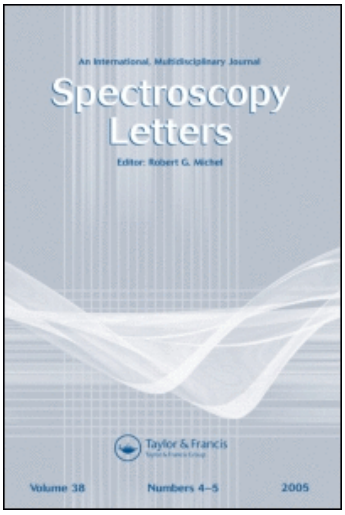

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ABSORPTION STATISTICS IN LINEAR DICHROISM

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Attention is called to an artifact in linear dichroism (LD), so called absorption statistics, which leads to reduced LD intensity in regions of high absorption. The reduction factor is larger than that governing the corresponding reduction in absorption, when LD is measured by using a Legrand-Grosjean circular dichroism spectrophotometer. In the case of infinite fibres at perfect order it coincides with the absorption statistical reduction factor of optical activity. The artifact was observed for β-carothene solubilized in lecithin liposomes oriented at flow.

The artifact generated by absorption statistics (Duysens' effect)[1] in suspensions manifests itself in the absorption spectrum by a decreased amplitude in spectral regions of high absorption by the particles. As has been recently shown by Gordon and Holzwarth[2] the effects on optical activity and circular dichroism are similarly decreased intensities in regions of high absorption. We here consider the corresponding influence on linear dichroism, of oriented suspensions of elongated dichroic particles.

Let us discuss a case in which absorbing elongated rectangular particles (dimensions $d_1 x d_s x d_s$, $d_1 >> d_s$) are arranged according to Figure 1, at complete order. Using Duysens' way of reasoning and the notations of Gordon and Holzwarth, the transmittance of h cm suspension, T_{sus}, will be given by

$$T_{sus} = \int_0^h P(z)\exp(-\alpha z)dz \qquad (1)$$

where P(z) is the probability of finding a path of length z through absorbing matter and l-z through the transparent solvent. The absorbance (base e) is consequently $A_{sus} = -\log_e T_{sus}$. The absorption statistics is due to P(z)=1, or that different "rays" have varying probability of interacting with a given number of particles. The absorption coefficient, α, of the particle is defined so that the solution of infinitely small particles at a concentration (=volume fraction) q has the absorbance (base e)

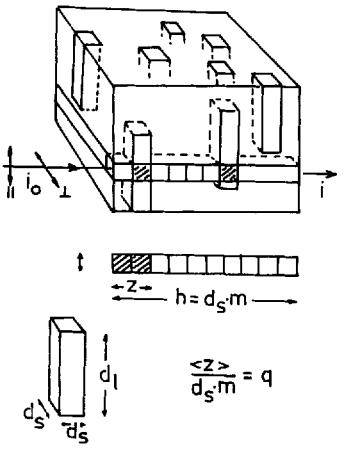

FIG. 1

$$A_{sol} = \alpha q h \qquad (2)$$

This is the Bouguer-Lambert-Beer law. If we look upon a horizontal layer of thickness d_s parallel to the direction of propagation of light we have a random distribution of cubic boxes cut out from the particle rods each having an edge d_s. Each beamlet $i_o \rightarrow i$ traverses a column of area d^2 and length h which can be divided into $m = h/d_s$ cubic solution boxes of volume d^3. The volume concentration q defines the probability that a given box will contain a particle and (1-q) the probability that it will contain only solvent. The net "particle path" z can assume discrete values $z = nd$, $n = 0,1,2 \ldots, m$. P(z) then becomes the binomial probability

$$P_n = \frac{m!}{n!\,(m-n)!}\, q^n (1-q)^{m-n} \qquad (3)$$

The average transmission of one particle is $T_p = e^{-\alpha d_s}$ (we have so far assumed isotropic particle absorption) and for the suspension

$$T_{sus} = \sum_{n=0}^{m} \frac{m!}{n!\,(m-n)!}\, q^n (1-q)^{m-n}\, T_p^{\,n} = 1 - q(1-T_p)^m$$

It is in general realistic to assume $q << 1$ so $A_{sus} \approx qm(1-T_p)$ or the absorption is given by

$$A_{sus} \equiv Q_A A_{sol} \equiv Q_A \alpha q h$$

$$\text{where } Q_A = (1 - e^{-\alpha d_s})/\alpha d_s \tag{4}$$

This is identical with Duysens' formula for a suspension of cubic particles. If the light is instead propagated along the particle fibre axes the effect of absorption statistics is strengthened according to $T_p = e^{-\alpha d_1}$, $m = h/d_1$, $A_{sus} \equiv qm(1-T_p)$, which is realized by dividing the solution into columns of cross-section $d_s x d_s$, containing h/d_1 non-cubic boxes, whereof n are absorbing).

If linear dichroism is obtained by measuring $A_{||}$ and $A_{\perp}$ separately, the same correction for absorption statistics applies:

$$(A_{||} - A_{\perp})_{sus} = Q_{LD}(A_{||} - A_{\perp})_{sol} \equiv Q_{LD}(\alpha_{||} qh - \alpha_{\perp} qh)$$

$$\text{with } Q_{LD} = (e^{-\alpha_{\perp} d_s} - e^{-\alpha_{||} d_s})/(\alpha_{||} - \alpha_{\perp})d_s \tag{5}$$

Here $\alpha_{||}$ and $\alpha_{\perp}$ denote specific absorption coefficients with polarization of the electric radiation field parallel and perpendicular to the particle fibre axis, respectively.

However, as in the case of circular dichroism detected with a Grosjean-Legrand instrument, linear dichroism measured differentially with similar photomodulation technique at a fixed incident light intensity, will depend linearly on z and is to be intensity averaged[2] according to

$$LD = \frac{\int_0^h P(z)(\alpha_{||} - \alpha_{\perp}) z e^{-\alpha z} dz}{\int_0^h P(z) e^{-\alpha z} dz} \tag{6}$$

$$(\alpha_{||} - \alpha_{\perp} << \alpha = (\alpha_{||} + 2\alpha_{\perp})/3)$$

From this follows that

$$Q_{LD} = e^{-\alpha d_s} \tag{7}$$

We may perhaps not apprehend d as the real particle dimension but more as an optical parameter of the model. Thus from knowledge of α (which is generally possible to determine separately) the experimental flattening in the absorption is obtained and Q_{LD} may be calculated from eqs. (4), (7).

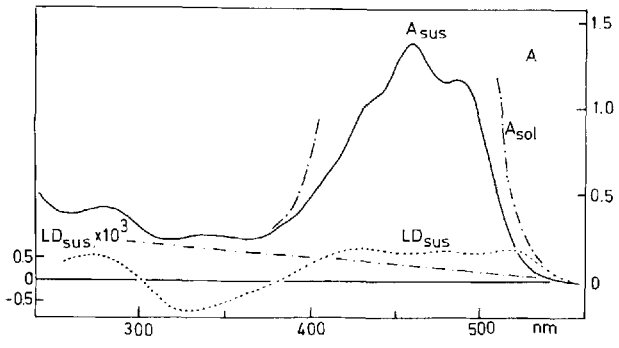

FIG. 2
Absorption statistical effect on LD of oriented lecithin/liposome/carothene solution

Generally the orientation is not complete but the particles are for instance distributed (we assume in a uniaxial way) at an average angle, say $0 \ll \langle\theta\rangle \ll 45^{o}$, to the orientation direction. The light path in a particle is then average $d_s(1 + 1/\cos\theta)/2$ ($d_l \gg d_s$) and

$$Q_{LD} \approx e^{-\alpha d_s(1 + 1/\cos\langle\theta\rangle)/2} \qquad (8)$$

A complete treatment requires the explicit expression of T_p, then Q_{LD} is obtained as $-qm\ (\partial T_p/\partial A_{sol})$. The result has to be averaged over the appropriate molecular distribution function, which implies a problem analogous with that of polydisperse solution.

An alternative way of approach is to consider, f, the order parameter be the fraction of completely aligned fibres, 1-f being a randomly oriented fraction. Then one obtains

$$LD_{sus,f} = fe^{-\alpha d_s}(\alpha_{||} - \alpha_{\perp})qh \qquad (9a)$$

$$A_{sus,f} \approx \{f[(1 - e^{-\alpha d_s})/\alpha d_s] +$$

$$+ (1 - f)[(1 - \exp\alpha(d_1 + 2d_s)/3)/\alpha(d_1 + 2d_s)/3]\}\alpha qh \qquad (9b)$$

Eq. (8b) may be used when A in LD/A refers to the random solution (f = 0).

Fig. 2 shows the effect of absorption statistics in a solution of lecithin liposomes containing solubilized β-carothene. A "new" LD maximum above 520 nm and a predominant negative LD band corresponding to weak absorption at 340 nm (known to have perpendicular polarization are characteristic point that may be noted. Due to possible solvent effects A_{sol} was difficult to estimate. However, from the knowledge that the broad absorption complex between 370-550 nm derives from a transition polarized parallel to the polyene chain we expect the LD curve to have the same shape as the A_{curve}. Hence the flattering of LD_{sus} as compared to A_{sus} proves that $\exp(-\alpha d_s)$ yields a harder reduction than $[1 - \exp\alpha(d_1 + 2d_s)/3]/\alpha(d_1 + 2d_s)/3$ does. We substitute d_1 and d_s with an average d and get the following hopefully useful equation holding for a band of pure polarization, that is one with a constant $LD(\lambda)_{sol}/A(\lambda)_{sol}$.

$$\frac{LD(\lambda)_{sus,f}}{A(\lambda)_{sus,f=0}} = \frac{f(\alpha_{||} - \alpha_{\perp})}{\alpha} \cdot \frac{Q_{LD}(\lambda)}{Q_A(\lambda)} \qquad (10)$$

Q_{LD} and Q_A may now be obtained as follows: 1. The wavelength-independent factor $f(\alpha_{||} - \alpha_{\perp})/\alpha$ is determined by observing LD_{sus}/A_{sus} at a wavelength of small absorption, where $Q_{LD}/Q_A = 1$. 2. Q_{LD}/Q_A is calculated at a "safe point", viz. the absorption maximum where influence by solvent shift can be neglected. 3. d is obtained by scaling any ε curve valid for a real solution.

The uncertain A spectrum for the β-carothene solution made us use instead a simulated example, the Gaussoid A_{sol}, Fig. 3. Q_{LD}/Q_A = 0.074 obtained at abs. max. in Fig.2 yields d=4.0. With $\alpha=9.2\cdot10^{4}$ cm^{-1}, $d=4.3\cdot10^{-5}$ cm. The liposomes may actually be as large as 10^{-4}cm. The LD_{sus} and A_{sus} spectra are then calculated according to the table.

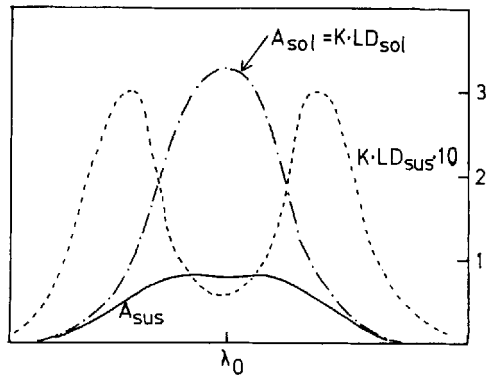

FIG. 3
Absorption statistics on A and LD for purely polarized band.

TABLE

A_{sol}	αd	Q_{LD}	Q_A	Q_{LD}/Q_A
3.3	4.00	0.018	0.245	0.074
3.0	3.64	0.026	0.267	0.098
2.5	3.03	0.048	0.314	0.154
2.0	2.42	0.089	0.376	0.236
1.5	1.82	0.162	0.460	0.352
1.0	1.21	0.298	0.580	0.514
0.5	0.61	0.543	0.749	0.726
0.25	0.30	0.741	0.864	0.858
0.10	0.12	0.886	0.951	0.930

The discussed case is only one example of a system prone to absorption statistics. We shall expect similar effect with a coloured solution in which large transparent particles are dispersed, with liquid crystals containing transparent domains, etc.

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