The Correction of the Relation of the Optical Density Ratio to the Stretch Ratio on the Dichroic Spectra*

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Previously,[1] in order to analyze the dichroic spectra and determine the transition directions of the electronic bands of molecules in the stretched PVA sheet, an expression was proposed for the density ratio ($R_d = D_{\parallel}/D_{\perp}$) as a function of the stretch ratio (R_s). In the course of the derivation, however, the author made a mistake in the description of the surface element, $\rho(\theta_0)$; therefore, the distribution function was not correct. For that reason, the proposed expression was also incorrect, though it could explain some experimental results obtained under certain conditions.[1,2]

In the present communication the author shall give the correct description of $\rho(\theta_0)$ and derive anew the distribution function $f(\theta)$ and the R_d expression. Further, it will be shown how the orientation angle of the transition moment can be obtained practically.

Figure 1 illustrates schematically the previous statement[1] of the deformation of a sphere with a unit radius into a spheroid with the same volume. The long axis of the spheroid is taken as the Z axis (the stretching direction). On the assumption that the deformation is made under a constant volume, the angle θ_0 of any unit vector in the sphere will be transformed into θ in the spheroid as follows:

$$\tan\theta_0 = R_s \tan\theta \tag{1}$$

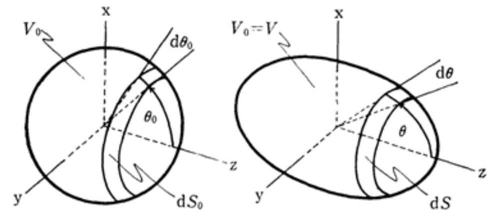
where both θ_0 and θ are defined in the region $0-\pi/2$. The distribution function, $f(\theta)$, after stretching, is expressed as:

$$f(\theta) = \int_0^{\pi/2} G(\theta,\theta_0) F(\theta_0) \mathrm{d}\theta_0 = \int_0^{\pi/2} \delta(\theta-\theta_0)\rho(\theta_0) F(\theta_0)\mathrm{d}\theta_0 \tag{2}$$

where $F(\theta_0)$ ($=\sin\theta_0$) is the distribution before stretching; $G(\theta, \theta_0)$, the transformation function, and δ, the delta function. From the relation $\mathrm{d}V_0 = \mathrm{d}V$ (Fig. 1), we have:

$$h/h_0 = \mathrm{d}S_0/\mathrm{d}S = \rho(\theta_0)$$

hence:



$$\mathrm{d}S_0 = 2\pi \sin\theta_0 \mathrm{d}\theta_0 \qquad \mathrm{d}S = \frac{2\pi R_s^{2/3} \sin\theta \,\mathrm{d}\theta}{\sqrt{1+(R_s^2-1)\sin^2\theta}}$$

$$\mathrm{d}V_0 = h_0 \mathrm{d}S_0 \qquad \mathrm{d}V = h \,\mathrm{d}S$$

Fig. 1. The schematic illustration for the deformation from a sphere to a spheroid under a constant volume.

$$\rho(\theta_0) = R_s^{-2/3}\sqrt{1+(R_s^2-1)\sin^2\theta}\,\frac{\sin\theta_0}{\sin\theta}\,\frac{\mathrm{d}\theta_0}{\mathrm{d}\theta} = R_s^{1/3}\sqrt{1+(R_s^2-1)\sin^2\theta}\,\frac{\sin\theta_0}{\sin\theta}\,\frac{\cos^2\theta_0}{\cos^2\theta}$$

because, by Eq. 1, we can write $\mathrm{d}\theta_0/\mathrm{d}\theta = R_s\cos^2\theta_0/\cos^2\theta$. Therefore, Eq. 2 becomes:

$$f(\theta) = \int_0^{\pi/2} \delta(\theta-\theta_0) R_s^{1/3}\sqrt{1+(R_s^2-1)\sin^2\theta} \times \frac{\sin^2\theta_0\cos^2\theta_0}{\sin\theta\cos^2\theta}\mathrm{d}\theta_0$$

$$= \int_0^{\pi/2} \delta(\theta-\theta_0) R_s^{1/3}\frac{\sqrt{1+(R_s^2-1)\sin^2\theta}}{\sin\theta\cos^2\theta} \times \frac{\tan^2\theta_0}{(1+\tan^2\theta_0)^2}\mathrm{d}\theta_0$$

By eliminating $\tan\theta_0$ by Eq. 1, that is to say, by carrying out the integration with respect to θ_0, we obtain:

$$f(\theta) = R_s^{1/3}\frac{\sqrt{1+(R_s^2-1)\sin^2\theta}}{\sin\theta\cos^2\theta} \times \frac{R_s^2\tan^2\theta}{(1+R_s^2\tan^2\theta)^2}$$

or

$$= R_s^{7/3}\sin\theta\{1+(R_s^2-1)\sin^2\theta\}^{-3/2}$$

The further integration of $f(\theta)$ with respect to θ in the region of $0-\pi/2$ gives $R_s^{1/3}$. Therefore, $R_s^{-1/3}f(\theta)$ is normalized. Rewriting this normalized function by $f(\theta)$ again, the distribution function becomes:

$$f(\theta) = R_s^2\sin\theta\{1+(R_s^2-1)\sin^2\theta\}^{-3/2} \tag{3}$$

* Dichroism of Dyes in the Stretched PVA Sheet. V. IV: Y. Tanizaki and H. Ono, This Bulletin, 33, 1207 (1960).

1) Y. Tanizaki, This Bulletin, 32, 75 (1959).
2) Y. Tanizaki, ibid., 33, 979 (1960).

Equation 3 is the corrected distribution function required.

The correct R_d equation against R_s for a parameter r, therefore, can be obtained as follows, using the same procedure as that described in the previous paper:[1)]

$$\left.\begin{aligned} R_d &= \frac{2+2(2r^2-1)T}{(2r^2+1)-(2r^2-1)T} \\ T &= \frac{R_s^2}{R_s^2-1}\left[1-\left\{\frac{\pi}{2}-\tan^{-1}(R_s^2-1)^{-1/2}\right\}\right. \\ &\qquad \left.\times(R_s^2-1)^{-1/2}\right] \\ R_s &> 1 \end{aligned}\right\} \quad (4)$$

The parameter r has the following meaning: $\cot^{-1} r$ provides the angle of the transition moment against the orientation axis which is considered to be peculiar to the molecular species.

If the orientation axis is peculiar to the molecular species, namely, if the r-value is independent of R_s, the orientation angle of the transition moment must be decided from Eq. 4 by substituting the observed R_d and R_s values. According to our experiences with the dichroic measurement, however, in some cases, the r-value is not invariant with R_s, as in the examples shown in Fig. 2. In that case, the r-value extrapolated to $R_s=1$ should be employed.

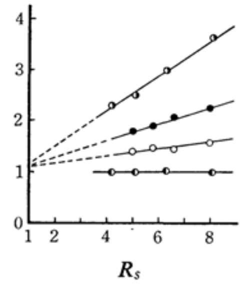


Fig. 2. Examples of the relations of r vs. R_s.
Sodium 4′-hydroxyazobenzene-4-sulfonate:
◑ at 365 mμ, ◐ at 244 mμ
Chrysoidine:
● at 460 mμ, ○ at 240 mμ

The warrant for the appropriate deformation of the sample sheet by stretching will be given by the fact that the ratio of $(D_{\parallel}+2D_{\perp})$ for any R_s to D for $R_s=1$ (i.e., nonstretching) at the same wavelength is invariant for the observed region.

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