D and S Order Parameters from Planar and Homeotropic Orientation Using Unpolarized Light

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Using cells of glass of quartz coated with transparent electrodes, it is easy to achieve either planar or homeotropic orientation of a nematic liquid crystal. Various surface treatments like rubbing the glass surface, coating the surface with polyvinylalcohol or polyimide, or evaporating oxides oblique to the surface, will give planar orientation.[1] When a d.c. or an a.c. voltage is applied, however, a homeotropic orientation will result for liquid crystals with positive dielectric anisotropy. By using a microscope hot stage with crossed polarizers the nematic to isotropic transition is easily seen. The transition takes place at the same temperature whether the liquid crystal is oriented by surface treatment, or by an electric field. The overall order of the phase is not influenced by the field, only the direction of the director. The behaviour of several anthraquinone dyes as guests in a liquid crystal host has recently been studied in this laboratory.[2] For this investigation it was of interest to develop a relationship between the absorption of light and the order parameter of the guests. In the present communication the relationship between the absorption of unpolarized radiation in the planar and homeotropic modes and the order parameters S and D will be derived.

Let us consider a rigid molecule with an axes system x', y', and z', in which z' is the long axis of the molecule. We shall be looking at a molecular absorption transition of oscillator strength f (proportional to the square of the transition moment) which makes an angle α with the z'-axis, and whose projection on the x' y'-plane makes an angle β with the x'-axis.

X, Y, Z is a macroscopic coordinate system with the Z-axis along the C_∞-axis of the nematic sample, usually refered to as the director of the sample. The angle between the Z-axis and the z'-axis of a given molecule is θ. The angle ϕ gives the orientation of the $x'z'$-plane of a molecule relative to the XZ-plane of the laboratory frame (see Fig. 1).

$$\text{Let } \begin{aligned} f_{x'} &= f \sin^2 \alpha \cos^2 \beta \\ f_{y'} &= f \sin^2 \alpha \sin^2 \beta \\ f_{z'} &= f \cos^2 \alpha \end{aligned} \tag{1}$$

By applying the Euler transformations, and calculating the ensemble average over the nematic sample Korte[3] has shown that the mean absorption along the three macroscopic axes will be:
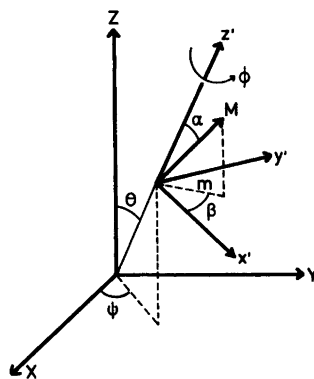

Fig. 1. The angles used to describe a transition moment M in the molecular frame of reference (x', y', z'), and angles describing the molecule in the laboratory frame (X, Y, Z).

$$\bar{f}_x = \bar{f}_y = f/3 \cdot \{1 - S \cdot [\tfrac{1}{2}(3\cos^2\alpha - 1)] + \tfrac{1}{2} \cdot D \cdot \sin^2\alpha \cos 2\beta\} \tag{2}$$

$$\bar{f}_z = f/3 \cdot \{1 + 2S \cdot [\tfrac{1}{2}(3\cos^2\alpha - 1)] - D \cdot \sin^2\alpha \cos 2\beta\} \tag{3}$$

Where the usual definitions of $S = \tfrac{1}{2}(3\,\overline{\cos^2\theta} - 1)$ and $D = \tfrac{3}{2}\,\overline{\sin^2\theta\,\cos 2\phi}$ are used.

The bars indicate an averaging over all molecules in the sample, and S gives the order of the long axis of the molecules with respect to the nematic director. D is an order parameter introduced[4] in order to describe the different tendency of the two molecular short axes to project onto the director. Therefore D is related to the biaxiality (λ) of the molecules. If γ is any tensor property of a molecule, λ can be expresssed as:

$$\lambda = \frac{\sqrt{6}}{4}\,\frac{\gamma_{yy} - \gamma_{xx}}{\gamma_{zz} - \tfrac{1}{2}\gamma_{yy} - \tfrac{1}{2}\gamma_{xx}}$$

Where γ_{zz}, γ_{yy}, γ_{xx} are the components of the tensor after it is diagonalized.[5] A numerical solution of D as a function of biaxility, γ, and the S order parameter has been given.[6]

We have called the absorbances in the planar and the homeotropic modes A_p and A_h, respectively. By a suitable surface treatment and in the absence of electric fields, the molecules of the nematic sample are supposed to have their long axis parallel to the glass plate, and therefore be oriented in the planar mode. The Z- and Y-axes will thus be parallel to the glass plate. The absorbances A_p and A_h are proportional to the concentration (c), thickness of the sample (d), and oscillator strenght (f), δ being the constant of proportionality. We introduce the normalized absorbances A'_p and A'_h to simplify the equations. $A'_p = A_p/\delta cd$ and correspondingly for A'_h.

$$A'_p = \bar{f}_z + \bar{f}_y = 2f/3 + f \cdot \{\tfrac{1}{3} \cdot S \cdot [\tfrac{1}{2}(3\cos^2\alpha - 1)] - \tfrac{1}{6} \cdot D \cdot \sin^2\alpha \cos 2\beta\} \tag{4}$$

After applying an electric field of sufficient strength (in the order of 10^4 V/cm), nematogens with positive dielectric anisotropy will be oriented normal to the glass plate. In this homeotropic orientation the Z-axis will be normal to the cell walls and we observe the absorption along the X- and Y-axes.

$$A'_h = 2f/3 - 2f \cdot \{\tfrac{1}{3} \cdot S \cdot [\tfrac{1}{2}(3\cos^2\alpha - 1)] - \tfrac{1}{6} \cdot D \cdot \sin^2\alpha \cos 2\beta\} \tag{5}$$

By combining eqns. (4) and (5) the following expressions are derived:

$$f = (A'_h + 2A'_p)\tfrac{1}{2} \tag{6}$$

$$A'_p - A'_h = f\{S[\tfrac{1}{2}(3\cos^2\alpha - 1)] - \tfrac{1}{2} \cdot D \cdot \sin^2\alpha \cos 2\beta\} \tag{7}$$

After substituting eqn. (6) into (7) and multiplying both the numerator and the denominator by δcd we obtain the present equation:

$$2(A_p - A_h)/(2A_p + A_h) = S \cdot \tfrac{1}{2}(3\cos^2\alpha - 1) - \tfrac{1}{2} \cdot D \cdot \sin^2\alpha \cos 2\beta \tag{8}$$

When the angles α and β are known for at least two transitions, either from independent measurements or from symmetry reasons, the order parameters S and D can be determined from eqn. (8). All the factors of the left hand side fraction can be determined from absorption spectra, and two transition bands are sufficient to determine S and D at a given temperature.

Transition moment directions for electronic transitions can be found using the stretched film method. See Thulstrup and Michl[7] for a recent review of the method. For stretching frequencies in the infrared region the transition moment vector will usually be parallel to the group in question, and the angles α and β can thus be determined by geometrical considerations.

The angles α and β are regarded as constants, and do not change with temperature. If three or more distinct bands are present one can thus always measure at several temperatures and will eventually get an overdetermined system of equations. Each new temperature introduced two new unknowns $S(T)$ and $D(T)$ which are temperature dependent, but also gives n independent equations, where n is the number of distinct bands.

An alternative method for obtaining the order parameters from absorption data involves measurements using polarized light. This procedure can lead to inaccuracies due to experimental difficulties,[8] because most photodetectors are not equally sensitive to all polarizations. Eventually, absorption measurements can be performed in the liquid crystalline and the isotropic liquid phases.[9] In view of the simple experimental setup and the few corrections necessary eqn. (8) should be useful for determining the order parameters in nematic liquid crystals.

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