and $\omega_0\tau_{CB}$, the value of which appears beside each curve.

(solid curves) the accuracy of the approximation deteriorates, particularly for $I = 3/2$, because the slow components are weighted heavier in a linewidth measurement than in a Carr-Purcell R_2 measurement. Large differences between R_2^{*a}

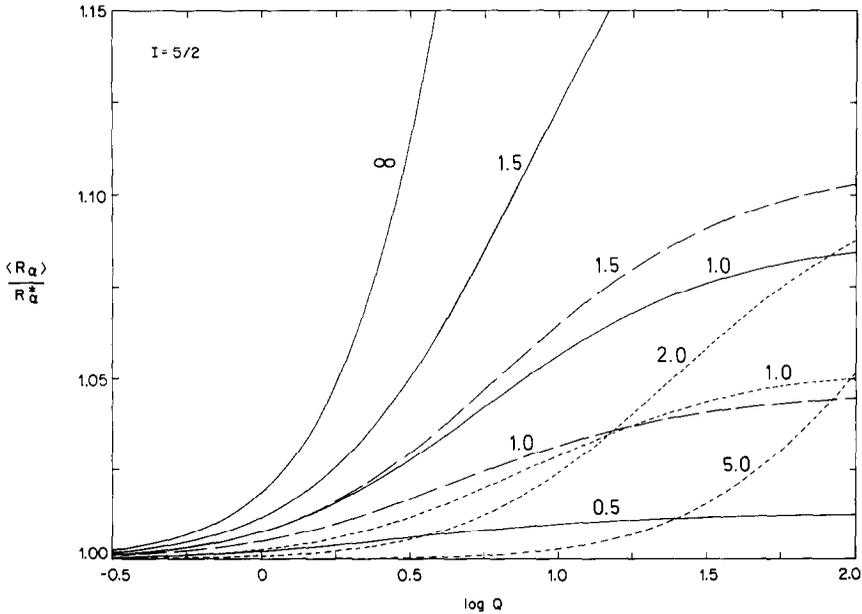


FIGURE 2

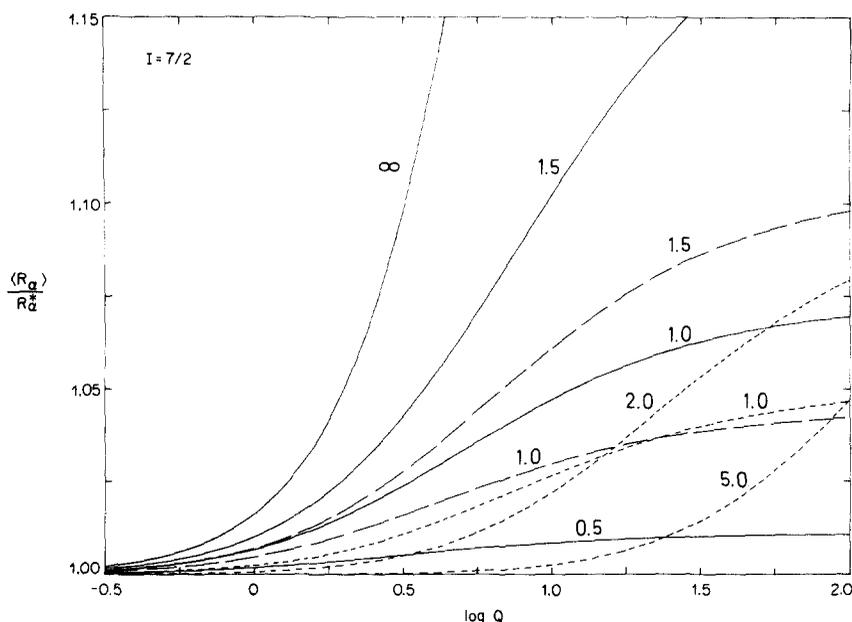


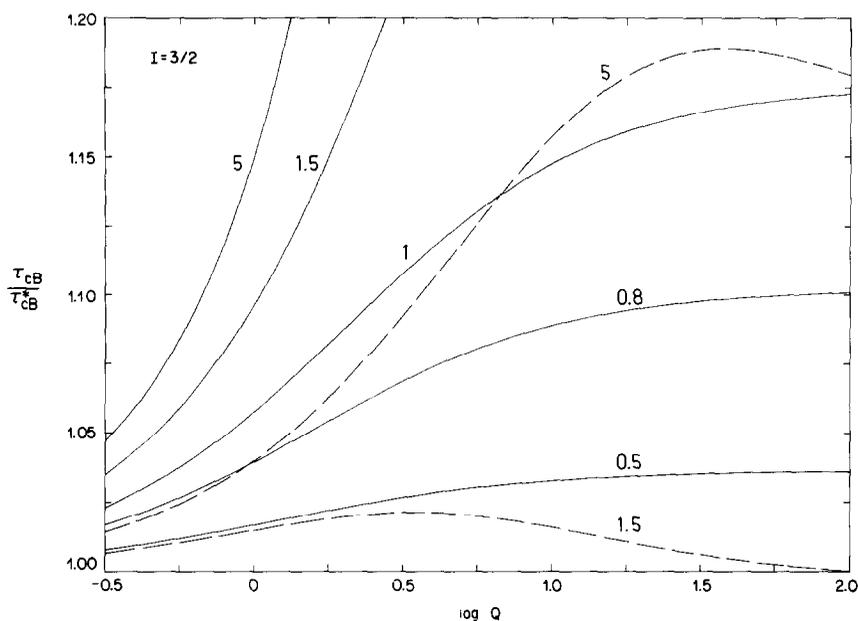
FIGURE 3

and R_2^{*e} have been observed for ^{23}Na ($I = 3/2$) in polyelectrolyte solutions (15). In electron spin resonance, it is customary to obtain R_2^* from the peak-to-peak distance in the derivative spectrum. The influence of the slowest component is then even greater. In fact, R_2^* measured in this way is nearly equal to the slowest component; e.g., for $I = 5/2$ the difference never exceeds 12%. This fact has been utilized in an ESR study of Fe^{3+} ($S = 5/2$) solutions (5).

For a given ratio $\langle R_2 \rangle / R_2^{*a}$, the deviation from Lorentzian lineshape becomes less pronounced with increasing spin I . It is doubtful whether, within the range of Figs. 1–3 ($\leq 15\%$ error), the slight ($\leq 10\%$) increase in amplitude in the wings of the absorption curve can be detected, even for $I = 3/2$. Moreover, within this range of error, the standard deviation of the exponential fits for determination of R_1^{*e} or R_2^{*e} is too small ($\leq 2\%$) to serve as an indicator of multiexponentiality. In the absence of reliable estimates of Q and $\omega_0\tau_{cB}$, the first-order expressions [14] should therefore be applied with caution.

The correlation time τ_{cB} for the B state may be obtained from the dispersion of either the longitudinal or the transverse relaxation rate. More commonly, however, τ_{cB} is calculated from the ratio of excess longitudinal and transverse rates at a single frequency. Since the ratio $\langle R_\alpha \rangle / R_\alpha^*$ is larger than one for the longitudinal as well as for the transverse rate, one would expect a cancellation effect in the error when evaluating τ_{cB} by this latter method. That this is indeed the case is shown in Figs. 4–6. Again, the accuracy is seen to improve dramatically in going from $I = 3/2$ to $5/2$. However, if R_2^* is obtained from a Carr–Purcell sequence (exponential fit) the accuracy is roughly independent of I . In agreement with previous calculations for $I = 3/2$ (24), Fig. 4 shows that, in this case, the error is negligible for $\omega_0\tau_{cB} \leq 1.5$.

The inherent anisotropy of the macromolecule–solvent interfacial region often



FIGS. 4-6. The ratio of the actual correlation time τ_{cB} and the apparent correlation time, τ_{cB}^* , obtained by equating the first-order relaxation rates with the corresponding apparent rates: R_1^{*e} and R_2^{*e} (dashed curves) or R_1^{*e} and R_2^{*a} (solid curves), for indicated spin I . The dimensionless parameters are Q , which is defined by Eq. [21], and $\omega_0\tau_{cB}$, the value of which appears beside each curve.

makes it convenient to regard the averaging of the quadrupole interaction as a two-step process: a fast local, slightly anisotropic reorientation and a slower, more extensive motion (25). If the local motion is sufficiently rapid (extreme narrowing)

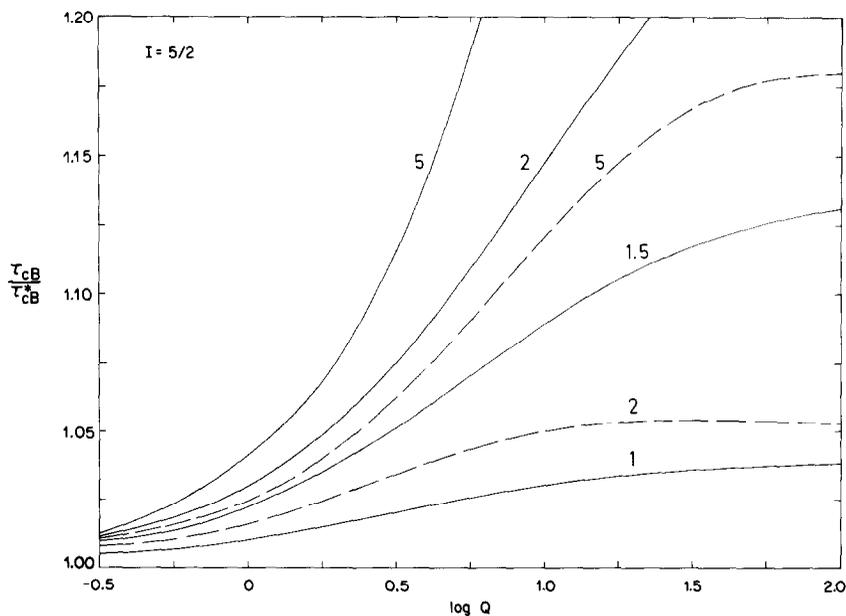


FIGURE 5

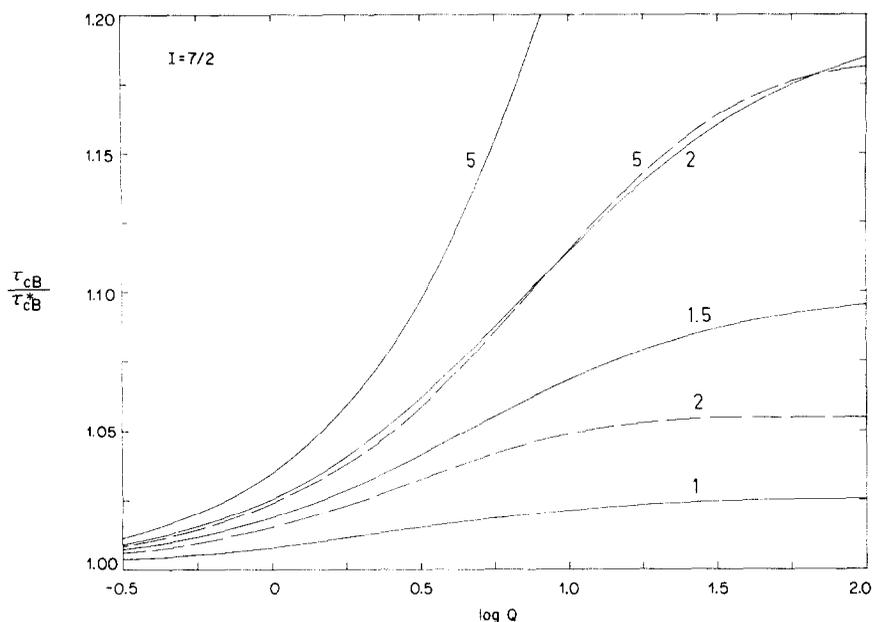


FIGURE 6

it will not contribute to the multiexponentiality, whereas for the slow motion the quadrupole coupling constant should, under certain conditions (25), be multiplied by an anisotropy factor A , the magnitude of which usually lies in the range 0.01 to 0.1. Thus by multiplying Q , as given by Eq. [21], by a factor A^2 , one obtains from Figs. 1–3 upper limits, corresponding to negligible contribution to the relaxation from the fast local motion, to the error appropriate for this model.

CONCLUSIONS

The perturbation treatment shows that the relaxation behavior is well described as a simple exponential decay with a rate given by Eq. [14], provided that the effective spectral density is only weakly frequency dependent. Calculations pertaining to a fast-exchange two-state model show that, for $I = 5/2$ and $7/2$, the first-order rates are accurate to within a few percent for Q values of the order of unity or less. For $I = 5/2$ and $7/2$ it seems, therefore, that the first-order expressions [14] will be useful in all cases, except, possibly, for large populations of species which are rigidly bound to large macromolecules.

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