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ON THE INFLUENCE OF MOLECULAR GEOMETRY, ORIENTATION, AND DYNAMICS ON ANGULAR
CORRELATION PATTERNS FROM ROTATIONALLY LABELED MACROMOLECULES

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ABSTRACT

In order to determine the sensitivity of gamma-ray angular correlation patterns from solute macromolecules labeled with rotational tracers such as ^{111m}Cd , a theoretical study was made of the behavior expected under certain conditions. A nucleus of spin $5/2$, acted upon by an axially symmetric electric field gradient, and bound to a rodlike macromolecule, was considered. Under static conditions (no molecular rotation), the time-dependent correlation pattern is quite sensitive to molecular orientation and, for oriented molecules, to the angle between the axis of the field-gradient tensor and the molecular axis. A general equation and results for selected geometric configurations are given. When molecular rotation is allowed, a classical model is applicable if the rotation is sufficiently slow. This model is used to calculate relaxation curves for several geometrical configurations under the condition that the macromolecules rotate about their long axes. These curves are shown to have considerable diagnostic value. Finally, the applicability of rotational tracers in the light of these results is discussed.

I. INTRODUCTION

Gamma-ray angular-correlation patterns from solute molecules labeled with radioisotopes--or "rotational tracers"--have been shown to be sensitive to molecular properties.¹⁻⁴ The rotational tracer method is of interest because of its extremely high sensitivity, the high penetrating power of γ rays, the relatively small disruption caused by binding a single tracer atom to a large molecule, and the rigor of angular correlation theory. As more sophisticated experiments become possible it is desirable to examine theoretically the sensitivity of γ -ray correlation patterns to molecular orientation and dynamics, and to evaluate the various possible experimental configurations systematically. The results of such a study are reported in this paper.

The theory of perturbed angular correlations is briefly reviewed in Sec. II. It is applied to the case of a spin-5/2 nucleus in an axially-symmetric electric field gradient. This spin was chosen because states of spin 5/2 in ^{133}Cs and ^{111}Cd have been used in the rotational tracer work to date. Much of the material in Sec. II can be found in the review articles by Steffen and Frauenfelder.⁵ It is included here in order to give a specific account of the assumptions upon which the results in Secs. III and IV are based, thus defining the extent of their validity.

Section III deals with the effects of static electric quadrupole interactions on the angular correlation pattern from a macromolecule labeled with a spin-5/2 rotational tracer. Macromolecules are considered whose shapes can be characterized by a single preferred axis (e.g., rods or discs). An equation is derived that relates the correlation pattern to molecular orientation and local properties of the tracer atom. Explicit calculations are presented for several experimental configurations.

Dynamical effects are considered in Sec. IV. A classical relaxation model is given that is applicable to solute macromolecules under certain conditions. The model is applied to several of the configurations considered in Sec. III. Conclusions are drawn in Sec. V.

II. TIME-INDEPENDENT QUADRUPOLE PERTURBATIONS

In this section the theory of angular correlations perturbed by static quadrupole interactions is discussed and applied to a particular case. Detailed treatments of this problem were given by Abragam and Pound⁶ and by Alder, et al.⁷ The development given below follows the exposition and notation of Steffen and Frauenfelder.⁵ The general expression for perturbed angular correlations (Eq. (1)) is specialized in several steps to an expression (Eq. (16)) for $\bar{\Gamma}_2(t)$, the rank-two perturbation coefficient arising from static quadrupole interaction of a spin-5/2 nucleus with an axially-symmetric electric field gradient. The assumptions embodied in each step of specialization are stated, in order to facilitate future applications to different systems.

The nuclear level scheme for a perturbed angular correlation experiment is illustrated in Fig. 1. A nucleus decays from an initial nuclear level to an intermediate level of spin I, emitting a γ quantum (γ_1). While in this intermediate level the nucleus interacts with extranuclear fields. The interaction, described by a hyperfine-structure Hamiltonian K, starts acting at the instant of formation of the intermediate level (time $t = 0$) and continues to act until this level decays by emission of the second γ quantum (γ_2). The nuclear mean life τ_N is usually in the 10^{-8} - 10^{-6} sec range in cases for which the rotational tracer method is most useful. Both γ_1 and γ_2 are detected and recorded, as in the time-interval between their emission. The three processes involving the intermediate level--formation, perturbation, and decay--are separable. The angular correlation between the two quanta γ_1 and γ_2 , emitted in the

directions \vec{k}_1 and \vec{k}_2 , respectively, is given by⁵

$$W(\vec{k}_1, \vec{k}_2, t) = \frac{e^{-t/\tau_N}}{4\pi\tau_N} \sum_{\lambda_1 \lambda_2 q_1 q_2} [(2\lambda_1 + 1)(2\lambda_2 + 1)]^{-1/2} A_{\lambda_1}(1) A_{\lambda_2}(2) \\ \times G_{\lambda_1 \lambda_2}^{q_1 q_2}(t) Y_{\lambda_1}^{q_1}(\theta_1, \phi_1)^* Y_{\lambda_2}^{q_2}(\theta_2, \phi_2) \quad (1)$$

Here λ_j and q_j denote tensor rank and components, $Y_{\lambda_j}^{q_j}(\theta_j, \phi_j)$ is a spherical harmonic in the angles between \vec{k}_j and an arbitrary co-ordinate frame, which we shall refer to later as the "atomic frame", and $A_{\lambda_j}(j)$ is a nuclear radiation parameter that depends only on the nuclear spins and multipolarities associated with the j^{th} transition. The perturbation factors $G_{\lambda_1 \lambda_2}^{q_1 q_2}(t)$ contain a complete description of the intermediate-state perturbations. They are in fact transformation coefficients for statistical tensors ρ_q^λ describing nuclear orientation in the intermediate state. If these tensors are defined in terms of the density matrix,⁸

$$\rho_q^\lambda = \sum_m (-1)^{I-m'+q-\lambda} \sqrt{2\lambda+1} \begin{pmatrix} I & I & \lambda \\ m' & -m & q \end{pmatrix} \langle m' | \rho | m \rangle \quad (2)$$

then the perturbation coefficients obey the relation⁹

$$\rho_q^{\lambda'}(t) = \sum_{\lambda q} G_{\lambda \lambda'}^{qq'}(t) \rho_q^\lambda(0) \quad (3)$$

An explicit expression for $G_{\lambda \lambda'}^{qq'}(t)$ may be written in terms of the time-evolution operator $\Lambda(t)$. This operator obeys the Schrödinger Equation. If K is time-independent, $\Lambda(t)$ may be written in terms of K as

$$\Lambda(t) = e^{-\frac{i}{\hbar} K(t)} \quad (4)$$

It follows that⁵

$$G_{\lambda_1 \lambda_2}^{q_1 q_2}(t) = \sum_{m_1 m_2} (-1)^{2I+m_1+m_2} [(2\lambda_1 + 1)(2\lambda_2 + 1)]^{1/2} \\ \times \begin{pmatrix} I & I & \lambda_1 \\ m_1' & -m_1 & q_1 \end{pmatrix} \begin{pmatrix} I & I & \lambda_2 \\ m_2' & -m_2 & q_2 \end{pmatrix} \langle m_2 | \Lambda(t) | m_1 \rangle \langle m_2' | \Lambda(t) | m_1 \rangle^* \quad (5)$$

In general K can be diagonalized by a unitary transformation U . If K has axial symmetry the problem is appreciably simplified, because then $U = 1$ and $\langle m_2 | \Lambda(t) | m_1 \rangle = \delta_{m m_1} \delta_{m m_2} e^{-i/\hbar E_m t}$, where E_m is the energy of the state $|Im\rangle$ in the diagonal representation. This relation, together with Eq. (5), requires $q_1 = q_2$. In the remainder of this paper K will be taken as axially symmetrical. The perturbation factor then takes the form⁵

$$G_{\lambda_1 \lambda_2}^{q q}(t) = \sum_m [(2\lambda_1 + 1)(2\lambda_2 + 1)]^{1/2} \begin{pmatrix} I & I & \lambda_1 \\ m' - m & q \end{pmatrix} \begin{pmatrix} I & I & \lambda_2 \\ m' - m & q \end{pmatrix} e^{\frac{i}{\hbar}(E_{m'} - E_m)t} \quad (6)$$

Specializing to axially-symmetric quadrupole interactions, the energy eigenvalues may be written

$$E_m = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I+1)] = -\frac{\omega_Q}{\hbar} [3m^2 - I(I+1)] \quad (7)$$

Thus for this case¹⁰

$$G_{\lambda_1 \lambda_2}^{q q}(t) = [(2\lambda_1 + 1)(2\lambda_2 + 2)]^{1/2} \sum_m \begin{pmatrix} I & I & \lambda_1 \\ m'-m & q & \end{pmatrix} \begin{pmatrix} I & I & \lambda_2 \\ m'-m & q & \end{pmatrix} e^{3i(m^2 - m'^2)\omega_Q t}. \quad (8)$$

Substitution of Eq. (8) into Eq. (1) would yield a general formal expression for the angular correlation function $W(\vec{k}_1, \vec{k}_2, t)$ in the presence of a static axially-symmetric quadrupole perturbation. In order to use this result in the most general cases, however, it would be necessary to know the values of the radiation parameters $A_{\lambda_1}(1)$ and $A_{\lambda_2}(2)$ of the two transitions separately. This information is usually not available because it cannot be obtained from unperturbed angular correlation studies on the same cascade, which yield only products of the form $A_{\lambda_1}(1) A_{\lambda_1}(2)$. Fortunately in many cascades this problem does not arise because λ takes only the values 0 and 2, and interference terms of the form $G_{0\lambda}^{qq}$ or $G_{\lambda 0}^{qq}$ vanish (Eq. (8)). This leaves only $A_0(1) A_0(2)$ and $A_2(1) A_2(2)$, which can be written A_{00} and A_{22} for brevity. The unperturbed correlation for such a cascade is given by

$$W(\vec{k}_1, \vec{k}_2, t) = \frac{e^{-t/\tau_N}}{4\pi\tau_N} [1 + A_{22}P_2(\cos\theta)] \quad (9)$$

Here the normalization condition

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} W(\vec{k}_1, \vec{k}_2, t) dt \sin\theta d\theta d\phi = 1 \quad , \quad (10)$$

has been used to set $A_{00} = 1$. In most cases A_{22} is determined experimentally from unperturbed correlation measurements. From Eqs. (1), (8), and (9), the angular correlation for axially-symmetric quadrupole perturbations and $\lambda_{\max} = 2$ can be written

$$W(\vec{k}_1, \vec{k}_2, t) = \frac{e^{-t/\tau_N}}{4\pi\tau_N} [1 + A_{22}\Gamma_2(\vec{k}_1, \vec{k}_2, t)] \quad , \quad (11)$$

where the response function $\Gamma_2(\vec{k}_1, \vec{k}_2, t)$ has the form

$$\begin{aligned} \Gamma_2(\vec{k}_1, \vec{k}_2, t) &= \frac{1}{5} \sum_q G_{22}^{qq}(t) Y_2^q(\theta_1, \phi_1)^* Y_2^q(\theta_2, \phi_2) \\ &= \sum_q \sum_m \begin{pmatrix} I & I & 2 \\ m' & -m & q \end{pmatrix}^2 e^{3i(m^2 - m'^2)\omega_Q t} Y_2^q(\theta_1, \phi_1)^* Y_2^q(\theta_2, \phi_2) \quad . \quad (12) \end{aligned}$$

The oscillations of $G_{22}^{qq}(t)$ in time can be written

$$G_{22}^{qq}(t) = \sum_n S_{nq}^{22} \cos n\omega_0 t \quad . \quad (13)$$

The factors

$$S_{nq}^{22} = 5 \sum_{mm'} \begin{pmatrix} I & I & 2 \\ m' & -m & q \end{pmatrix}^2 \quad , \quad (14)$$

have been tabulated by Alder, et al.⁷ The frequency ω_0 corresponds to the smallest energy-level separation in the quadrupole pattern. The sum in Eq. (14) is taken over all pairs for which $m - m' = q$. For half-integer spins $\omega_0 = 6\omega_Q$, and the index n in Eq. (13) takes all positive integer values¹¹
 $n = |m^2 - m'^2|/2$.

The spin-5/2, $T_{1/2} = 84$ nsec level¹² at 247 keV in ¹¹¹Cd and the spin-5/2, $T_{1/2} = 6.3$ nsec level¹² at 81 keV in ¹³³Cs have been used in rotational tracer

experiments to date. The following discussion will be made explicitly for a spin-5/2 level, perturbed by an axially-symmetric field gradient, and detected by a cascade with $\lambda_{\max} = 2$. Some generality is lost by this restriction, but the qualitative conclusions reached should apply for other spins. The object of this paper is to evaluate the sensitivity of perturbed angular correlations to molecular properties for a realistic case. The shortest path is taken to this end, using relatively pedestrian mathematical techniques, at the expense of developing further formalism.

For spin $I = 5/2$, n takes the values $n = 0, 1, 2, 3$, and 7

$$G_{22}^{00} = 1$$

$$G_{22}^{11}(t) = G_{22}^{-1-1}(t) = \frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t$$

$$G_{22}^{22}(t) = G_{22}^{-2-2}(t) = \frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 2\omega_0 t \quad (15)$$

Finally, the explicit expression for the response function, which will be the basic equation for the rest of this paper, is

$$\begin{aligned} \Gamma_2(\vec{k}_1, \vec{k}_2, t) = & \frac{1}{4} [3\cos^2\theta_1 - 1] [3\cos^2\theta_2 - 1] \\ & + 3 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2 \cos(\phi_2 - \phi_1) \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ & + \frac{3}{4} [1 - \cos^2\theta_1] [1 - \cos^2\theta_2] \cos 2(\phi_2 - \phi_1) \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \quad (16) \end{aligned}$$

Here the angles θ_i, ϕ_i express the \vec{k}_i direction to the i^{th} detector in a coordinate frame in which the symmetry axis of the electric field gradient tensor serves as

the z axis. This relationship is illustrated in Fig. 2. This will be called the atomic frame, and the cartesian axes in this frame will be denoted by xyz .

III. STATIC INTERACTIONS IN CRYSTALS AND ORIENTED MOLECULES

From Eq. (16) it is evident that the choice of experimental geometry will strongly affect the form of $\Gamma_2(\vec{k}_1, \vec{k}_2, t)$. It is important to choose an optimum geometry in which Γ_2 is sensitive to the molecular parameters of interest. The best choice of geometry is often not obvious, however, particularly when studying a system for which certain structural information is missing. For example, in studying an assembly of molecules with unknown orientation, one would not know the relative orientation of the atomic and laboratory coordinate systems. Thus the angles θ_1 , ϕ_1 , θ_2 , and ϕ_2 would be unknown (although relations among them would be known). Before attacking this complicated case it is useful first to consider the well-known case of a crystalline source.

A. Crystalline Sources

The variety of forms for $\Gamma_2(t)$ that are encompassed by Eq. (16) may easily be displayed by selecting sets of angles $(\theta_1, \phi_1, \theta_2, \phi_2)$ that emphasize oscillations of particular frequencies. The set $(0 \ 0 \ \pi \ \pi)$, which will be called Geometry 1, yields the time-independent result

$$\Gamma_2(t)_1 = 1 \quad (17)$$

In fact it is well known that orientation of either \vec{k}_1 or \vec{k}_2 along the symmetry axis of a static Hamiltonian will yield a $\Gamma_2(t)$ of the "unperturbed" form.⁵

For the set of angles $(\frac{\pi}{2} \ 0 \ \frac{\pi}{2} \ \pi)$, which will be called Geometry 2, the frequency $3\omega_0$ is prominent:

$$\Gamma_2(t)_2 = \frac{1}{4} + \frac{27}{56} \cos \omega_0 t + \frac{15}{56} \cos 3\omega_0 t \quad (18)$$

The intermediate frequency $2\omega_0$ is best displayed in Geometry 3(3'), with angles $(\frac{\pi}{4}, 0 \pm \frac{\pi}{4}, \frac{\pi}{4})$. For these cases

$$\Gamma_2(t)_{3, 3'} = \frac{1}{16} \pm \frac{3\sqrt{2}}{28} \cos \omega_0 t \pm \frac{15\sqrt{2}}{28} \cos 2\omega_0 t \quad (19)$$

Here Geometry 3 takes the + sign, and Geometry 3' the - sign.

In some geometries $\Gamma_2(t)$ vanishes identically. These geometries may be useful for normalization. One such case is described by the angles $(0, \phi_1, \cos^{-1} \sqrt{\frac{1}{3}}, \phi_2)$. For a polycrystalline source, in which the z axes are oriented randomly relative to \vec{k}_1 , the well-known polycrystalline curve⁵ is observed

$$\Gamma_2(t)_{\parallel} = \frac{1}{35} [7 + 13 \cos \omega_0 t + 10 \cos 2\omega_0 t + 5 \cos 3\omega_0 t] \quad (20)$$

Here the \parallel sign denotes parallel geometry, in which $\vec{k}_1 = -\vec{k}_2$. This result is easily obtained by general methods,⁵⁻⁷ or it can be derived from Eq. (16) by ensemble-averaging over the angles under the constraints $\theta_2 = \pi - \theta_1$, $\phi_2 = \phi_1 + \pi$. The polycrystalline response function, together with those for Geometries 1-3, is plotted in Fig. 3.

B. Oriented Molecules

Let us now consider a sample of macromolecules labeled with rotational tracers. If the molecules are randomly oriented, $\Gamma_2(t)$ will be described by Eq. (20), and there is nothing more to be said about static interactions. However, if the molecules are oriented preferentially along some direction in space, the observed perturbation coefficients can be very informative. To

explore this problem systematically, let us define a molecular coordinate frame with cartesian axes XYZ and an orientation direction \vec{E} . The methods by which macromolecules can be oriented will not be discussed, but it will be assumed that the direction \vec{E} is known relative to the laboratory frame (\vec{E} could be the direction of an electric field, for example).

In the single-crystal case the two "parallel" geometries--Geometries 1 and 2--yielded response functions that suffice to describe the static interactions. A similar result holds for oriented macromolecules, but now the detector positions must be defined in terms of the symmetry axis of the ensemble, namely \vec{E} . The two geometries are thus defined by

$$\vec{E} \parallel \vec{k}_1 = -\vec{k}_2 \quad (\text{Geometry 1'}) ,$$

$$\vec{E} \perp \vec{k}_1 = -\vec{k}_2 \quad (\text{Geometry 2'}) . \quad (21)$$

This choice of geometry has a theoretical advantage because calculations of $\Gamma_2(t)$ are relatively simple at symmetry points of the system. An experimental advantage is that the two geometries may be interchanged without moving the detectors, facilitating normalization. Two practical advantages are: 1) The measured effect is maximized, and $\Gamma_2(0) = 1$ for both geometries, and 2) If the direction \vec{E} is in doubt it may be determined efficiently with parallel geometries.

Any static orientation mechanism can be described by an orientation Hamiltonian \mathcal{H} . The observable average of a quantity such as $\Gamma_2(t)$ is just its canonical average over the stationary states of \mathcal{H} . These states may be described, for the purpose of calculating $\Gamma_2(t)$, by specifying the relative orientations of

\vec{E} , the molecular frame (XYZ), and the atomic frame (xyz), as well as the quadrupole frequency ω_0 . It is sometimes necessary in addition to average \vec{k}_1 and \vec{k}_2 over an angle of rotation about \vec{E} and \vec{Z} . This kind of average will be denoted by a single bar, i.e., $\bar{\Gamma}_2(t)$. It is made over states that are energetically equivalent but differently related to \vec{k}_1 and \vec{k}_2 . The subsequent canonical average over states of different energies,

$$\bar{\bar{\Gamma}}_2(t) = Q^{-1} \sum_i \bar{\Gamma}_2(\epsilon_i, t) P(E_i) \quad ,$$

where $P(E_i)$ denotes the probability of the system having energy ϵ_i and Q the partition function, will not be considered further in this paper. The evaluation of $\bar{\bar{\Gamma}}_2(t)$ from $\bar{\Gamma}_2(t)$ is straightforward if \mathcal{H} is known.

In the derivation of Eq. (16) the electric-field-gradient tensor was assumed to be cylindrically symmetrical with z as the symmetry axis. In the discussion below a similar assumption will be made about the macromolecules. Specifically, it will be assumed that the energy of the system is essentially invariant to rotations about a single molecular axis, the Z axis. This will be taken in Sec. II, as the axis about which rotational relaxation is fastest. Thus the following discussion is most readily applicable to rodlike, or perhaps disklike, molecules. This set of assumptions was selected as representing the most important single example. For other sets of assumptions the methods for evaluation of $\bar{\Gamma}_2(t)$ would be similar to those given below.

To evaluate $\bar{\Gamma}_2(t)$ for either geometry (1' or 2') the relative orientations of the four vectors \vec{E} , Z , \vec{z} , and \vec{k}_1 must be specified, and angular averages must be taken where appropriate. For a given labeled molecular species

and confirmation there is a fixed angle β between \vec{z} and \vec{Z} , and in a given state \vec{Z} makes an angle δ with \vec{E} . In Geometry 1', represented in Fig. 4, \vec{k}_1 and \vec{E} are parallel, and the angle of rotation of \vec{z} about \vec{Z} (the angle γ in Fig. 4) completes the description of the stationary state that is necessary for calculating $\bar{\Gamma}_2(t)$. It remains only to express θ_1 , ϕ_1 , θ_2 , and ϕ_2 in terms of β , γ , and δ in Eq. (16) and to average over γ . In fact $\phi_2 = \phi_1 + \pi$; thus the factors $\cos(\phi_2 - \phi_1)$ and $\cos 2(\phi_2 - \phi_1)$ can be replaced forthwith by their values of -1 and +1, respectively. In averaging over θ_1 and θ_2 the relation $\theta_1 + \theta_2 = \pi$ must be retained. Thus

$$\begin{aligned} \overline{\cos^2 \theta_2} &= \overline{\cos^2 \theta_1} \quad , \\ \overline{\cos^2 \theta_1 \cos^2 \theta_2} &= \overline{\cos^4 \theta_1} \quad , \\ \overline{\sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2} &= \overline{\cos^4 \theta_1} - \overline{\cos^2 \theta_1} \quad . \end{aligned} \quad (22)$$

The cosine law gives

$$\cos \theta_1 = \cos \beta \cos \delta + \sin \beta \sin \delta \cos \gamma \quad . \quad (23)$$

After Eqs. (16), (22), and (23) are combined and the average over γ taken, the perturbation factor for geometry 1' is

$$\begin{aligned} \Gamma_2(t)_{1'} &= \frac{9}{4} C^2 + \frac{27}{4} CS + \frac{27}{32} S^2 - \frac{3}{2} C - \frac{3}{4} S + \frac{1}{4} \\ &+ [-3C^2 - 9CS - \frac{9}{8} S^2 + 3C + \frac{3}{2} S] [\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t] \\ &+ [\frac{3}{4} C^2 + \frac{9}{4} CS + \frac{9}{32} S^2 - \frac{3}{2} C - \frac{3}{4} S + \frac{3}{4}] [\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t]. \end{aligned} \quad (24)$$

Here $C = \cos^2 \beta \cos^2 \delta$ and $S = \sin^2 \beta \sin^2 \delta$.

In Geometry 2' \vec{k}_1 is perpendicular to \vec{E} , and specification of the relative orientation of \vec{k}_1 and \vec{z} involves an additional azimuthal angle η and a polar angle ϵ that relates \vec{z} to \vec{E} , as shown in Fig. 5. From the cosine law

$$\cos \theta_1 = \sin \epsilon \cos \eta$$

$$\cos \epsilon = \cos \beta \cos \delta + \sin \beta \sin \delta \cos \gamma \quad . \quad (25)$$

Except for the additional average taken over η , the calculation of $\bar{\Gamma}_2(t)_2$ is similar to that for $\bar{\Gamma}_2(t)_1$. The result is

$$\begin{aligned} \bar{\Gamma}_2(t)_2 = & \frac{27}{32} C^2 + \frac{81}{32} CS + \frac{81}{256} S^2 - \frac{15}{16} C - \frac{15}{32} S + \frac{11}{32} \\ & + \left[-\frac{9}{8} C^2 - \frac{27}{8} CS - \frac{27}{64} S^2 + \frac{3}{4} C + \frac{3}{8} S + \frac{3}{8} \right] \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ & + \left[\frac{9}{32} C^2 + \frac{27}{32} CS + \frac{27}{256} S^2 + \frac{3}{16} C + \frac{3}{32} S + \frac{9}{32} \right] \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right]. \quad (26) \end{aligned}$$

Again $C = \cos^2 \beta \cos^2 \delta$ and $S = \sin^2 \beta \sin^2 \delta$.

The sensitivity of $\bar{\Gamma}_2(t)$ to molecular geometry and orientation is best illustrated by example. Let us consider the four cases that can be constructed with the macromolecules oriented parallel or perpendicular to \vec{E} and the electric-field-gradient axis parallel or perpendicular to the molecular symmetry axis. These will be denoted

Case I: $\vec{E} \parallel \vec{Z} \parallel \vec{z}$

Case II: $\vec{E} \parallel \vec{Z} \perp \vec{z}$

Case III: $\vec{E} \perp \vec{Z} \parallel \vec{z}$

Case IV: $\vec{E} \perp \vec{Z} \perp \vec{z}$

By combining these four cases with Geometries 1' and 2' a total of eight configurations can be constructed. These are designated by the notation I1', I2', etc. The angles describing these eight configurations are set out in Table I.

The dependence of $\bar{\Gamma}_2(t)$ on β and δ in Eqs. (24) and (26) only through even powers of $\cos \beta \cos \delta$ and $\sin \beta \sin \delta$ portends considerable symmetry in $\bar{\Gamma}_2(t)$. This expectation is realized in the eight configurations I1' - IV2', which yield only four distinct curves. These curves, labeled A, B, C, and D, have the forms

$$\bar{\Gamma}_2(t)_A = 1$$

$$\bar{\Gamma}_2(t)_B = \frac{1}{4} + \frac{27}{56} \cos \omega_0 t + \frac{15}{56} \cos 3\omega_0 t$$

$$\bar{\Gamma}_2(t)_C = \frac{11}{32} + \frac{129}{448} \cos \omega_0 t + \frac{15}{56} \cos 2\omega_0 t + \frac{45}{448} \cos 3\omega_0 t$$

$$\bar{\Gamma}_2(t)_D = \frac{49}{256} + \frac{1443}{3584} \cos \omega_0 t + \frac{15}{64} \cos 2\omega_0 t + \frac{615}{3584} \cos 3\omega_0 t \quad (27)$$

These four curves A - D are distributed among configurations I1' - IV2' as indicated in the last column of Table I. They are plotted in Fig. 6 for intercomparison and for comparison with the single-crystal results shown in Fig. 3. In assessing the diagnostic value of $\Gamma_2(t)$, we note that either Geometry, 1' or 2', would suffice to distinguish among Cases I, Cases II or III, and Case IV, but that II and III are undistinguishable because of the $\beta - \delta$ symmetry in Eqs. (24) and (26).

A more general case of some practical importance, which will be called Case V, is encountered when the molecules are completely oriented along \vec{E} (i.e., $\delta = 0$) and the electric-field-gradient axis \vec{z} makes an arbitrary angle β with the molecular symmetry axis \vec{Z} . The response functions are

$$\begin{aligned} \bar{\Gamma}_2(t)_{V1} &= \frac{1}{4} [3 \cos^2 \beta - 1]^2 + \frac{3}{4} \sin^2 2\beta \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ &\quad + \frac{3}{4} \sin^4 \beta \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \\ \bar{\Gamma}_2(t)_{V2} &= \frac{27}{32} \sin^4 \beta + \frac{3}{4} \sin^2 \beta + \frac{1}{4} \\ &\quad + \left[\frac{3}{2} \sin^2 \beta - \frac{9}{8} \sin^4 \beta \right] \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ &\quad + \left[\frac{3}{4} - \frac{3}{4} \sin^2 \beta + \frac{9}{32} \sin^4 \beta \right] \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \quad . \quad (28) \end{aligned}$$

The high sensitivity of $\bar{\Gamma}_2(t)_{V1}$, and $\bar{\Gamma}_2(t)_{V2}$, to the angle β can easily be appreciated by referring to Fig. 6. As β is increased from 0 to $\pi/2$, $\bar{\Gamma}_2(t)_{V1}$, changes continuously from Curve A to Curve B, while $\bar{\Gamma}_2(t)_{V2}$, changes from Curve B to Curve C.

Let us examine the sensitivity of $\bar{\Gamma}_2(t)$ to the degree of molecular orientation, for arbitrary β . If the molecules are randomly oriented, evaluation of the angular averages $\cos^2 \delta$, $\sin^2 \delta$, etc., in Eqs. (24) and (26) leads to the expected random result, Eq. (21), for both geometries. Together with Eq. (28), describing $\bar{\Gamma}_2(t)$ for a completely oriented system, this suggests that for a wide range of values of β , $\bar{\Gamma}_2(t)$ would be a sensitive indicator of molecular orientation. As the molecules in a given experiment become oriented, the observed

$\bar{\Gamma}_2(t)$ will vary continuously from the random result, Eq. (21), to $\bar{\Gamma}_2(t)_{V1',2'}$, Eq. (28). For the extreme cases $\beta = 0$ (Case I) or $\beta = \pi/2$ (Case II), this variation is very striking, with $\bar{\Gamma}_2(t)_1$, and $\bar{\Gamma}_2(t)_2$, for the completely oriented systems following Curves A and B for $\beta = 0$ and Curves B and C for $\beta = \pi/2$. Systems with intermediate β values will show less sensitivity to orientation, although any value of β will yield some variation in $\bar{\Gamma}_2(t)_1$, or $\bar{\Gamma}_2(t)_2$, with orientation.

This discussion has shown that $\bar{\Gamma}_2(t)$ has considerable sensitivity as a diagnostic tool in studying the static properties and orientation of macromolecules labeled with rotational tracers. At the same time the symmetry of $\bar{\Gamma}_2(t)$ in the angles β and δ limited this sensitivity. Much of this symmetry is removed, and the sensitivity of $\bar{\Gamma}_2(t)$ is consequently enhanced, if dynamic properties are considered, as discussed below.

IV. RELAXATION IN THE CLASSICAL LIMIT

In angular correlation studies relaxation is observed "directly" as decay of the response function $\bar{\Gamma}_\lambda(t)$ in time, rather than as a broadening of spectral lines. In principle these two manifestations of relaxation are equivalent, being related by a Fourier transformation.

Several theoretical discussions of the effect of relaxation on angular correlations. Abragam and Pound⁶ considered weak random perturbations and found that $\bar{\Gamma}_\lambda(t)$ decays exponentially. For strong perturbations, Dillenburg and Maris¹³ predicted multiexponential decay. Recently Gabriel¹⁴ has developed the formalism for a non-Markoffian theory. These approaches are all quantum-mechanical in nature. A quantum-mechanical description of relaxation is necessary when the rotational correlation time is short compared with the reciprocal interaction frequency, i.e., $\omega_0\tau_c \ll 1$. For ¹¹¹Cd in complexes and small molecules this condition obtains:^{2,3} ω_0 is in the 10^8 Hz range, while τ_c may be 10^{-10} sec or less. In macromolecules, however, the opposite situation, $\omega_0\tau_c \gg 1$, is often to be expected, and for this situation a simple classical approach, given below, is simpler and more appropriate.

Let us consider a rotational tracer atom that is bound in a rigid macromolecule in such a way as to be effectively shielded from the environment. The tracer nucleus is subject to two interactions, the static quadrupole interaction and relaxation caused by solvent-macromolecule collisions. However, since each collision induces only a very small rotation in the macromolecule, their combined effect on the tracer site is a random rotation of the coordinate frame. If this rotation is slow compared to the frequencies associated with the static interaction (i.e., if $\omega_0\tau_c \gg 1$), then the nucleus can follow adiabatically. We may

therefore write a formal expression for the ensemble average $\bar{\Gamma}_2(t)$ in the presence of relaxation as

$$\bar{\Gamma}_2(t) = \int_{\Omega'} \int_{\Omega} P(\theta_2 \phi_2) C(\theta_2, \phi_2; \theta_2'(t), \phi_2'(t)) \Gamma_2(\theta_2', \phi_2', t) d\Omega d\Omega' . \quad (28)$$

Here $\Gamma_2(\theta_2', \phi_2', t)$ is given by Eq. (16) (with $\theta_2' \phi_2'$ in place of $\theta_2 \phi_2$), $P(\theta_2 \phi_2)$ is the probability of finding $\vec{k}_2(t=0)$, a vector directed toward the second detector, initially at angles θ_2 and ϕ_2 in the atomic frame. The correlation function $C(\theta_2, \phi_2; \theta_2'(t), \phi_2'(t))$ expresses the compound probability that the z axis (in the atomic system) will move in time t to an orientation such that $\vec{k}_2(t)$ is at angles θ_2', ϕ_2' . Thus $P(\theta_2 \phi_2)$ depends on the geometry of the experiment, including molecular geometry (e.g., the angles β, γ, δ , and η), $C(\theta_2, \phi_2; \theta_2'(t), \phi_2'(t))$ contains the dynamics as well as being geometry-sensitive, and $\Gamma_2(\theta_2', \phi_2', t)$ describes the static perturbations. The adiabaticity of this model is manifest in the dependence of $C(\theta_2, \phi_2; \theta_2'(t), \phi_2'(t))$ on angles rather than on spin operators.

As written above Eq. (28) is of formal interest only, because it contains no actual mechanism for relaxation. Such a mechanism is discussed below for the cylindrical molecules treated in Sec. III.

Let us assume that the rotational motion of the molecules is characterized by fast relaxation about their Z axes and slow relaxation of the Z-axial direction. If the time scales of the two modes of relaxation are sufficiently different that they may be taken as separable, the function $C(\theta_2, \phi_2; \theta_2'(t), \phi_2'(t))$ may be replaced by the product $F(\alpha, t) S(\theta, \phi, t)$, where $F(\alpha, t)$ and $S(\theta, \phi, t)$ describe the fast and slow relaxation, respectively.

The angles θ and ϕ in $S(\theta, \phi, t)$ give the orientation of \vec{Z} with respect to the orientation axis \vec{E} . The slow component of relaxation will not be discussed in detail.

The angle α in $F(\alpha, t)$ describes the rotation of the atomic frame about Z . Referring to Fig. 5, $\alpha(t)$ may be defined by

$$\alpha(t) = \gamma(t) - \gamma(0) \quad , \quad (29)$$

where $\gamma(t)$ is the value of the angle γ at time t . If $S(\theta, \phi, t)$ varies sufficiently slowly compared to $F(\alpha, t)$, it may be taken as essentially constant, and as having the value unity, during the interval in which fast relaxation takes place. Thus in this interval Eq. (28) can be approximated by

$$\bar{F}_2(t) \cong \int_{\Omega'} \int_{\Omega} P(\theta_2, \phi_2) F(\alpha, t) \Gamma_2[\theta_2'(\alpha), \phi_2'(\alpha), t] d\Omega d\Omega' \quad . \quad (30)$$

Here the dependence of θ_2' and ϕ_2' on α is indicated specifically. Of course θ_2' and ϕ_2' also depend on other angles.

The time-evolution of $\alpha(t)$ can be treated as a random-walk process around the perimeter of a circle. For a macromolecule the step size $\Delta\alpha$ is very small and the number of steps required to produce a substantial angular displacement is very large, because rotation is caused by collisions with small solvent molecules. Thus $F(\alpha, t)$ may be taken as having Gaussian form,

$$F(\alpha, t) = \left(\frac{\tau_c}{4\pi t}\right)^{1/2} e^{-\frac{\tau_c \alpha^2}{4t}} \quad . \quad (31)$$

Here τ_c was chosen as the correlation time of $\cos \alpha(t)$, i.e.,

$$\langle \cos \alpha(0), \cos \alpha(t) \rangle = \int_{-\infty}^{\infty} \cos \alpha F(\alpha, t) d\alpha = e^{-t/\tau_c} \quad (32)$$

The normalization condition is

$$\int_{-\infty}^{\infty} F(\alpha, t) d\alpha = 1 \quad (33)$$

Even with the approximations entailed in Eq. (30), the calculation of $\bar{\Gamma}_2(t)$ when relaxation is present would be very involved. Rather than attacking this problem generally let us evaluate $\Gamma_2(t)$ for some of the specific configurations discussed in Sec. III. The relaxation calculations are relatively simple for these configurations, and the results nicely illustrate the effects of relaxation on the curves in Fig. (6).

In configuration I1', $\theta_1 = \pi - \theta_2 = 0$ and these angles are unaffected by rotation about Z. In fact $\phi_2(t) = \phi_2(0) + \alpha(t)$, but the terms in Eq. (16) that depend on ϕ_2 have vanishing coefficients. Thus there are no observable effects of fast relaxation, and

$$\bar{\Gamma}_2(t)_{I1'} \cong 1 \quad (34)$$

In configuration I2', θ_2 is time-independent in spite of fast relaxation about Z, and the terms in θ_1 and θ_2 can be evaluated immediately. From the relation $\phi_2(t) = \phi_2(0) + \alpha(t)$, Eq. (16) becomes

$$\Gamma_2(t) = \frac{1}{4} + \frac{3}{4} (\cos 2\alpha) \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \quad (35)$$

Integration on $F(\alpha, t)d\alpha$ gives

$$\bar{\Gamma}_2(t)_{I2'} = \frac{1}{4} + \frac{3}{4} e^{-\frac{4t}{\tau_c}} \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \quad (36)$$

Configuration III' gave Curve B in Fig. 6 in the absence of relaxation, as did configuration I2'. With fast relaxation about Z, however, they behave very differently. Neither θ_2 nor ϕ_2 is affected by fast relaxation in about Z in configuration III', and

$$\bar{\Gamma}_2(t)_{III'} = \frac{1}{4} + \frac{27}{56} \cos \omega_0 t + \frac{15}{56} \cos 3\omega_0 t \quad (37)$$

In fact the results for configuration II' and III' are examples of the general rule that relaxation about an axis parallel to \vec{k}_1 or \vec{k}_2 is not observable. This rule is the analogue for dynamic interactions of the well-known rule for static interactions that was mentioned after Eq. (17).

The calculation of fast relation effects for configuration II2' is more involved. The angle θ_2 becomes $\theta_2(t) = \theta_2 + \alpha(t)$, and $\phi_2 - \phi_1$ becomes $\phi_2(t) - \phi_1$. This latter angle presents a special problem because it changes abruptly from 0 to π , and vice-versa, whenever the z or -z axis crosses through the \vec{k}_2 direction. The $\cos^2[\phi_2(t) - \phi_1]$ term is unaffected, but $\cos[\phi_2(t) - \phi_1]$ changes sign abruptly. In fact

$$\cos[\phi_2(t) - \phi_1] = -\text{SIGN}[\sin(\theta_2 + \alpha(t))] \quad .$$

The approximation

$$\cos[\phi_2(t) - \phi_1] \cong -\frac{15\pi}{32} \sin[\theta_2 + \alpha(t)] \quad ,$$

has been used in the calculation below in order to retain the simple analytical procedures used for the other configurations. The normalization factor $\frac{15\pi}{32}$ was introduced to give the correct initial value of $\bar{\Gamma}_2(t)$. After a rather tedious calculation the result for configuration II 2' is

$$\begin{aligned} \bar{\Gamma}_2(t)_{II2'} \cong & \frac{1}{16} + \frac{9}{32} e^{-\frac{4t}{\tau_c}} + \left[\frac{15}{64} e^{-t/\tau_c} + \frac{9}{64} e^{-9t/\tau_c} \right] \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ & + \left[\frac{3}{16} + \frac{3}{32} e^{-\frac{4t}{\tau_c}} \right] \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \end{aligned} \quad (38)$$

This result is of special interest because an oscillatory term of maximum amplitude $\pm 3/16$ remains after fast relaxation is complete, in addition to the constant "fast" hard-core term of magnitude $\frac{1}{16}$. A fast hard-core value of $\frac{1}{4}$ was present for configuration I2' (Eq. (36)), while configurations II' and III' showed no fast relaxation effects. Slow relaxation will always lead to a limiting value $\bar{\Gamma}_2(t \rightarrow \infty) = 0$, provided that the relaxation is unrestricted. Incidentally the limiting values of $\bar{\Gamma}_2(t)$ are easily checked. For $t = 0$ (or $\tau_c = \infty$), Eqs. (36) and (37) must reduce to Curve B and Eq. (38) to Curve C. The limiting values after fast relaxation are obtained by taking uncorrelated averages of θ_1, θ_2 , etc., within the constraints set by each configuration. Thus for configuration II2', $(3 \cos^2 \theta_1 - 1)(3 \cos^2 \theta_2 - 1) = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right) = \frac{1}{4}$, etc.

The sensitivity of these relaxation curves to the experimental configuration is striking. This sensitivity is illustrated by Cases II and III, for which $\bar{\Gamma}_2(t)$ was identical in the absence of relaxation (Table I). The expressions for $\bar{\Gamma}_2(t)_{III'}$, and $\bar{\Gamma}_2(t)_{II2'}$, in the presence of fast relaxation are given above. The two configurations I2' and IIII' will give identical forms of $\bar{\Gamma}_2(t)$ even in the presence of fast relaxation, because they are related by a rotation

of the entire system. (The same is true of configurations II2' and IV1'.) Thus $\bar{\Gamma}_2(t)_{\text{IIII1}}$, is given by Eq. (36). Finally, $\bar{\Gamma}_2(t)_{\text{IIII2}}$, is easily calculated since only $\phi_2 - \phi_1$ is affected by fast relaxation (it is also necessary to average over θ_1). The result is

$$\begin{aligned} \bar{\Gamma}_2(t)_{\text{IIII2}} = & \frac{11}{32} + \frac{3}{8} e^{-t/\tau_c} \left[\frac{2}{7} \cos \omega_0 t + \frac{5}{7} \cos 2\omega_0 t \right] \\ & + \frac{9}{32} e^{-\frac{4t}{\tau_c}} \left[\frac{9}{14} \cos \omega_0 t + \frac{5}{14} \cos 3\omega_0 t \right] \quad . \end{aligned} \quad (39)$$

The fast relaxation curves $\bar{\Gamma}_2(t)$ for Cases II and III are plotted in Fig. 7. Their diagnostic value is obvious. With fast relaxation these two cases give very different results, whereas with only static interactions they were undistinguishable.

Little generalization is possible on the basis of the few configurations studied above. However, it is clear that in some instances angular-correlation studies of relaxation in rotationally-labeled macromolecules can yield information about the molecular geometry at the binding site (specifically ω_0 and the angle β) and about the molecular orientation, as well as elucidating the dynamical behavior itself.

V. CONCLUSIONS AND OUTLOOK

It has been shown that, for a particular set of circumstances, rotational tracer studies should yield results that are sensitive to molecular geometry. In addition, this technique should prove to be a good indicator of molecular orientation. In fact it is an absolute indicator of orientation, because angular correlation theory is rigorous. Finally, the response function measured in rotational tracer experiments is sensitive to the dynamic properties of molecules. In favorable cases it may be possible to study molecular dynamics in some detail. For example, different relaxation rates about different axes would yield results that could be calculated by a straightforward extension of the methods used in Sec. IV. These features of rotational tracers are especially interesting because of the possibility of in vivo studies and other biological applications. It is not difficult, for instance, to think of biologically interesting problems for which a knowledge of molecular orientation is pertinent. Let us therefore examine briefly the range of validity of the results obtained in Secs. III and IV.

First, although the above results were obtained explicitly for a nuclear level with spin $5/2$, similar calculations could just as easily have been done with any other spin (a spin $I \geq 1$ is required for quadrupole interactions). The restriction $\lambda_{\max} = 2$ presents no real problem either: the appropriate combination of $A_{\lambda_1}(1)$ and $A_{\lambda_2}(2)$ could if necessary be determined in auxiliary experiments. The restriction to axial symmetry in the electric field gradient was made to simplify the calculation. With an asymmetric field gradient, $\bar{\Gamma}_2(t)$ would be oscillatory but aperiodic. The calculations are more involved but the results are qualitatively similar. The criterion $\omega_0 \tau_c \gg 1$ that is necessary

if the classical relaxation model is to be valid will often not be met, but other theoretical approaches^{6,13,14} can be used, and the resulting relaxation curves should not be grossly different. Thus none of the restrictions made for the derivations given in Secs. III and IV are qualitatively serious: if different assumptions were made, the resulting curves would be different, but similar.

Finally, however, two problems that could seriously affect the usefulness of rotational tracers can be conveniently discussed in connection with the above curves. First, the nuclear lifetime τ_N , together with other experimental parameters, will usually limit the number of cycles that can be observed in a practical experiment to no more than 5-10, and often less. More serious is the problem of the uniqueness of the quadrupole coupling constant. Even if the electric field gradient tensor is asymmetric, which is highly probable at the binding site of a macromolecule, the response function $\bar{\Gamma}_2(t)$ can exhibit large (albeit aperiodic) oscillations, because the interactions are temporally coherent in the ensemble (with all systems referred to the same time origin $t = 0$ by γ_1). This coherence is lost, however, when there is a distribution of quadrupole frequencies at the binding site. A distribution is often expected: it could arise, for example, from small conformational changes in neighboring functional groups. The resultant "inhomogeneous broadening" leads to a decay in $\bar{\Gamma}_2(t)$ that could (but should not) be mistaken for relaxation. Two features that distinguish this broadening from relaxation are: (1) With inhomogeneous broadening, the maxima and minima in $\bar{\Gamma}_2(t)$ will broaden as t increases. Relaxation leaves the widths of these features unchanged. (2) With only static interactions, $\bar{\Gamma}_2(t)$ tends to a finite hard-core value. Even if these two differences enable one to distinguish

relaxation from inhomogeneous broadening, however, the latter may still modify $\bar{\Gamma}_2(t)$ enough to result in considerable loss of information.

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FOOTNOTES AND REFERENCES

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Table I. Classification of the Configurations

Configuration	β	δ	θ_1	Static Curve	Dynamic Curve ^a
I 1'	0	0	0	A	Eq. (34)
I 2'	0	0	$\pi/2$	B	Eq. (36)
II 1'	$\pi/2$	0	$\pi/2$	B	Eq. (37)
II 2'	$\pi/2$	0	$0-\pi$	C	Eq. (38) ^c
III 1'	0	$\pi/2$	$\pi/2$	B	Eq. (36)
III 2'	0	$\pi/2$	$0-\pi$	C	Eq. (39)
IV 1'	$\pi/2$	$\pi/2$	$0-\pi$	C	Eq. (38) ^c
IV 2'	$\pi/2$	$\pi/2$	$0-\pi$ ^b	D	--
V 1'	any	0	β	Eq. (28)	--
V 2'	any	0	$\frac{\pi}{2}-\beta$	Eq. (28)	--

^aFast component only.

^bAveraged around both \vec{E} and \vec{Z} .

^cApproximate. See text.

FIGURE CAPTIONS

Fig. 1. Typical nuclear level diagram for angular correlation experiment. Substates of intermediate level are shown schematically. The notation is explained in text.

Fig. 2. Relations of the γ -ray propagation directions \vec{k}_1 and \vec{k}_2 to the atomic frame, in which the \vec{z} direction is taken along the symmetry axis of the electric field gradient tensor.

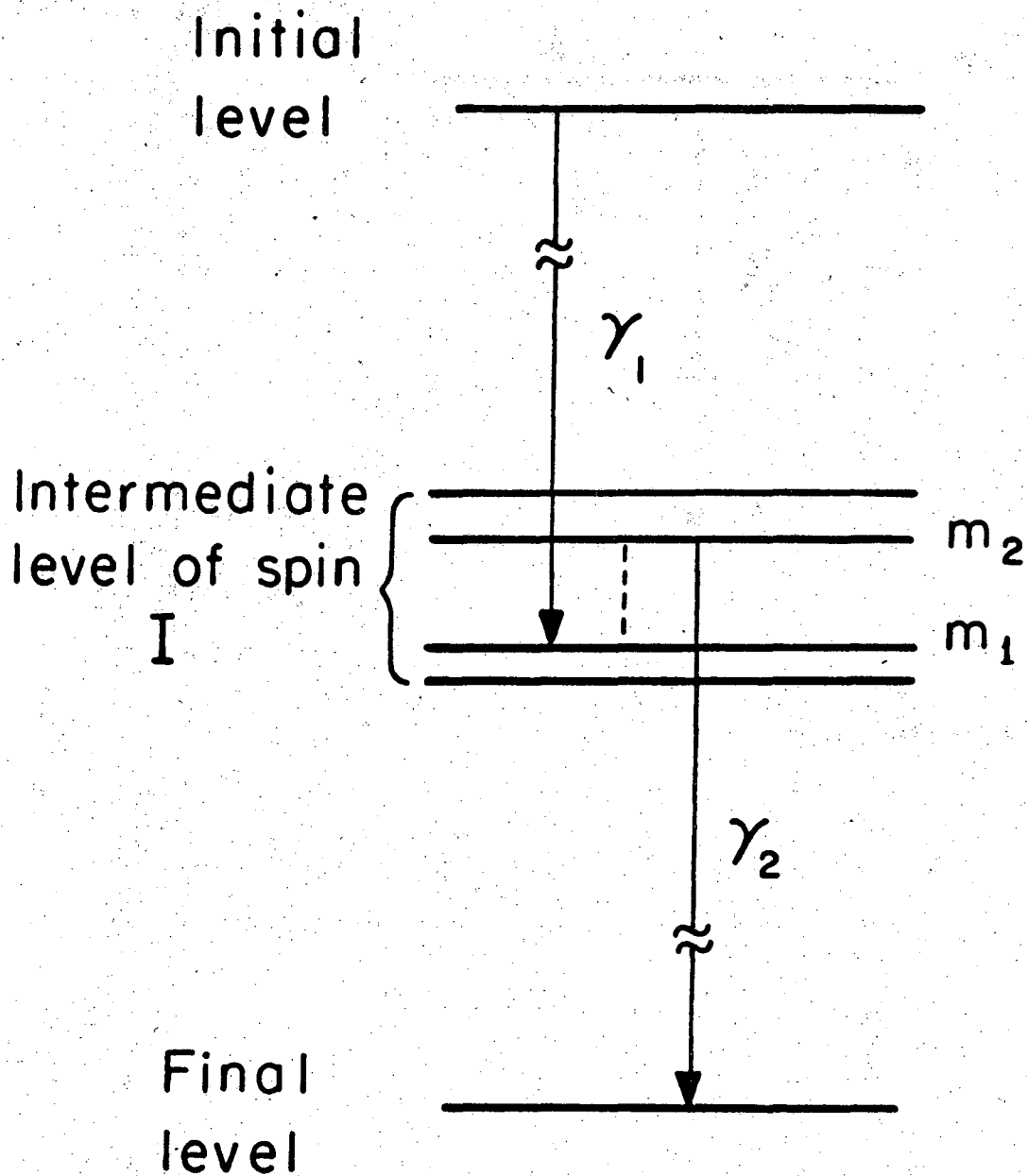
Fig. 3. Response functions $\Gamma_2(t)$ for crystals, using Geometries 1-3, and for a polycrystalline source (random geometry). In each case $I = 5/2$ and the electric field gradient has axial symmetry.

Fig. 4. Orientation of vectors in Geometry 1'.

Fig. 5. Orientation of vectors in Geometry 2'.

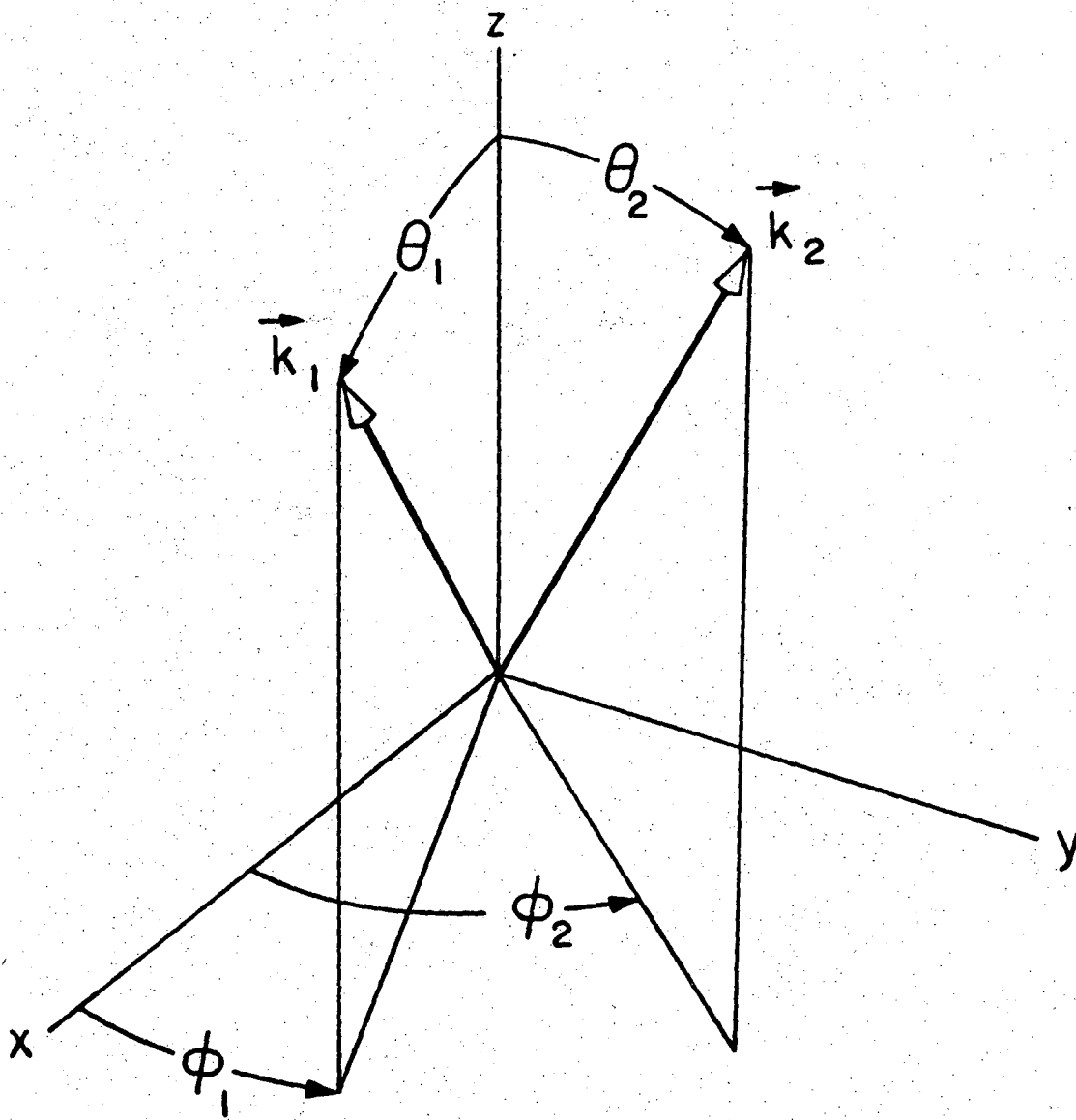
Fig. 6. The four curves for static interactions, in oriented molecules, for Cases I - IV and Geometries 1' and 2'. The nuclear spin is taken as $5/2$, and the electric field gradient has axial symmetry.

Fig. 7. Calculated response functions for oriented macromolecules in the presence of fast relaxation. See Table I and text.



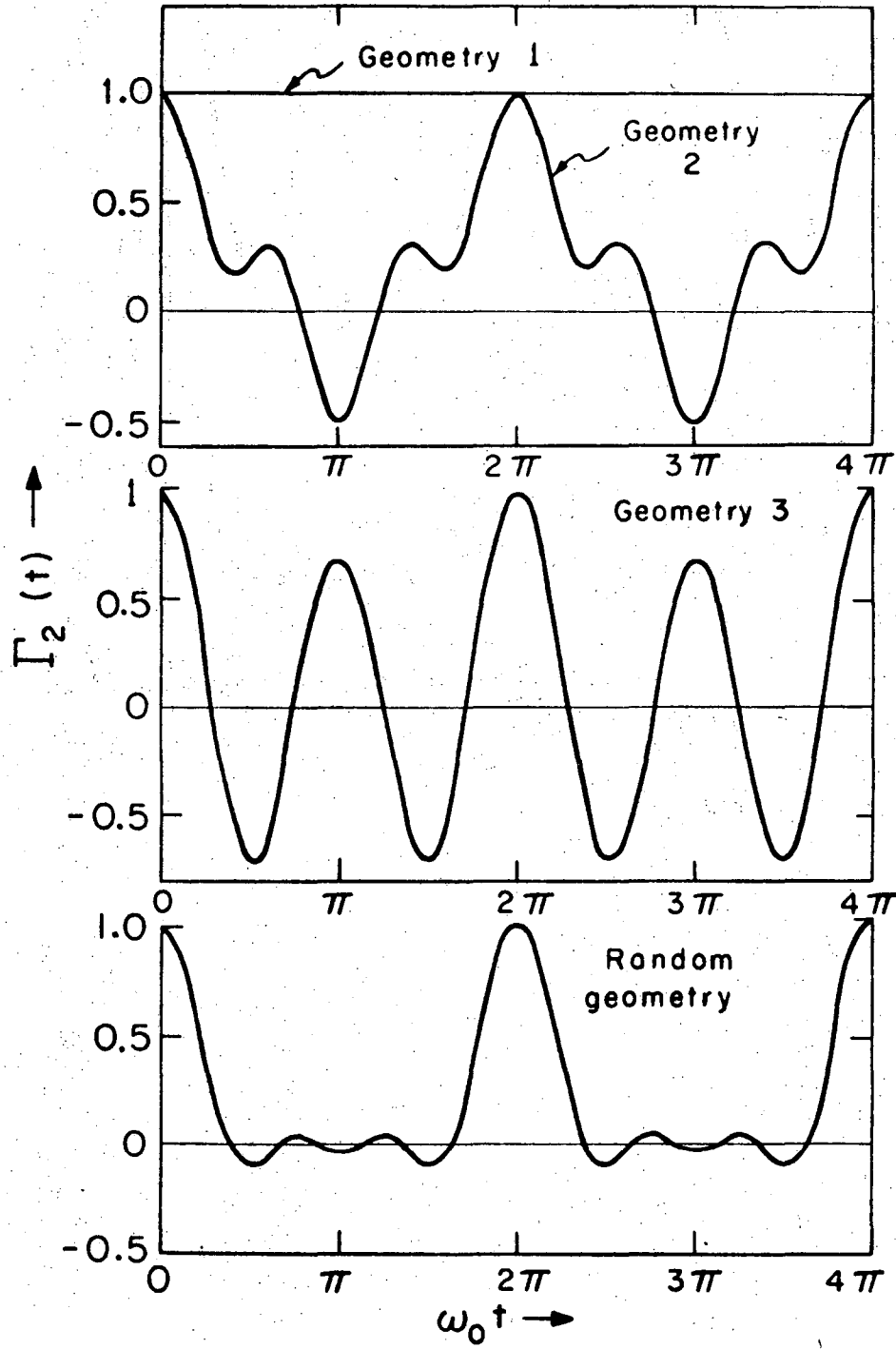
XBL7011-4154

Fig. 1



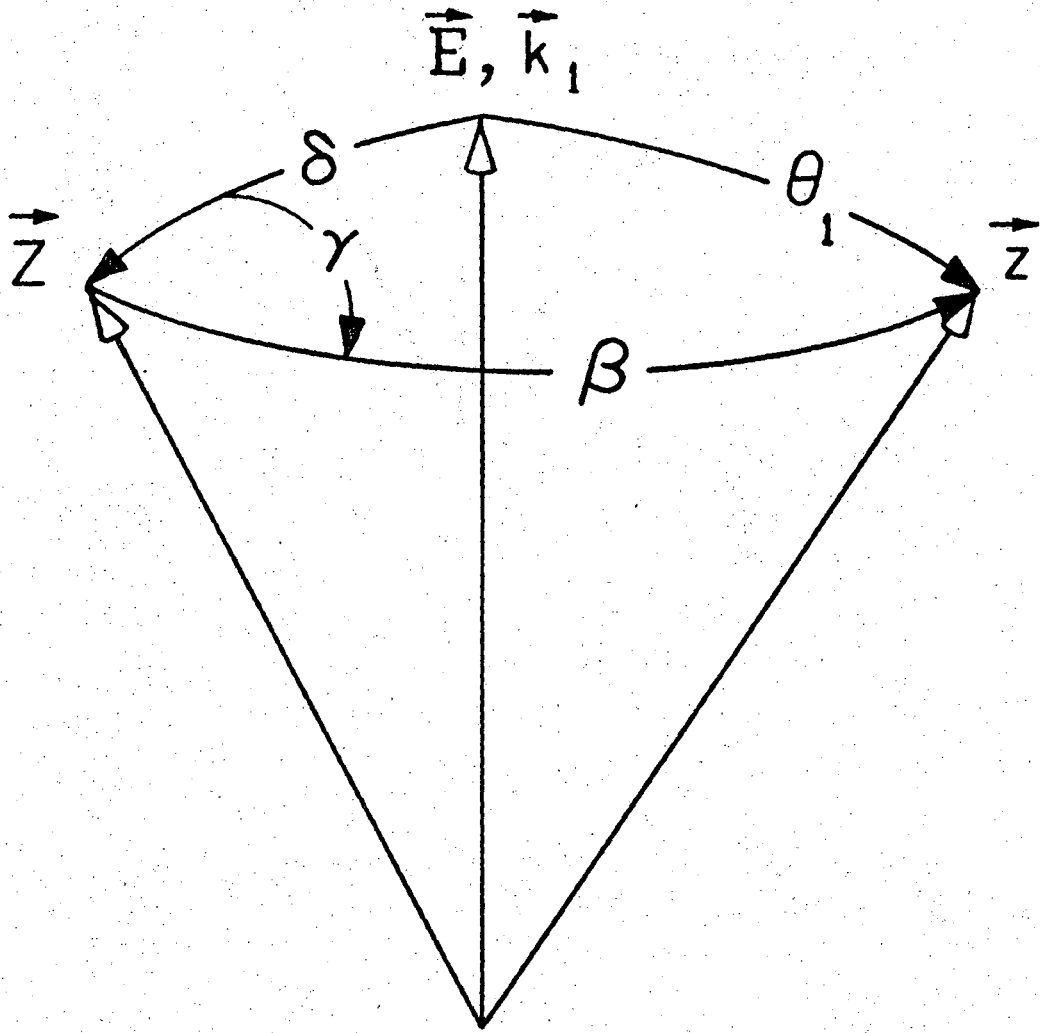
XBL7011-4153

Fig. 2



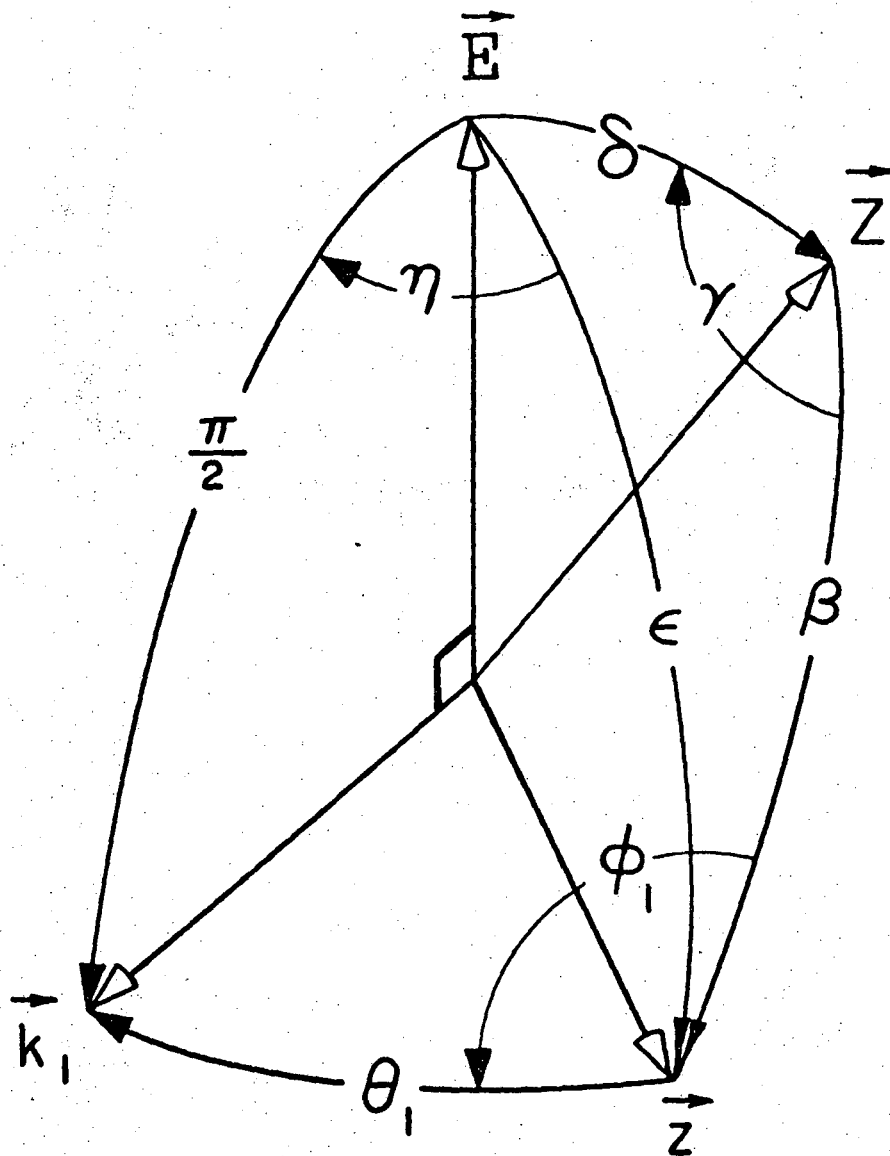
XBL7011-4150

Fig. 3



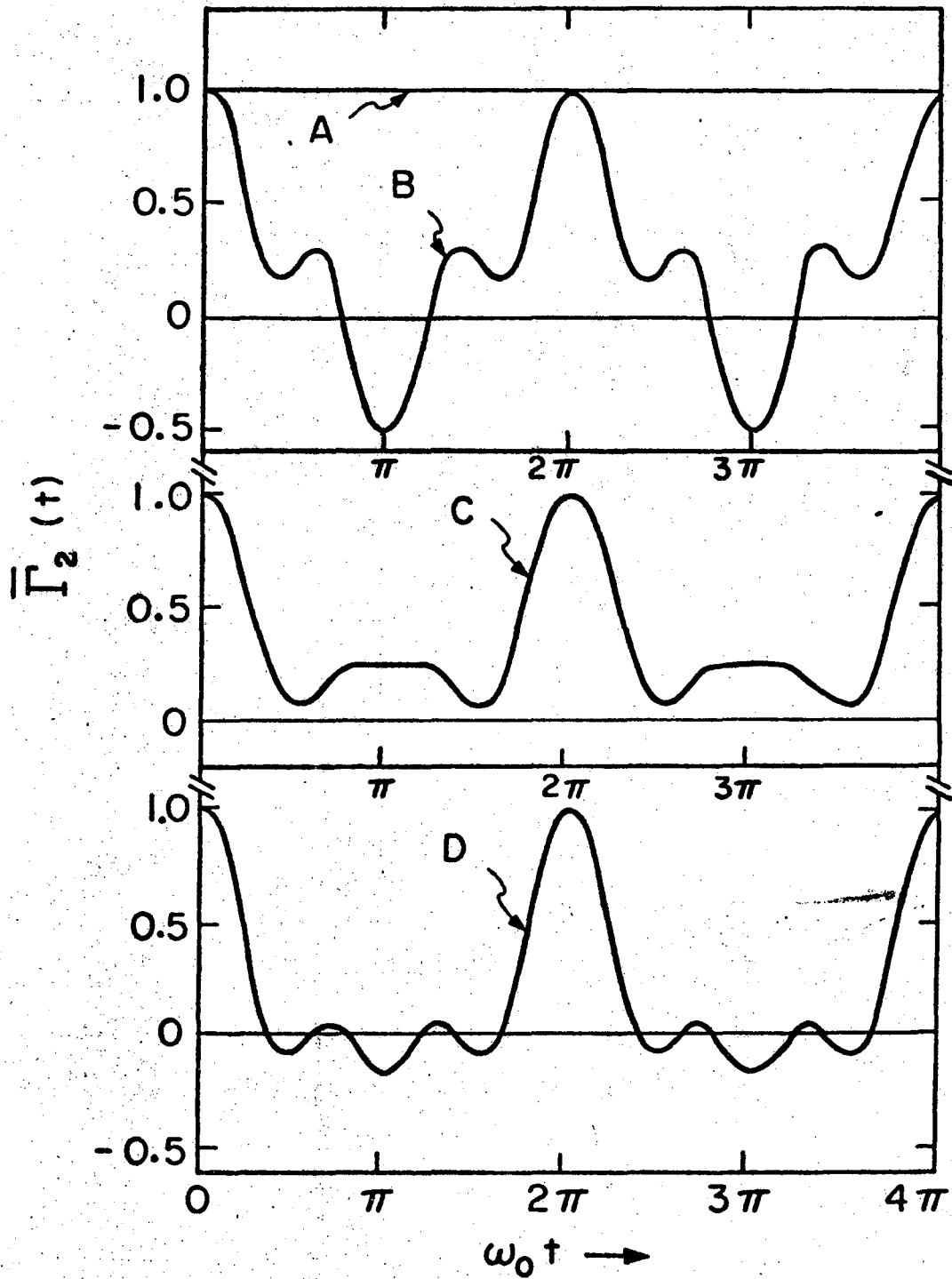
XL7011-4147

Fig. 4



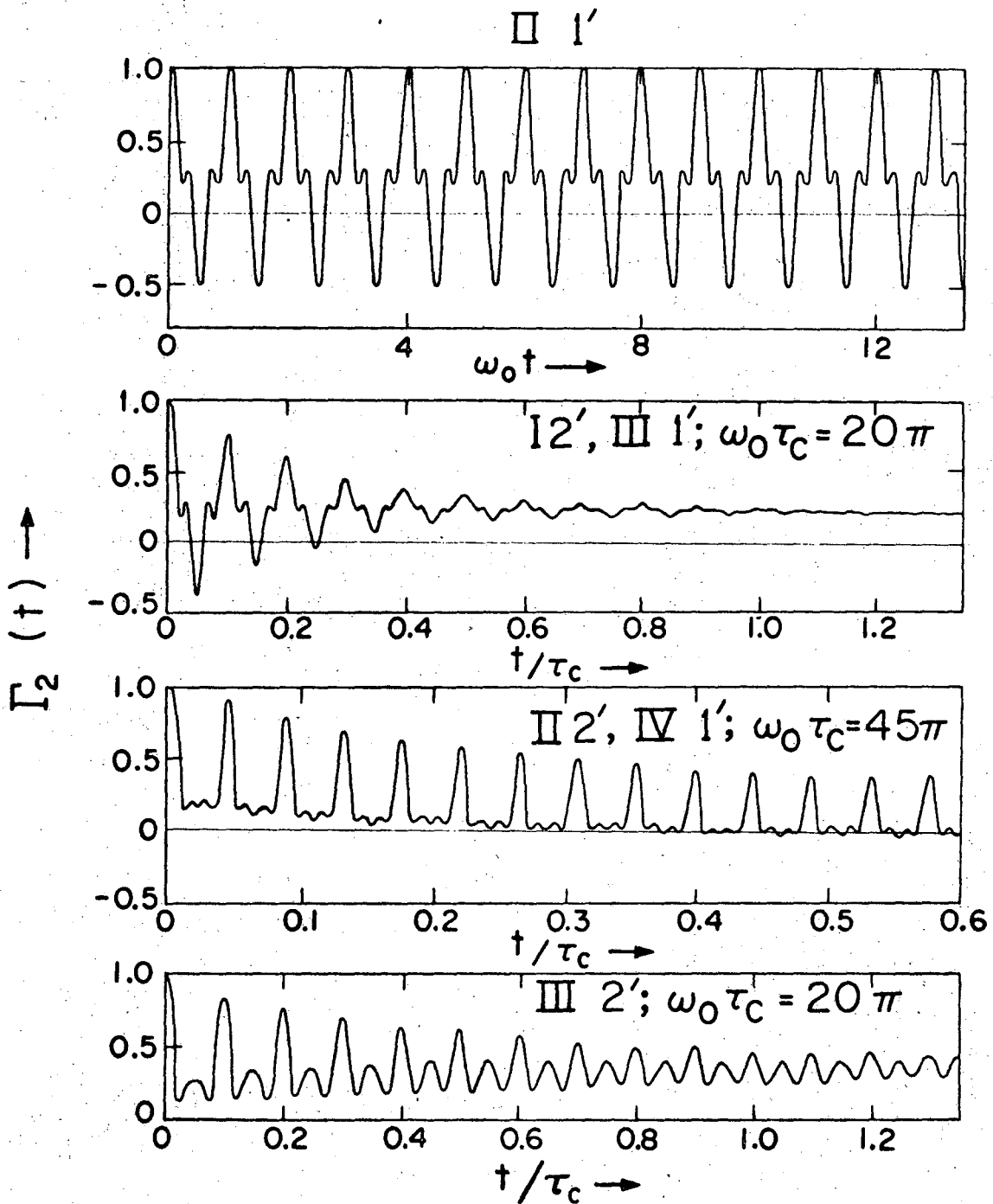
XBL 7011-4148

Fig. 5



XBL7011-4151

Fig. 6



XBL7011-4149

Fig. 7

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