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Abstract

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PHYSICS

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CALCULATION OF THE STATIONARY VALUE OF REVERSIBLE PHOTODICHROISM IN VISCOUS SOLUTIONS

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To investigate the phenomenon of reversible orientational photodichroism in viscous dye solutions described in (^{1}), it is necessary to establish the relation between the measured characteristics of the phenomenon and the properties of the system under study.

The proposed calculation is carried out for a model according to which a dye molecule located in a continuous viscous medium, represented in the form of a classical oscillator, after absorbing a light quantum turns with probability β through some mean angle α. In this case, turns in all directions relative to the initial orientation of the oscillator representing the molecule are assumed equally probable. It is also assumed that the stationary function of the orientational distribution of the dye molecules differs only slightly from the function of the isotropic distribution, equal to $1/4\pi$.

Fig. 1

The calculation was performed according to the following scheme:

1. The orientational flux arising as a result of the sharp anisotropy of molecular absorption when the solution is illuminated with polarized light in the region of the absorption band is calculated.
2. From the condition of equality of the orientational flux and the flux of rotational diffusion, which restores the initial isotropy of the system, the stationary function of the orientational distribution of the oscillators describing the dye molecules is calculated.
3. From the known orientational distribution function, by integration over all orientations and over the thickness of the solution layer, the stationary value of the dichroism of the solution is found.

The calculation was carried out in spherical coordinates; the direction of the electric vector in the orienting light beam was chosen as the z-axis (see Fig. 1).

1. Calculation of the flux. It is obvious that the orientational distribution function has axial symmetry with respect to the direction z—the electric vector in the beam of orienting light. As a result, only the meridional component of the orientational flux can be different from zero. To calculate this component at points on the circle $\theta' = \theta$ (where θ' is the variable azimuthal angle, i.e., the angle between the axis of the oscillator and the Z-axis, and θ is the angle fixed during the calculation of the orientational flux), one should sum the meridional components of the fluxes from spherical layers $d\theta'$, taking into account the dependence of the probability of absorption on θ' (for the oscillator $k_{\theta'} = k\cos^2\theta'$) and taking into account only the meridional components α_{m} of the oscillator rotation angle α (see Fig. 1).

In integrating, it should be borne in mind that the contribution of each elementary layer $d\theta'$ to the flux on the circumference $\theta' = \theta$ is determined by the fraction of absorbing molecules for which the meridional component α_{m} of the oscillator rotation angle α is greater than $|\theta - \theta'|$. The corresponding factor is, as can be shown:

$$\frac{1}{4\pi}\arccos\frac{|\theta-\theta'|}{\alpha} \simeq \frac{1}{4\pi}\left(1-\frac{|\theta-\theta'|}{\alpha}\right). \tag{1}$$

Under stationary conditions, in the layer $(\theta', \theta' + d\theta')$, per unit time $2\pi\beta nkNf(\theta')\cos^2\theta'\sin\theta'\,d\theta'$ molecules undergo rotation. Here β is the probability of rotation of a molecule that has absorbed a quantum; n is the number of molecules per unit volume; k is the molecular absorption coefficient; N is the number of quanta incident per unit time per unit surface of the solution.

The flux from the layer $(\theta', \theta' + d\theta')$ at the points of the circumference $\theta' = \theta$ is equal to

$$\frac{1}{\pi}\beta nkNf(\theta')\cos^2\theta'\left(1-\frac{|\theta-\theta'|}{\alpha}\right)d\theta', \tag{2}$$

and the total photoorientation flux is

$$I_{\mathrm{op}}(\theta) = \frac{1}{\pi}\beta nkN\left[\int_{\theta-\alpha}^{\theta} f(\theta')\cos^2\theta'\left(1-\frac{|\theta-\theta'|}{\alpha}\right)d\theta' - \int_{\theta}^{\theta+\alpha} f(\theta')\cos^2\theta'\left(1-\frac{|\theta-\theta'|}{\alpha}\right)d\theta'\right]. \tag{3}$$

According to the assumption made above, $f(\theta)$ differs little from $1/4\pi$; therefore, in the interval $\theta \pm \alpha$ we put $f(\theta') = f(\theta)$.

The orientation flux is then equal to:

$$I_{\text{op}}(\theta) = \frac{4\alpha^2}{3\pi}\beta kn\, N f(\theta)\sin 2\theta. \tag{4}$$

2. Calculation of the distribution function

The stationary function of the orientational distribution is found from the condition $I_{\text{op}} = I_{\text{diff}}$, where $I_{\text{diff}} = B\,\partial f(\theta)/\partial\theta$, and B is the constant of rotational diffusion.

The equation for $f(\theta)$ is obtained in the form

$$\frac{4}{3\pi}\alpha^2\beta kn\, N f(\theta)\sin 2\theta = B\,\frac{\partial f(\theta)}{\partial\theta} \tag{5}$$

or

$$\frac{\partial f}{\partial\theta} = \gamma f\sin 2\theta,$$

where

$$\gamma \equiv \frac{4}{3\pi}\alpha^2\beta k\, Nn\,\frac{1}{B}. \tag{5a}$$

Hence

$$f(\theta) = Ce^{-\frac{\gamma}{2}\cos 2\theta}. \tag{6}$$

The expression obtained can be replaced by the first terms of its expansion in a series in powers of γ, taking into account that, according to the assumption made above, $f(\theta)$ differs little from the isotropic distribution. In the linear approximation,

$$f(\theta) = C\left(1 - \frac{\gamma}{2}\cos 2\theta\right). \tag{7}$$

The constant C can be obtained from the normalization condition

$$8\int_0^{\pi/2}\int_0^{\pi/2} f(\theta)\sin\theta\, d\theta\, d\varphi = 1. \tag{8}$$

From (7) and (8) it follows that

$$f(\theta) = \frac{(1 - \frac{\gamma}{2}\cos 2\theta)}{4\pi\left(1 - \frac{\gamma}{6}\right)}. \tag{9}$$

3. Calculation of the dichroism. By definition, the dichroism is equal to:

$$d = \frac{D_\perp - D_\parallel}{D_\perp + D_\parallel} \simeq \frac{D_\perp - D_\parallel}{2D},$$

where $D_\perp$ and $D_\parallel$ are the optical densities corresponding to two mutually perpendicular directions of the electric vector in the measuring light beam. The signs $\parallel$ and $\perp$ in our case determine the direction of polarization of the measuring beam relative to the polarization of the orienting beam.

To calculate $D_\parallel$, a new variable x is introduced, describing the length of the path of light in the solution. We assume that the Bouguer–Beer law holds, i.e., $N(x) = N_0 e^{-knx}$, where $N(x)$ is the quantum intensity of light as a function of the path traversed by the light.

On the basis of (5a) one can write $\gamma(x) = \gamma_0 e^{-knx}$, where $\gamma_0 = 3a^2knN_0/4\pi B$. $D_\parallel$ is found by integrating $f(\theta)\cos^2\theta$ over all orientations and over the thickness of the solution layer, taking into account the dependence $\gamma = \gamma(x)$:

$$D_\parallel = 8kn\int_0^{x_0} dx \int_0^{\pi/2}\int_0^{\pi/2} f(\theta)\cos^2 \sin\theta\, d\theta\, d\varphi = \frac{knx_0}{3} - \frac{4}{45}\gamma_0(1 - T), \tag{10}$$

where x_0 is the thickness of the solution layer, and $T = e^{-knx_0}$ is its transmittance.

It is obvious that $knx_0/3 = D$, where D is the optical density of the layer under study for an isotropic distribution of molecules.

To calculate $D_\perp$ it is necessary to pass to a new coordinate system (ψ, η), associated not with the orienting beam but with the measuring beam, in which the z-axis is directed along the electric vector of the measuring beam:

$$D_\perp = 8kn\int_0^{x_0} dx \int_0^{\pi/2}\int_0^{\pi/2} f'(\psi, \eta)\sin\psi\, d\psi\, d\eta. \tag{11}$$

Integrating, we find

$$D_\perp = \frac{knx_0}{3} + \frac{2}{45}\gamma_0(1 - T). \tag{12}$$

From (10) and (11) we obtain the required expression for the stationary value of the orientational photodichroism:

$$d_0 = \frac{2}{15}\frac{\gamma_0(1-T)}{2D} = \frac{2}{15}\frac{3a^2\beta kn}{4\pi B}\frac{1-T}{2D}. \tag{13}$$

The value of d_0 obtained in this way is the linear term in the expansion of the true value d_0 in powers of γ_0. Usually this approximation proves sufficient, since d_0 and, correspondingly, γ_0 are very small. But in some cases d_0 reaches several percent under experimental conditions. In that case, it becomes impossible to restrict oneself to the linear approximation for describing the phenomenon.

The calculation of the second approximation is somewhat more complicated than the one given above, and since no new physical assumptions were made in the course of the calculation, only its result is given here; the first term of it coincides with (13):

$$d_0^{(2)} = \left[\frac{2}{15}\gamma(1-T) - \frac{1}{60}\gamma^2(1-T^2)\right]/2D. \tag{14}$$

Analysis of experimental data with the aid of this expression apparently may help in clarifying the principal question of the study: what are the causes and what is the mechanism of reorientation of molecules after absorption of a light quantum.

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CITED LITERATURE

[1] B. S. Neporent, O. V. Stolbova, *Optics and Spectroscopy*, **10**, 278 (1961).

Note: Figure translations are in progress. See original paper for figures.

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