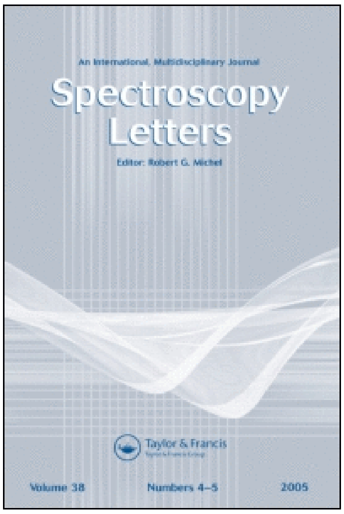

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Interpretation of Polarized Absorption and Emission Spectra of Molecules Incorporated in Stretched Polymer Films

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INTERPRETATION OF POLARIZED ABSORPTION AND EMISSION SPECTRA OF MOLECULES INCORPORATED IN STRETCHED POLYMER FILMS

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Different methods for the interpretation of linear dichroic spectra of molecules incorporated in uniaxial matrices are discussed. A method based on the combination of both polarized absorption and emission measurements is described for the resolution of absorption and emission spectra into their different polarized components, and for the investigation of molecular distributions in the oriented matrix. The distributions of some planar molecules of different shapes incorporated in stretched polyethylene films are presented.

In this article we shall discuss some methods for the interpretation of linear dichroism (LD) spectra of molecules incorporated in stretched polymers. The distribution of the incorporated molecules in these matrices is of crucial importance for such interpretation. In order to overcome the lack of sufficient information about these distributions, different models have been suggested. Many attempts have been made to analyze LD spectra using one parameter of orientation.[1-11]. An expression that has been widely used for the dichroic ratio d_o is

$$d_o = \frac{A_{\parallel}}{A_{\perp}} = \frac{f \cos^2\alpha + \frac{1}{3}(1 - f)}{\frac{1}{2} f \sin^2\alpha + \frac{1}{3}(11 - f)} \tag{1}$$

where A and A are the absorption intensities for light polarized parallel and perpendicular to the stretching direction, respectively, f is an orientational parameter and α is the angle between the transition moment vector and the orientational axis of the molecule.

It was shown that eq. (1) is valid for matrices possessing uniaxial symmetry and where the incorporated molecules have uniform distribution around their orientational axes.[12]

Eq. (1) can not be solved for a single spectrum without previous knowledge of either the orientation (f) or the polarization of the transition (α). Besides the case of molecules possessing a manyfold axis of symmetry (rod-like, disk-like), "a priori" it is very difficult to know whether eq. (1) can be applied for a certain molecular geometry or not. In the following we shall present a method by which this equation was used (and its validity proved) in the interpretation of LD of steroid molecules who do not have the mentioned axial symmetry. The method is based on the use of a "small" chromophore which can be positioned in different sites of the molecular skeleton, under the assumption that this modification does not affect the geometry of the molecule, and hence its orientation in the polymeric matrix.[13]

We have measured the dichroic ratio in stretched polyethylene of the seven α,β -unsaturated ketones of the cholestane series shown in Figure 1.

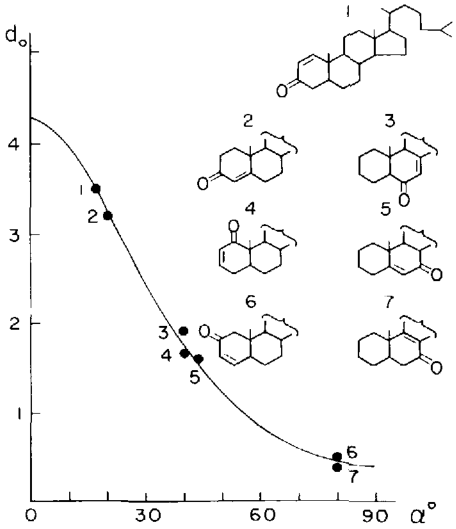

FIGURE 1: Plot of d_0 vs. α according to eq.(1) for f=0.5 The circles are measured d_0 values of cholestenones plotted vs. α values estimated from molecular models.

Assuming that the direction of the transition moment with respect to the chromophore is independent of its position in the molecular skeleton, the shifts in the direction of the transition moments when passing from one compound to another, can be estimated from crystallographic data or from molecular models. By substituting the values of the dichroic ratios of selected pairs of compounds in eq. (1), the value of f and the direction of both the orientational axes and the transition moment can be elucidated. The f value for the cholestane series was found to be 0.5 and the direction of polarization of the transition is shown in Figure 2 for the case of compound 2.

In figure 1 the curve describing the relation between α and d_0 as calculated from eq. (1) using f=0.5 is shown together with the experimental values. The close fit between the two sets of values proves that eq. (1) can be used to analyze the LD of molecules possessing a cholestane skeleton.

Similarly, using the same chromophore, we have proved the validity of eq. (1) for other steroids such as the androstane series, carboxylic esters of cholesterol and of different androstanols.

Using the same procedure, we have been able to analyze the LD spectra of these steroids containing other chromophores such as the isolated double bond[9] and the saturated ketone.[11] In all these cases eq. (1) was found to be valid, and the same f values were found for the corresponding series of molecules. In both the cholestane and androstane steroids the orientational axes determined by the above described method coincide with the longitudinal principal axes of inertia as calculated from X-ray data.[1,14,15]

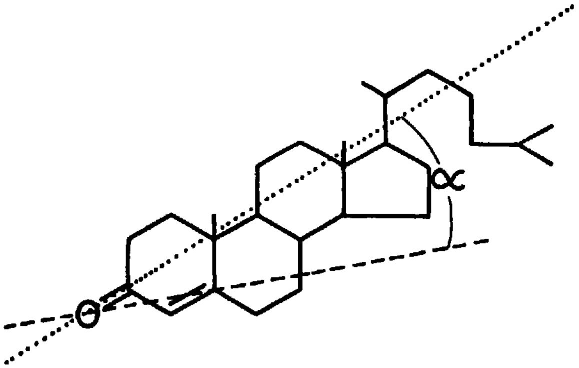

FIGURE 2: Direction of (---) the π -π* transition moment vector and (...) the longitudinal axis of Δ^4 - cholesten-3-one.

All these results were obtained without making any assumption on the polarization of the electronic transitions or the orientation of the molecules in the matrix. These results demonstrate that eq.(1) is also applicable to a variety of compounds which do not fulfillthe symmetry requirements which have been previously proposed.[12]

In cases in which the molecule contains polar groups, the possibility of association with the matrix or with other molecules should be considered.[16]

It is noteworthy that eq. (1) can also be applied for studying the conformation, configuration and association of the incorporated molecules.[8,16,17]

In all cases where eq. (1) is valid, the medium has axial symmetry and therefore eq. (2) must also be valid:

$$A_0(\lambda) = \frac{1}{3}\left[A_{\parallel}(\lambda) + 2A_{\perp}(\lambda)\right] \qquad (2)$$

where $A_0(\lambda)$ is the intensity of absorption of light by the same assembly of molecules randomly distributed. We shall refer to $A_0(\lambda)$ as to the "isotropic spectrum". Overlaping transitions in the isotropic spectrum can be resolved by using the α values obtained from eq. (1) and simple trigonometric relationships.

Although eq. (1) was found to be valid for a great variety of compounds, there is no solution to this equation in the case of bicyclic compounds like decalones and naphtalene. For these and similar cases overlapping transitions can be resolved into their components if the overlap at two different wavelengths is known. In the case where these wavelengths correspond to two pure transitions 1 and 2, the partial contributions of these transitions to the total absorption intensity is given by eqs. (3) and (4).

$$A_1 = \frac{(\underline{d}_0-\underline{d}_2)(\underline{d}_1+2)}{3(\underline{d}_1-\underline{d}_2)}A_{\perp} = \frac{(\underline{d}_0-\underline{d}_2)(\underline{d}_1+2)}{3\underline{d}_0(\underline{d}_1-\underline{d}_2)}A_{\parallel} \qquad (3)$$

$$A_2 = \frac{(\underline{d}_1-\underline{d}_0)(\underline{d}_2+2)}{3(\underline{d}_1-\underline{d}_2)}A_{\perp} = \frac{(\underline{d}_1-\underline{d}_0)(\underline{d}_2+2)}{3\underline{d}_0(\underline{d}_1-\underline{d}_2)}A_{\parallel} \qquad (4)$$

where d_1 and d_2 are the dichroic ratios of the two pure transitions.

A more general treatment based on the identification of specific features in the absorption spectrum has been suggested by Eggers et al. and has been widely used recently.[18-25]

Since these methods depend on the assumptions on the polarization of the transitions at at least two different wavelengths, they can not be used as an experimental tool for testing these assumptions. In principle it is impossible to obtain more information from absorption measurements only, as long as the molecular distribution is not known. Additional information can be obtained from polarized emission experiments.

In the following we shall present a method based on the combination of both polarized absorption and polarized emission measurements. We shall describe the application of such a method to the resolution of the absorption and emission spectra into their different polarized components.

Let us consider two transition moments P and Q (Figure 3), the former defined in the molecular coordinate system a,b,c, the latter in terms of a', b', c, and which are responsible respectively for the absorption and

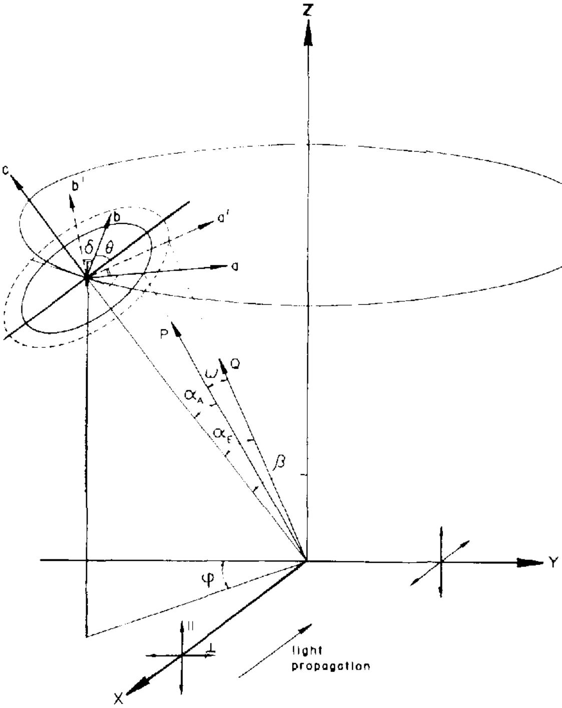

FIGURE 3

emission of light by a single molecule. These coordinate systems are chosen in such a way that the c axis coincides with a molecular axis (which we shall call the "orientational axis") and the transition moments P and Q are localized in the ac and a'c planes respectively.

The individual components of these vectors in each of the two molecular coordinate systems are related to their components in the laboratory-fixed coordinate system x, y, z (Fig. 1) by the transformation matrix T and T' respectively.

$$\begin{pmatrix} \underline{P}_x \\ \underline{P}_y \\ \underline{P}_z \end{pmatrix} = T \begin{pmatrix} \underline{P}_a \\ \underline{P}_b \\ \underline{P}_c \end{pmatrix} \quad ; \quad \begin{pmatrix} \underline{Q}_x \\ \underline{Q}_y \\ \underline{Q}_z \end{pmatrix} = T' \begin{pmatrix} \underline{Q}_{a'} \\ \underline{Q}_{b'} \\ \underline{Q}_c \end{pmatrix}$$

where

$$T = \begin{pmatrix} \cos\phi\cos\theta-\cos\beta\sin\phi\sin\theta & -\cos\phi\sin\theta-\cos\beta\sin\phi\cos\theta & \sin\beta\sin\phi \\ \sin\phi\cos\theta+\cos\beta\cos\phi\sin\theta & -\sin\phi\sin\theta+\cos\beta\cos\phi\cos\theta & -\sin\beta\cos\phi \\ \sin\beta\sin\theta & \sin\beta\cos\theta & \cos\beta \end{pmatrix}$$

T' has the same expression as T but with θ replaced by $(\theta+\delta)$.

$$\underline{P}_a = P \sin\alpha_A \qquad \underline{P}_b = 0 \qquad \underline{P}_c = P\cos\alpha_A$$

$$\underline{Q}_{a'} = Q \sin\alpha_E \qquad \underline{Q}_{b'} = 0 \qquad \underline{Q}_c = Q\cos\alpha_E$$

The intensity of absorption of light polarized in a certain direction is proportional to the sum of the squares of the scalar products between the electric vector of the light and the components of the transition moments $\underline{P}$ in that direction, of all the molecules in the light path. The probability that an excited molecule will emit light polarized in a certain direction will be proportional to the square of the corresponding component of $\underline{Q}$.

For fluorescence measured at right angles to the exciting beam we define the fluorescence polarization ratios R_z and R_x as the ratios of the intensities of fluorescence polarized in the z and x directions respectively, for exciting light polarized along z and along y (Figure 3).

For the dichroic ratio d_0 and the fluorescence polarization ratios R_z and R_x we can write:

$$d_0 = \frac{A_z}{A_y} = \frac{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta,\ \theta,\phi) P_z^2 \, d\phi \, d\theta \, d\beta}{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta,\ \theta,\phi) P_y^2 \, d\phi \, d\theta \, d\beta} \tag{6}$$

$$R_z = \frac{F_{zz}}{F_{zy}} = \frac{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta\ \theta\ \phi) P_z^2 \, Q_z^2 \, d\phi \, d\theta \, d\beta}{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta\ \theta\ \phi) P_y^2 \, Q_z^2 \, d\phi \, d\theta \, d\beta} \tag{7}$$

$$R_x = \frac{F_{xz}}{F_{xy}} = \frac{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta\ \theta\ \phi) P_z^2 \, Q_x^2 \, d\phi \, d\theta \, d\beta}{\int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} g\,(\beta\ \theta\ \phi) P_y^2 \, Q_x^2 \, d\phi \, d\theta \, d\beta} \tag{8}$$

$g(\beta,\ \theta,\ \phi)$ is a distribution function which gives the fraction of molecules oriented as defined by the angles β, θ and ϕ (Figure 3).

So far we have considered single electronic transitions involved in the absorption and emission processes. Usually electronic transitions overlap to a great extent. There could be also cases in which more than one polarization is involved in the emission process. Therefore, eqs. (6) - (8) should be extended to include the case of overlapping polarizations in both absorption and emission. Moreover, there are cases in which the distribution of the oriented molecules cannot be described by a single distribution function. Such is the case, for example, of molecules partitioned between two different phases of an orientational matrix. In these cases, the expressions for the dichroic ratio and fluorescence polarization ratios should be modified to include the partial contribution to each of the polarized absorption or emission intensities by the different fractions of molecules each distributed according to a different distribution function.

When different transitions contribute to the total absorption intensity, each by a fraction $\underline{h_i}$ and with its transition moment making an angle $\underline{\alpha_{A_i}}$ with the orientational axis of the molecule; and $\underline{n}$ transitions contribute to the total emission each by a fraction $\underline{k_j}$ and with its transition moment making an angle $\underline{\alpha_{E_j}}$ with the orientational axis, then we can write, for the case of two different distribution functions 1 and 2, and for an uniaxial distribution,

$$d_o = \frac{\sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_z + (1-f)\ K_2\, {}^2g(\beta)\, {}^2G_z]\ d\beta}{\sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_y + (1-f)\ K_2\, {}^2g(\beta)\, {}^2G_y]\ d\beta} \tag{9}$$

$$R_z = \frac{\sum_{j=1}^{n} k_j \sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_{zz} + (1-f)K_2\, {}^2g(\beta)\, {}^2G_{zz}]\ d\beta}{\sum_{j=1}^{n} k_j \sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_{zy} + (1-f)K_2\, {}^2g(\beta)\, {}^2G_{zy}]\ d\beta} \tag{10}$$

$$R_x = \frac{\sum_{j=1}^{n} k_j \sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_{xz} + (1-f)K_2\, {}^2g(\beta)\, {}^2G_{xz}]\ d\beta}{\sum_{j=1}^{n} k_j \sum_{i=1}^{m} h_i \int_0^{\pi} [f\ K_1\, {}^1g(\beta)\, {}^1G_{xy} + (1-f)K_2\, {}^2g(\beta)\, {}^2G_{xy}]\ d\beta} \tag{11}$$

K_1 and K_2 are normalization constants, f and $1-f$ are the fractions of molecules distributed according to the distribution functions ${}^1g\ (\beta)$ and ${}^2g\ (\beta)$ respectively, and ${}^1G$ and ${}^2G$ are functions of the angles β α_{A_j}, α_{E_j} and δ_{ij}. Their expressions depend on the symmetry of the distribution. If both distributions are of the same symmetry, G may be factorized out of the square brackets of equations (9)-(11).

The above equations may be used to solve the orientation [f,g (β)] and to resolve the absorption and emission spectra into their different polarized components [h_i (λ) and k_j (λ), respectively].

We have studied the orientation of elongated and of planar molecules incorporated in stretched polyethylene films.

In the case of elongated molecules like 4,4' - dimethylstilbene and anthracene, the best fit with the experimental results was obtained when the distribution was described by two functions. The first function describes the number of molecules possessing isotropic distribution around their orientational axes ("axial" distribution) and as its maximum at $\beta = \pi/2$. This function corresponds to the random distribution [$g\ (\beta\ ) = \sin\beta$]. The second function possess a sharp maximum at around $\beta = o$. In this case an "axial" distribution is indistinguishable from a distribution in which all the molecules are with their planes parallel to the direction of stretching ("planar" distribution). Figure 4 shows the distribution of anthracene in the stretched film.

These distributions may be rationalized in view of the structural properties of stretched polyethylene films. It is now well established that when polyethylene is stretched, its molecules tend to orient themselves in the stretching direction. According to the model proposed by Hosemann[26,27] we may consider the stretched polymer as composed of domains in which the molecular chains are oriented parallel to each other and to the direction of stretching (the so called "paracrystals"), and domains in which no order can be observed. Accordingly, the two curves shown in Figure 4 may represent the distribution of molecules incorporated in the oriented domains of the polymer.

These observations may explain the fact that many compounds which do not possess a manyfold axis of symmetry fulfill the requirements of eq. (1)

According to this model bicyclic compounds which do not fulfill these requirements are also partitioned between the two phases of the stretched polyethylene. However, the oriented fraction exhibits a "planar" distribution. The distribution of naphtalene, as shown in Figure 5, may serve as an example of the distributions of these kind of compounds.

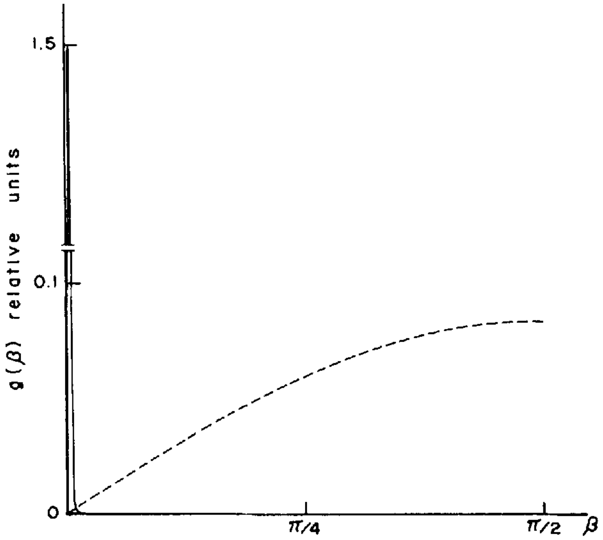

FIGURE 4: Distribution of anthracene molecules in stretched polyethylene: (——) oriented fraction, (---) unoriented fraction.

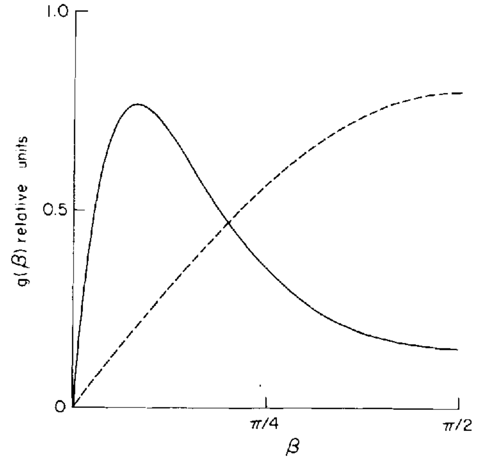

FIGURE 5: Distribution of naphthalene molecules in stretched polyethylene: (——) "planar" distribution, (---) "axial" distribution.

In case of disk-like molecules, the molecules in the oriented domains have isotropic distribution within their planes, as examplified by the distribution of coronene shown in Figure 6.

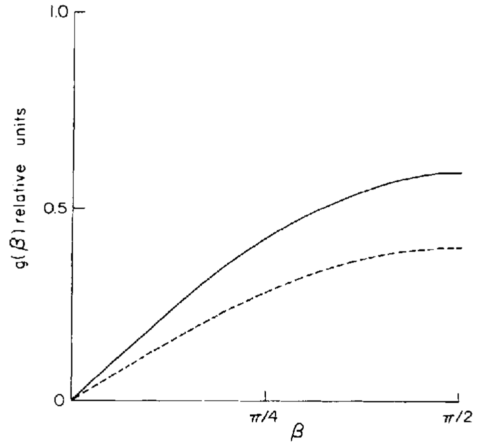

FIGURE 6: Distribution of coronene molecules in stretched polyethylene: (——) "planar" distribution, (---) "axial" distribution.

Since in the stretched polyethylene film the compound is partitioned between two different phases, this method can be applied only to molecules which have the same absorption spectrum and the same quantum efficiency of fluorescence in the two phases. Molecules which are strongly deformed in the excited state do not fulfill this requirements and, therefore, they can not be studied by this method. For example, tetraphenylbutatriene shows a strong Stokes shift in isotropic media which is strongly diminished in the crystalline state, in stretched polyethylene and in nematic phases. This behaviour is accompanied by an increase in the fluorescence intensity and by a strong increase in the quantum yield of photodimerization.[28] Similar effects have been observed in cynamic acid derivatives.

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