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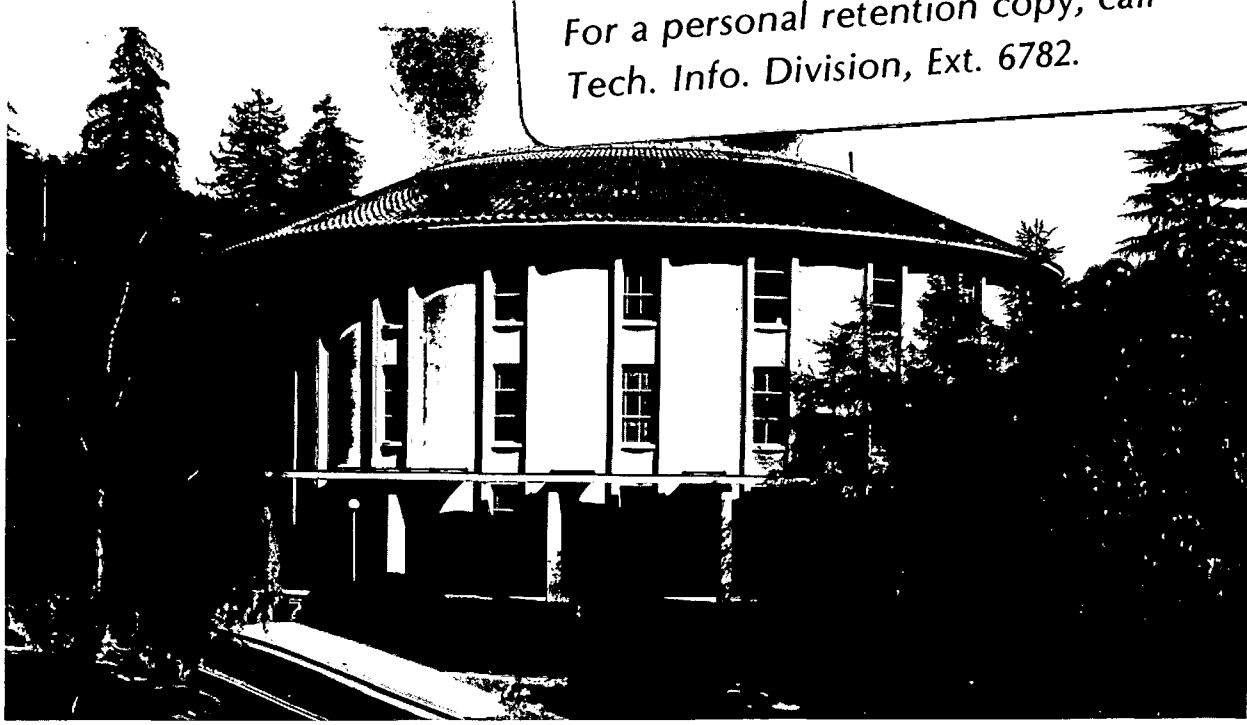

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CIRCULAR INTENSITY DIFFERENTIAL SCATTERING OF LIGHT

IV. RANDOMLY ORIENTED SPECIES.

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ABSTRACT

The theory of circular intensity differential scattering (CIDS) of light by a solution of randomly oriented molecules of arbitrary geometry has been derived. The molecules are treated as a set of polarizing tensors. The CIDS as a function of scattering angle is obtained in closed form. The CIDS depends on the distances and angle between all the polarizabilities in the molecule. Numerical calculations of helices made up of uni-axial polarizabilities, directed along the tangent to the helix, are shown as a function of helical geometry. The calculated values of the CIDS indicate that they should provide a useful, new experimental technique to determine the structures of biomolecular aggregates.

INTRODUCTION

The theory of the circular intensity differential scattering (CIDS) of oriented chiral molecules has been published recently.[1-4] Measurement of the CIDS as a function of scattering angle can give structural information about chiral macromolecular systems. The CID scattering patterns contain more detail and information than the corresponding total scattering patterns; the sign of the CIDS signal is directly related to the handedness of the chiral scatterer. While the traditional chiroptical methods, such as circular dichroism and optical rotatory dispersion give information about the short range structure of the optically active species (less than approximately 20Å), the CIDS contains structural information about molecular dimensions of the order of the wavelength of light used in the scattering experiment. CIDS is not restricted to wavelengths of light within the absorption band of the chromophores in the scatterers; different wavelengths can thus probe different critical dimensions in the macromolecules.

In this paper we will consider the case of randomly oriented molecules. A molecule is represented by an arbitrary set of polarizability tensors, and the scattering pattern is averaged over all orientations of the molecule. The organization of the paper is as follows: In part I the spatial averagings of the CIDS equations will be presented, in part II the resulting expressions will be applied to a helical scatterer, and in part III, numerical computations of the CIDS vs. the scattering angle will be presented.

I. The Spatial Averaging of CIDS Equations.

The circular intensity differential scattering (CIDS) is defined by:[5]

$$\text{CIDS} = \frac{I_L(\phi,\chi) - I_R(\phi,\chi)}{I_L(\phi,\chi) + I_R(\phi,\chi)}$$

where $I_{L,R}(\phi,\chi)$ is the intensity of light scattered in the direction (ϕ,χ) in space when left or right circularly polarized light is incident upon the sample. For a homogeneous solution of scatterers the scattered intensities in a chosen direction are measured to provide,[6] alternatively, $\langle I_L - I_R \rangle_{av.}$ and $\langle I_L + I_R \rangle_{av.}$. The measured signal is $\langle \text{CIDS} \rangle_{av.} = \langle I_L - I_R \rangle_{av.} / \langle I_L + I_R \rangle_{av.}$. We must therefore find the average of the numerator and the denominator of the CIDS ratio. Instead of deriving the averaged total scattered intensity for right and left circularly polarized light $(I_L + I_R)$, we will derive $\langle I_{\parallel} + I_{\perp} \rangle_{av.}$ where $I_{\parallel}$ and $I_{\perp}$ are the intensities scattered in a given direction, when the incident light is polarized parallel and perpendicular to the scattering plane. The total scattered intensity is independent of the orthogonal states used to characterize the incident radiation, but the derivation is simpler this way.

Theory

Let the scatterer be described by a set of point polarizability tensors. The field scattered by this array, due to field, $\underset{\sim}{E}_0$, is given by:

$$\underset{\sim}{E}(\underset{\sim}{r}') = C\, e^{-ikr'} (\underset{\sim}{1} - \hat{\underset{\sim}{k}}\hat{\underset{\sim}{k}}) \cdot \sum_j e^{i\Delta \underset{\sim}{k} \cdot \underset{\sim}{r}_j} \underset{\sim}{\alpha}_j \cdot \underset{\sim}{E}_0 \qquad (1)$$

where j labels each polarizability in the scatterer; k and $\hat{\underset{\sim}{k}}$ are the modulus and a unit vector along the scattered wave-vector of the radiation; $\underset{\sim}{r}_j$ and $\underset{\sim}{\alpha}_j$ are the position and the polarizability tensor for each j, respectively;

r' is the position of observation in space, $\Delta\underset{\sim}{k} = \underset{\sim}{k}-\underset{\sim}{k}_0$, and C is a proportionality constant containing some inverse distance factors. Next we define the incident circular polarizations of the radiation:

$$\begin{aligned} \underset{\sim}{E}_{0,L} &= \underset{\sim}{A} + i\underset{\sim}{B} \\ \underset{\sim}{E}_{0,R} &= \underset{\sim}{A} - i\underset{\sim}{B} \end{aligned} \tag{2}$$

with $\underset{\sim}{A}$ and $\underset{\sim}{B}$ two arbitrary orthogonal vectors, both perpendicular to the direction of incidence of the light. Similarly, the polarizability tensor can be written in terms of its components along principal axes $\underset{\sim}{e}_j$.

$$\underset{\sim}{\alpha}_j = \alpha_j \, \underset{\sim}{e}_j\underset{\sim}{e}_j \tag{3}$$

where in general there will be three components for each tensor. From (1) and using (2) and (3), we can write the difference in scattered intensity for incident left and right circularly polarized light at a given direction in space, as:

$$I_L - I_R = 2iC^2 \sum_{ij}\sum e^{i\Delta\underset{\sim}{k}\cdot(\underset{\sim}{r}_j-\underset{\sim}{r}_i)} \alpha_j \alpha_i^* [(\underset{\sim}{A}\times\underset{\sim}{B})\cdot(\underset{\sim}{e}_j\times\underset{\sim}{e}_i)][(\underset{\sim}{e}_j\cdot\underset{\sim}{e}_i)-(\underset{\sim}{e}_j\cdot\hat{\underset{\sim}{k}})(\underset{\sim}{e}_i\cdot\hat{\underset{\sim}{k}})] \tag{4}$$

Equation (4) is the expression in the numerator of the CIDS ratio that must be averaged; it involves the product between space fixed ($\underset{\sim}{A}$, $\underset{\sim}{B}$, $\Delta\underset{\sim}{k}$, $\hat{\underset{\sim}{k}}$) and molecule-fixed quantities ($\underset{\sim}{e}_j$, $\underset{\sim}{e}_i$, $\underset{\sim}{r}_j$, $\underset{\sim}{r}_i$). In order to do the averaging, we must define space and molecule-fixed frames, in terms of whose axes the corresponding quantitites can be written.

First we define a molecule-fixed coordinate system, with orthogonal unit vectors $\underset{\sim}{i}'$, $\underset{\sim}{j}'$ and $\underset{\sim}{k}'$. We orient this frame so that without loss of

generality, $\underset{\sim}{e}_i$ is chosen to lay in the plane $\underset{\sim}{i}', \underset{\sim}{k}'$, while $\underset{\sim}{e}_j$ is completely arbitrary with components along the three orthogonal axes. Furthermore, the $\underset{\sim}{k}'$ axis of the molecular frame is oriented along the distance vector $\hat{\underset{\sim}{R}}_{ij}$ between polarizabilities i and j in the scatterer, with $\underset{\sim}{R}_{ij} = \underset{\sim}{r}_j - \underset{\sim}{r}_i$. The space-fixed frame with axes labeled $\underset{\sim}{a}$, $\underset{\sim}{b}$ and $\underset{\sim}{c}$ is oriented so that one of its axes (the $\underset{\sim}{c}$ axis) is along the momentum transfer vector of light, $\Delta\underset{\sim}{k} = \underset{\sim}{k} - \underset{\sim}{k}_0$; the scattering plane defined by $\underset{\sim}{k}$ and $\underset{\sim}{k}_0$ coincides with the $\underset{\sim}{c}, \underset{\sim}{b}$ plane. We can now express the space-fixed quantities in terms of the axes of this frame:

$$\begin{aligned} \Delta\underset{\sim}{k} &= (4\pi/\lambda)\ \sin\beta\ \underset{\sim}{c} \\ \hat{\underset{\sim}{k}} &= \cos\beta\ \underset{\sim}{b} + \sin\beta\ \underset{\sim}{c} \\ \hat{\underset{\sim}{k}}_0 &= \cos\beta\ \underset{\sim}{b} - \sin\beta\ \underset{\sim}{c} \end{aligned} \tag{5}$$

where $\hat{\underset{\sim}{k}}$ and $\hat{\underset{\sim}{k}}_0$ are unit vectors along the scattered and incident wave-vectors; β is one-half of the scattering angle subtended between these two vectors.

Having defined this space-fixed coordinate system we can now rewrite the polarization vectors of light (2) as:

$$\underset{\sim}{E}_{0,L,R} = \underset{\sim}{A} \pm i\underset{\sim}{B} = \frac{1}{\sqrt{2}}\ [\underset{\sim}{a} \pm i(\sin\beta\ \underset{\sim}{b} + \cos\beta\ \underset{\sim}{c})] \tag{6}$$

where the + sign must be used for L and the - sign for R. Similarly we can write, from (6):

$$\underset{\sim}{A} \times \underset{\sim}{B} = \frac{1}{2}\ (\sin\beta\ \underset{\sim}{c} - \cos\beta\ \underset{\sim}{b}) \tag{7}$$

Equations (5) - (7) together with the corresponding expression of $\underset{\sim}{e}_i$, $\underset{\sim}{e}_j$, $\underset{\sim}{e}_i \times \underset{\sim}{e}_j$ written in terms of the molecular frame, can be replaced in Equation (4). The resulting expression will contain the dot products between the axes of the two frames. Notice that because of our particular choice in orienting these two frames, the exponential $e^{i\Delta \underset{\sim}{k} \cdot \underset{\sim}{R}_{ij}}$ can be written as $e^{i(\underset{\sim}{c} \cdot \underset{\sim}{k}')}$, i.e., in terms of the dot product between just one axis or each frame. Indeed, the product $(\underset{\sim}{c} \cdot \underset{\sim}{k}')$ in the exponential is a constant for any orthogonal transformation between the two coordinate systems, with the exception of the transformation involving the angle θ between $\underset{\sim}{c}$ and $\underset{\sim}{k}'$. This greatly simplifies the derivations.

To relate the space-fixed vectors to the molecule-fixed vectors, we use the Euler transformation matrix[7] to express any product between space-fixed and molecule-fixed basis-vectors, in terms of the three Euler angles (θ,χ,ϕ) (see Figure 1). The spatial averaging of any function $f(\theta,\chi,\phi)$ of the Euler angles involves the spatial integrations over the three Euler angles:

$$\langle f(\theta,\chi,\phi)\rangle = \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} f(\theta,\chi,\phi)\sin\theta d\theta d\chi d\phi \Big/ \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sin\theta d\theta d\chi d\phi \tag{8}$$

Using the Euler matrix, it can be shown that the only terms that survive the averaging process (see Equation 8) are the combinations of dot products between the molecule and space-fixed frames, such that the integration with respect to the polar angle θ:

$$\int_0^{\pi} e^{iq\cos\theta} f(\theta)\sin\theta d\theta \qquad \text{with} \qquad q \equiv \frac{4\pi}{\lambda} R_{ij} \sin\beta \tag{9}$$

is a purely imaginary number. This is related to the fact that Equation (9) is the Fourier transform of $f(\theta)\sin\theta$ in the q-space, and a necessary and sufficient condition[8] for this result is that $f(\theta)\sin\theta$ be an odd function of its argument, i.e., f must be an even function of θ. The imaginary result of the averaging integrations is of course necessary for Equation (4) to be real. Here we will just give only the results of the integrals that appear in the averaging of $I_L - I_R$:

$$\int_0^\pi e^{iq\cos\theta}\cos\theta\sin\theta d\theta = 2i\ j_1(q)$$

$$\int_0^\pi e^{iq\cos\theta}\cos\theta\sin^3\theta d\theta = 4i\ j_2(q) \tag{10}$$

$$\int_0^\pi e^{iq\cos\theta}\cos^3\theta\sin\theta d\theta = 2i(j_1(q) - 2j_2(q)/q)$$

where $j_1(q)$ and $j_2(q)$ are the first and second order spherical Bessel functions, respectively, defined by:[9]

$$j_1(q) = \frac{\sin q}{q^2} - \frac{\cos q}{q}$$

$$j_2(q) = \left(\frac{3}{q^3} - \frac{1}{q}\right)\sin q - \frac{3}{q^2}\cos q \tag{11}$$

The resulting averaged expression for $I_L - I_R$ in terms of (10) and (11) is then:

$$\frac{\langle I_L - I_R\rangle_{av}}{C^2} = \sum_i \sum_j \frac{\alpha_i^* \alpha_j\ (\underset{\sim}{e}_j \times \underset{\sim}{e}_i)\cdot\hat{\underset{\sim}{R}}_{ij}}{2} \{[(\underset{\sim}{e}_i\cdot\underset{\sim}{e}_j)(j_2/q - j_1)$$

$$- (\underset{\sim}{e}_i\cdot\hat{\underset{\sim}{R}}_{ij})(\underset{\sim}{e}_j\cdot\hat{\underset{\sim}{R}}_{ij})(5j_2/q - j_1)](\sin\beta + \sin^3\beta)\} \tag{12}$$

where the argument of the spherical Bessel functions, q (see Equation (9)), has been omitted for simplicity. In Equation (12) the geometry of the scatterer has been left completely general. The whole expression is multiplied by the factor:

$$(\underset{\sim}{e}_j \times \underset{\sim}{e}_i)\cdot\hat{\underset{\sim}{R}}_{ij} \tag{13}$$

Clearly this form-factor vanishes for any two groups in the scatterer whose relative orientation possesses a center of symmetry, i.e. for nonchiral arrays of point dipoles in space. Expression (13) can be rearranged to yield:

$$(\underset{\sim}{e}_j \times \underset{\sim}{e}_i)\cdot\hat{\underset{\sim}{R}}_{ij} \equiv (\underset{\sim}{e}_i \times \hat{\underset{\sim}{R}}_{ij})\cdot\underset{\sim}{e}_j = \underset{\sim}{m}_i\cdot\underset{\sim}{e}_j \tag{14}$$

which resembles the expression for the rotational strength in optical activity theory:[10] indeed, $\underset{\sim}{m}_i \equiv \underset{\sim}{e}_i \times \hat{\underset{\sim}{R}}_{ij}$ is the transition magnetic dipole associated with electronic transition $\underset{\sim}{e}_i$. The last expression in (14) shows that the factor (13) is the product of an axial and a polar vector. Axial or pseudovectors do not change sign when an inversion of their coordinates is carried out; as a result, expression (12) will have the same value, but opposite sign for a chiral molecule and its mirror image. This chiral discrimination appearing in the averaged equations makes CIDS much more sensitive than regular light scattering to the structure of optically active molecules. Only β (equal to one-half of the scattering angle) appears in Equation (12); this simple dependence gives the differential scattering pattern the "ring structure" of constant intensities similar to those observed in powder patterns in crystallography.[11] For small values of $q = \frac{4\pi R_{ij}}{\lambda}\sin\beta$, (i.e., for $\lambda \gg R_{ij}$), we can expand the spherical Bessel functions in terms of powers of their

arguments to obtain:

$$\lim_{q\to 0} j_1(q) = \frac{1}{3} q \tag{15a}$$

and

$$\lim_{q\to 0} j_2(q)/q = \frac{1}{15} q \tag{15b}$$

From these expressions, an asymtotic equation for $\langle I_L - I_R \rangle_{av}$ can be obtained:

$$\lim_{q\to 0} \frac{\langle I_L - I_R \rangle_{av}}{C^2} = \frac{2\pi R_{ij}}{\lambda} \sum_i \sum_j \alpha_i^* \alpha_j (\underset{\sim}{e}_j \times \underset{\sim}{e}_i) \cdot \hat{\underset{\sim}{R}}_{ij} (\underset{\sim}{e}_i \cdot \underset{\sim}{e}_j)(\sin^2\beta + \sin^4\beta) \tag{16}$$

Clearly, in the forward direction ($\beta = 0$, $q = 0$) $\langle I_L - I_R \rangle_{av}$ and therefore the CIDS ratio, vanishes. This conclusion is only valid within the first Born approximation[12] to the local field, used in deriving the above equations. Now we must obtain the spatial averaging for the total scattering. The scattering intensity due to a collection of polarizable points in space, each characterized by a polarizability tensor $\underset{\approx}{\alpha}_i = \alpha_i \underset{\sim}{e}_i \underset{\sim}{e}_i$, is:

$$\frac{I(r)}{C^2} = \sum_{i,j} \sum e^{iq\cos\theta} \alpha_i^* \alpha_j [\hat{\underset{\sim}{E}}_0^* \cdot \underset{\sim}{e}_i \underset{\sim}{e}_i \cdot \underset{\sim}{e}_j \underset{\sim}{e}_j \cdot \hat{\underset{\sim}{E}}_0 - \hat{\underset{\sim}{E}}_0^* \underset{\sim}{e}_i \underset{\sim}{e}_i \cdot \hat{k}\hat{k} \cdot \underset{\sim}{e}_j \underset{\sim}{e}_j \cdot \hat{\underset{\sim}{E}}_0] \tag{17}$$

where α_i, α_j, $\underset{\sim}{e}_i$, $\underset{\sim}{e}_j$, $\hat{\underset{\sim}{k}}$, q, and θ have the same meaning as before. $\hat{\underset{\sim}{E}}_0$ is the incident electric unit vector. For light polarized perpendicular to the scattering plane

$$\hat{\underset{\sim}{E}}_0 = \underset{\sim}{a} \tag{18a}$$

and for light polarized parallel to the scattering plane:

$$\hat{\underset{\sim}{E}}_0 = \cos\beta\ \underset{\sim}{b} + \sin\beta\ \underset{\sim}{c} \tag{18b}$$

The scattered intensity for light perpendicular to the scattering plane is then:

$$\frac{I_\perp}{C^2} = \sum_i \sum_j e^{iq\cos\theta} \alpha_i^* \alpha_j [(\underset{\sim}{a}\cdot\underset{\sim}{e}_i)(\underset{\sim}{a}\cdot\underset{\sim}{e}_j)\underset{\sim}{t}_i\cdot\underset{\sim}{t}_j - (\underset{\sim}{a}\cdot\underset{\sim}{e}_i)(\underset{\sim}{e}_i\cdot\hat{\underset{\sim}{k}})(\underset{\sim}{e}_j\cdot\hat{\underset{\sim}{k}})(\underset{\sim}{a}\cdot\underset{\sim}{e}_j)] \tag{19}$$

and the scattered intensity of light incident parallel to the scattering plane is given by:

$$\frac{I_\parallel}{C^2} = \sum_i \sum_j e^{iq\cos\theta} \alpha_i^* \alpha_j [(\underset{\sim}{e}_i\cdot\underset{\sim}{e}_j) - (\underset{\sim}{e}_i\cdot\hat{\underset{\sim}{k}})(\underset{\sim}{e}\cdot\hat{\underset{\sim}{k}})]\{\sin^2\beta(\underset{\sim}{b}\cdot\underset{\sim}{e}_i)(\underset{\sim}{b}\cdot\underset{\sim}{e}_j) +$$

$$\cos^2\beta(\underset{\sim}{c}\cdot\underset{\sim}{e}_i)(\underset{\sim}{c}\cdot\underset{\sim}{e}_j) + \sin\beta\cos\beta[(\underset{\sim}{b}\cdot\underset{\sim}{e}_i)(\underset{\sim}{c}\cdot\underset{\sim}{e}_j) + (\underset{\sim}{c}\cdot\underset{\sim}{e}_i)(\underset{\sim}{b}\cdot\underset{\sim}{e}_j)]\} \tag{20}$$

Equations (19) and (20) must be spatially averaged. The derivation follows closely along the lines shown for $I_L - I_R$, We will omit the details and will present only the results. The spatially averaged total scattered intensity is: (details of the derivations can be found elsewhere)[13]

$$\frac{\langle I_\perp + I_\parallel \rangle}{c^2} = \frac{8}{15} \sum_i |\alpha_i|^2 (1-\sin^2\beta \cos^2\beta) + \sum_{ij} \alpha_i \alpha_j^* \{ (\underset{\sim}{t}_i \cdot \hat{\underset{\sim}{R}}_{ij})(\underset{\sim}{t}_j \cdot \hat{\underset{\sim}{R}}_{ij})$$

$$\{[(j_0 - j_1/q) + \sin^2\beta(3j_1/q - j_0)](\underset{\sim}{t}_i \cdot \underset{\sim}{t}_j) - 2(\underset{\sim}{t}_i \cdot \underset{\sim}{R}_{ij})(\underset{\sim}{t}_j \cdot \underset{\sim}{R}_{ij})$$

$$[(j_1/q - 4j_2/q^2) - \sin^2\beta\, j_2/q^2 + \sin^4\beta(j_1/q - 3j_2/q^2)]\} +$$

$$(\underset{\sim}{t}_i \times \hat{\underset{\sim}{R}}_{ij}) \cdot (\underset{\sim}{t}_j \times \hat{\underset{\sim}{R}}_{ij}) \{ \tfrac{1}{2}[(j_0 + j_1/q) + \sin^2\beta(j_0 - 3j_1/q)](\underset{\sim}{t}_i \cdot \underset{\sim}{t}_j) -$$

$$\tfrac{1}{2}(\underset{\sim}{t}_i \cdot \hat{\underset{\sim}{R}}_{ij})(\underset{\sim}{t}_j \cdot \hat{\underset{\sim}{R}}_{ij})[(16j_2/q^2 - 3j_1/q + j_0) + \sin^2\beta(4j_2/q^2 -$$

$$3j_1/q + j_0) - 4\sin^4\beta(j_1/q - 3J_2/q^2)]\} - (1 - \tfrac{1}{2}((\hat{\underset{\sim}{R}}_{ij} \times \underset{\sim}{t}_i)^2 +$$

$$(\hat{\underset{\sim}{R}}_{ij} \times \underset{\sim}{t}_j)^2))[(5j_2/q^2 - j_1/q) + \sin^2\beta(j_0 - j_1/q) - \sin^4\beta(j_0 -$$

$$3j_2/q^2)] - ((\underset{\sim}{t}_i \times \underset{\sim}{R}_{ij}) \cdot (\underset{\sim}{t}_j \times \underset{\sim}{R}_{ij}))^2 [(1/8)(-9j_2/q^2 + 2j_1/q + j_0) -$$

$$(1/4)\sin^2\beta(3j_2/q^2 - 4j_1/q - j_0) - (1/8)\sin^4\beta(9j_2/q^2 + 2j_1/q +$$

$$3j_0)] - (\underset{\sim}{t}_j \cdot (\hat{\underset{\sim}{R}}_{ij} \times \underset{\sim}{t}_i))^2 [(1/8)(5j_2/q^2 + 2j_1/q - j_0) + \tfrac{1}{4}\sin^2\beta$$

$$(-5j_2/q^2 + 2j_1/q + j_0) + (1/8)\sin^4\beta(13j_2/q^2 - 6j_1/q - j_0)]\} \qquad (21)$$

where $j_0 = \frac{\sin q}{q}$ is the first order spherical Bessel function. Equation (21) gives the total scattering as a function of the scattering angle (2β), due to an ensemble of scatterers (each described by a set of point polarizable groups), adopting all possible orientations in space. In this expression only three sperical Bessel functions contribute: j_0, j_1 and j_2. All the Bessel functions

in this equation appear in the form, j_n/q^n, which is always symmetric in β. This together with the fact that only the 0th, 2nd and 4th power of sin β are present means that the scattering pattern must be symmetric about the direction of incidence of light. Equation (21) is an extension of the spatially averaged scattering of a collection of point polarizable groups, originally derived by Debye[14] for the case of spherically symmetric point polarizabilities. A somewhat different form of Equation (21) has been derived by Horn[15] for polymers which are rigid rods or Gaussian chains.

II. CIDS of an Ensemble of Randomly Oriented Helices.

Here we will apply the results of the last section to the case of a helical scatterer made up of uniaxial point polarizable groups which are evenly spaced. The position of the jth group in the helical scatterer with respect to an arbitrary coordinate system (see Figure 2) can be written:

$$\underset{\sim}{r}_j = a \cos j\tau_0 \, \underset{\sim}{e}_1 + a \sin j\tau_0 \, \underset{\sim}{e}_2 + \frac{Pj\tau_0}{2\pi} \, \underset{\sim}{e}_3 \tag{22}$$

with a, the radius of the helix; τ, the winding angle of the helix groups in radians; and P, the pitch of the helix. Next we assume that the single principal axis of each polarizability ($\underset{\sim}{t}_j$) is tangential to the helix,

$$\underset{\sim}{t}_j = -(a/M)\sin j\tau_0 \, \underset{\sim}{e}_1 + (a/M)\cos j\tau_0 \, \underset{\sim}{e}_2 + (P/2\pi M) \, \underset{\sim}{e}_3 \tag{23}$$

where M is a normalization constant: $M = (a^2 + P^2/4\pi^2)^{1/2}$. From Equations (22) and (23) and using the corresponding definition for the unit vector distance between groups i^{th} and j^{th}, $\hat{R}_{ij} = \underset{\sim}{r}_j - \underset{\sim}{r}_i \,/\, |\underset{\sim}{r}_j - \underset{\sim}{r}_i|$, we can write

Equation (13) for the case of a helical scatterer. Due to the symmetry of the helix, the result is that both the total $(I_{\parallel} + I_{\perp})$ and the differential scattering $(I_L - I_R)$ can be written in terms only of the angular distance τ_{ij} between groups i^{th} and j^{th}, $(\tau_{ij} \equiv (j-i)\tau_0)$:

$$\frac{\langle I_L - I_R \rangle_{av}}{c^2} = (a^2 P/4\pi M^2) \sum_i \sum_j (1/G_{ij})[2(1-\cos\tau_{ij}) - \tau_{ij}\sin\tau_{ij}]$$

$$\{(1/M^2)[(a^2\cos\tau_{ij} + P^2/4\pi^2)(j_2/q - j_1) - (1/G_{ij})[a^2\sin\tau_{ij} +$$

$$(P^2/4\pi^2)\tau_{ij}]^2(5j_2/q - j_1)\} \qquad (24)$$

with: $G_{ij} \equiv [2a^2(1-\cos\tau_{ij}) + (P\tau_{ij}/2\pi)^2]$

By exploiting the helical symmetry, Equation (24) can be greatly simplified for the purpose of calculations, allowing us to write it in terms of a single summation. The result is similar to (24) with $\tau_{ij} \equiv \tau_k$ and $G_{ij} = G_k$, and the two summations replaced by $\sum_{k=1}^{N-1} (N-k)$.

An equivalent expression for the denominator of the CIDS ratio can be obtained for the helix, but we will not write it here to save space.

III. Numerical Calculations.

We have carried out calculations using Equation (24) and its equivalent for the total scattering, for an ensemble of randomly oriented helices in solution as a function of the helix parameters and the wavelength of light. Figure 3 shows the polar plots of CIDS (labeled CIDS AV)

and total scattering (labeled SCAT AV) vs. the scattering angle, for three different values of pitch (P), radius (R) and wavelength of light. Positive values of the CIDS are depicted with light lines and negative values with dark lines (see figure caption for details). The first thing to notice in this figure is how much more sensitive CIDS (left column) is to a change in the helical parameters, when compared to the total scattering (right column). It is also remarkable that even for ratios of P/λ close to 0.5 and $R/\lambda \sim 0.3$ the CID scattering pattern shows at least one zero. The CID and total scattering values have been normalized for the purpose of the plotting; the order of magnitude of the CIDS ratio calculated ranged between 10^{-2} and 10^{-7} (see figure caption for maximum values obtained). Such values are commonly measured in the typical CD experiment, and therefore from these calculations we can predict that the CIDS effect corresponding to helical molecules of this size could in principle be detected.

Figure 4 shows the dependence of the magnitude of the CID and total scattering on the length of the helices in solution. The pitch of the helices is 34 Å and the radius 11 Å. The lengths are given in number of turns as follows: upper plate = 500 turns, middle = 73 and lower plate = 7.3 turns. Notice that while the total scattering becomes more spherically symmetric for smaller helices, the CIDS pattern does not change much. The plots have been normalized for comparison, since both CIDS and total scattering values decrease with the decreasing length of the helix. The independence of CIDS to the length of highly symmetric and periodic chiral scatterers, frequently found in biological aggregates, indicates the sensitivity and uniqueness of the CIDS signal. It will characterize the chiral nature of certain elements of an object, but it will not respond to other elements.

CONCLUSIONS

In this paper the theory of circular intensity differential scattering presented earlier[1-4] has been extended to include the general case of chiral scatterers of arbitrary geometry which are randomly oriented in space. The relevant equations are equations (12) and (21) whose ratio give the spatially averaged CIDS. It can be seen that in the process of averaging, the phase relationship between two point-polarizable groups in the scatterer is lost. This result formally means that an inverse Fourier transformation of (12) and (21), or their ratio, cannot be done to obtain direct geometric information from the measured CIDS signal. This is not different from any other spatially averaged optical signal, therefore the use of equations (12) and (21) to interpret CIDS in terms of structure is necessarily restricted to the comparison of model-structures with experimental data. On the other hand, the equations derived here, and the calculations performed, show that CIDS is much more sensitive than averaged total scattering to the geometry and structure of chiral molecules. In all numerical computations shown here, the absolute values of the CIDS ratio obtained were found between 10^{-2} to 10^{-7}, a range accessible to the measuring devices of current CD spectropolarimeters.

Acknowledgments

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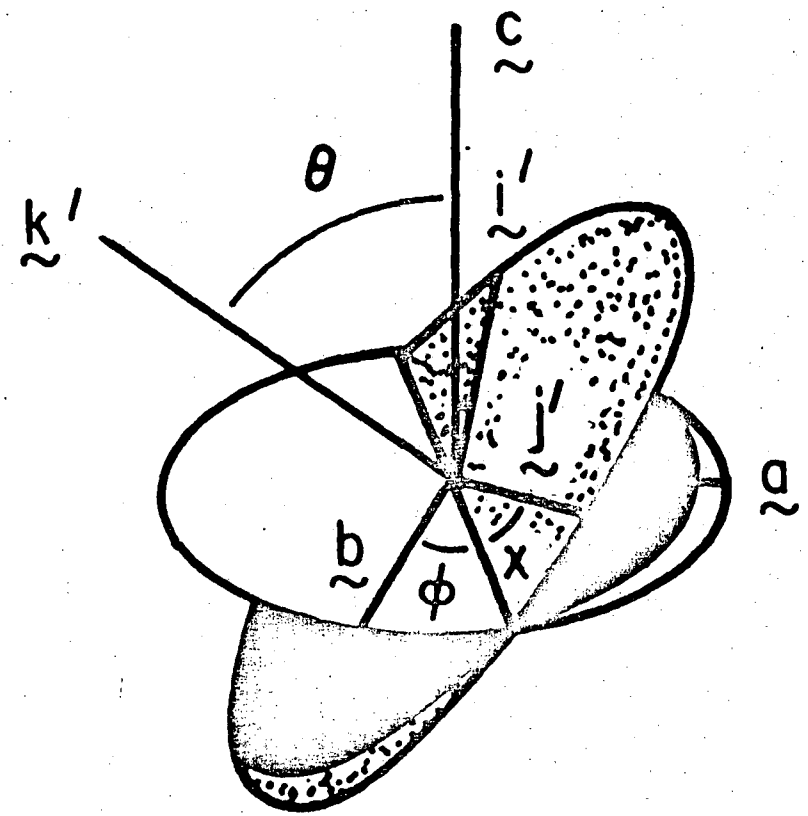
FIGURE CAPTIONS

Figure 1. The three Euler angles between the space-fixed and the molecule-fixed coordinate system, are shown. In the text $\underset{\sim}{c}$ and $\underset{\sim}{k}'$ are the polar axes of these frames.

Figure 2. A helix of polarizabilities. The polarizabilities are shown as ellipsoids of revolution whose symmetry axes are directed along the vectors $\underset{\sim}{t}_1$, t_2,.....etc, shown in the figure to be tangential to the helix. In our calculations the other two axes of the polarizability were taken equal to zero. τ_o is the angular distance between the dipoles; a is the radius of the helix and p its pitch.

Figure 3. Polar plots of total scattering(left column) and CIDS(right column) for ramdomly oriented helices, for different values of pitch P, radius A and wavelength of light W.The angular distance between the polarizabilities is 0.682 radians.The maximun CIDS value was obtained for the top case and was 2.81×10^{-3}.The thick lines indicate negative lobes whereas the thin ones correspond to positive CIDS values.

Figure 4. Polar plots of CIDS (left column) and total scattering (right column) for randomly oriented helical scatterers. Three different lengths are shown with the other parameters of the helix kept constant.(top) length = 500 turns, (middle) length = 73 turns and (bottom) length = 7.3 turns. The wavelength of light is 4442 Å, radius = 11 Å, pitch = 34 A. Notice that in the bottom figure the total scattering of the helix is like the scattering from a point, with the scattering intensity at right angles equal to one-half of that in the forward direction.



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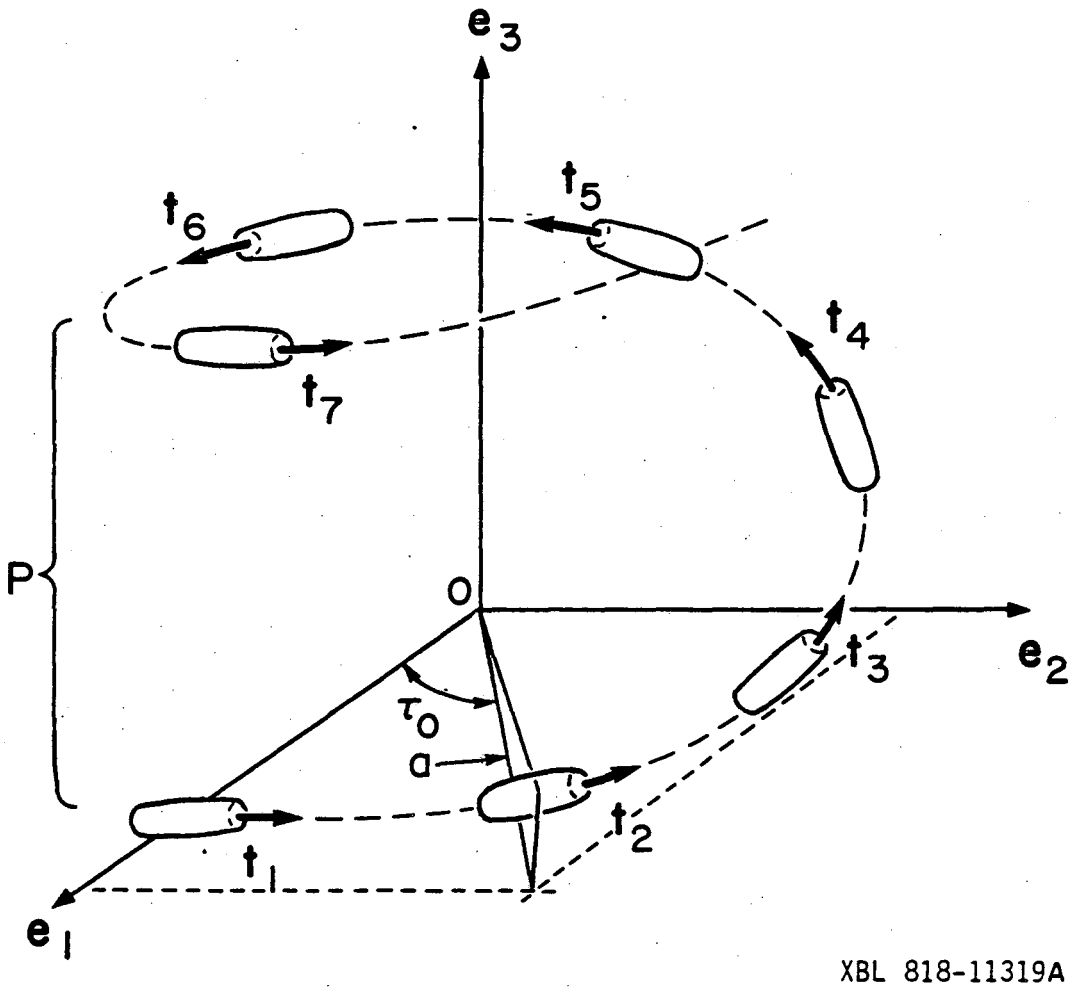

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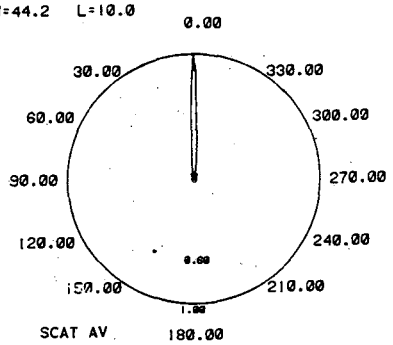

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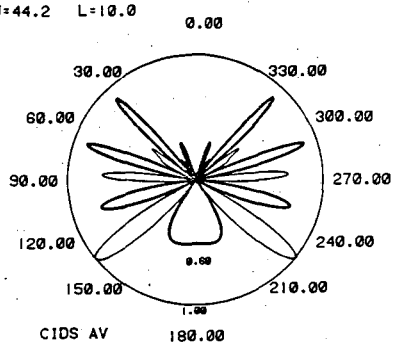

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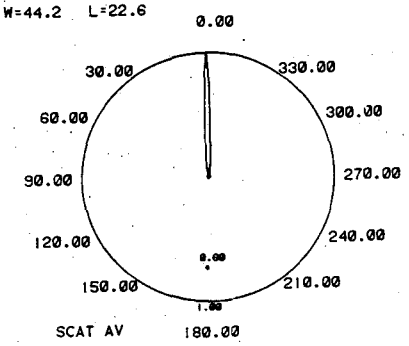

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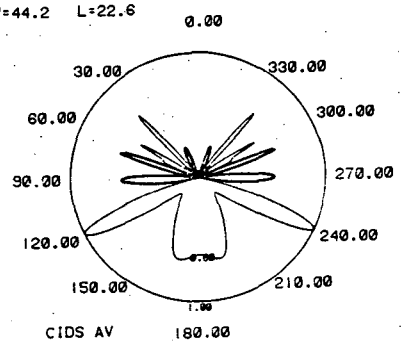

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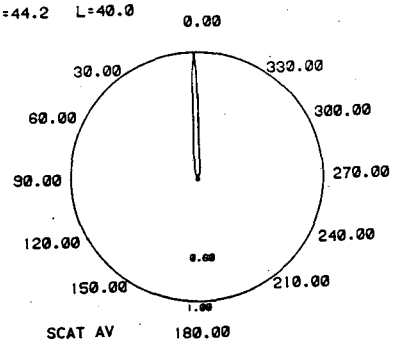

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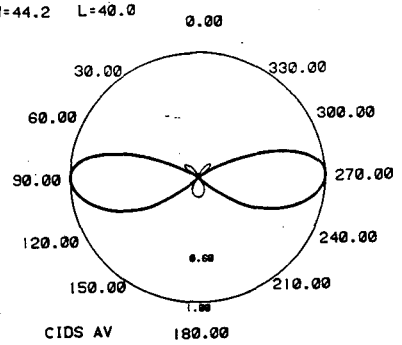

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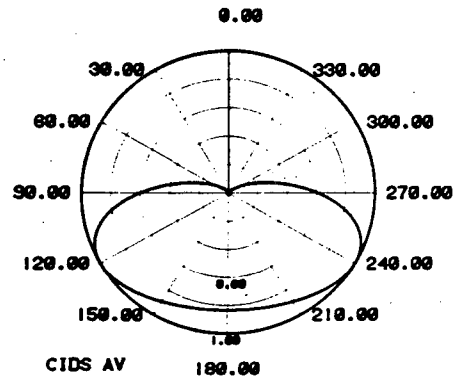

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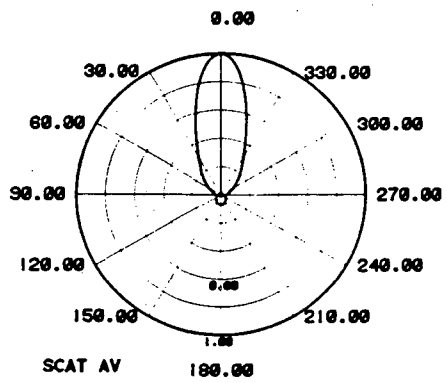

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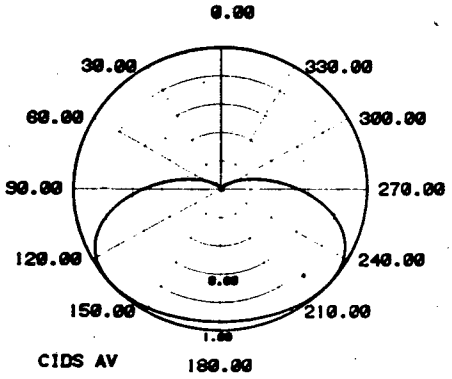

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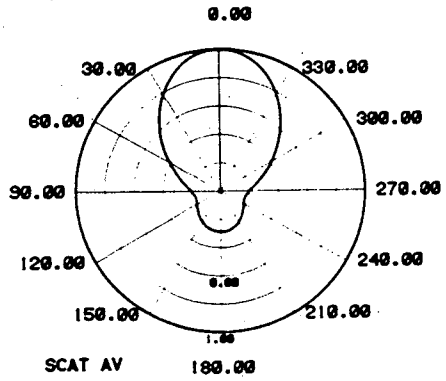

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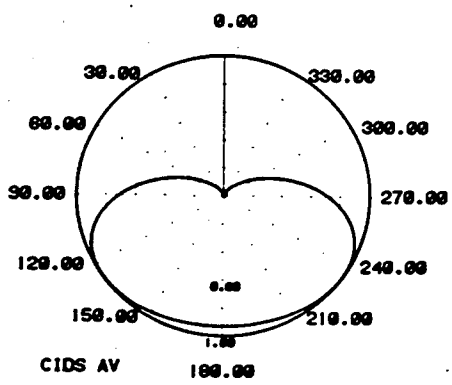

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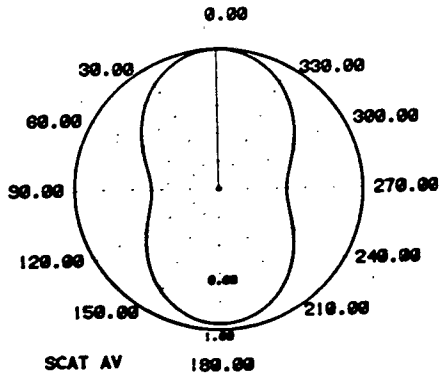

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