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Structural ordering and spectral properties of smectic A with biaxial solute molecules

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The influence of (i) orientational-translational ordering of solvent and solute molecules, (ii) anisotropic intermolecular solute-solvent interactions and (iii) the features of the electronic structure of biaxial solute molecules dissolved in a smectic A phase on the spectral position of polarized bands of a solute electronic absorption has been investigated. Equations for the positional-orientational pseudopotential in a pure smectic A doped with biaxial solute molecules have been obtained within the framework of the molecular statistical approach. The question about the correlation of contributions of partial orientational and translational molecular ordering to the spectral properties of a molecular system has been answered.

1. Introduction

The spectral properties of anisotropic media with partial orientational-translational ordering are of interest for the development of optical recording devices. Liquid crystals with a wide range of thermodynamically stable phases and a combination of different types of orientational and translational molecular ordering are convenient models of such media. In consequence, the influence of anisotropic intermolecular interactions and the structural features of smectics on the spectral properties of these systems is a significant problem.

The spectral features of the electronic absorption of uniaxial solute molecules dissolved in a smectic A phase have been studied theoretically [1]. However solute molecules of practical interest (e.g. condensed ring systems) have a biaxial shape, which can change from lath-like (acenes) to disc-like (porphins, porphyrins, phthalocyanines). In consequence, the case of biaxial solute molecules requires special consideration in relation to both the molecular electronic structure (the orientation of the transition moments) and the orientational-translational statistics in a smectic phase, since the molecular biaxiality modifies qualitatively the anisotropic intermolecular interaction and hence the molecular pseudopotential in nematic and smectic phases.

Here, we study the influence of anisotropic intermolecular solute-solvent interactions, orientational-translational ordering of the solvent and solute as well as the features of the electronic structure of biaxial solute molecules in a smectic A on the position of polarized bands in the solute electronic absorption. General properties of the structural parameters characterizing the ordering and the orientational-translational statistics of biaxial solute molecules in a smectic A are investigated in §2. Equations for the positional-orientational pseudopotential in a smectic A formed of biaxial molecules and for biaxial solutes in a smectic A formed of uniaxial and biaxial molecules are developed in §3. Section 4 is concerned with translational-orientational effects on the spectral position of polarized bands of the solute electronic absorption.

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2. The orientational-translational statistics for the solute dissolved in a smectic A

A theory for the spectral properties of a partially aligned molecular media has to be based on a molecular statistical theory of these objects and to use the structural parameters of the system, which can be determined directly or indirectly from experiment. We shall consider smectic A phases formed of non-chiral molecules and solute molecules with C_{2v} , D_2 or D_{2h} symmetry. The solute concentration is considered to be so low that solute-solute interactions can be ignored.

The frame $(x_1y_1z_1)$ of a solute molecule is selected to diagonalize the Saupe ordering matrix

$$S_{ii} = \langle 3 \cos^2 \theta_{ir} - 1 \rangle / 2, \quad (i = x_1y_1z_1). \quad (1)$$

Here θ_{ir} is the angle made by the i th axis of the molecular frame with the director \mathbf{r} and the brackets $\langle \dots \rangle$ denote a statistical average. The axis z_1 corresponds to the maximum value of the principal components S_{ii} . For flat molecules with C_{2v} and D_{2h} symmetry the x_1 axis is in the plane of the molecule and the y_1 axis is perpendicular to this plane. The orientation of the director in the frame $(x_1y_1z_1)$ is determined by the polar angle $\theta = \theta_{ir}$ and the azimuthal angle ψ made by the x_1 axis with the projection of \mathbf{r} to the plane x_1y_1 . Orientational-translational ordering of the solute is characterized by the order parameters [2]

$$\langle D_{0n}^L(\theta, \psi) \cdot \cos k\xi \rangle = \int_0^d dz \int_0^{2\pi} d\psi \int_{-1}^1 d \cos \theta D_{0n}^L(\theta, \psi) \cos k\xi f(\theta, \psi, z), \quad (2)$$

where $D_{0n}^L(\theta, \psi)$ are Wigner rotation matrices of rank L , d is the smectic structure period, $\xi = 2\pi z/d$ and z is the translational coordinate of the centre of mass of a solute molecule along the axis $z \parallel \mathbf{r}$. The index $L \geq 0$ takes even values, the index $|n| \leq L$ takes zero and even values, the index k takes integer values. The single particle distribution function $f(\Omega, z)$ is subject to the normalization constraint

$$\int \int f(\Omega, z) dz d\Omega = 1. \quad (3)$$

From the solute absorption dichroism of the bands studied it is possible to determine the following orientational order parameters of the solute [3-5]

$$\left. \begin{aligned} S = S_{z_1z_1} &= \langle D_{00}^2 \rangle \equiv \langle P_2(\cos \theta) \rangle \equiv \langle P_2 \rangle, \\ G = S_{x_1x_1} - S_{y_1y_1} &= (3/2)^{1/2} \langle D_{0,2}^2 + D_{0,-2}^2 \rangle = 3 \langle \sin^2 \theta \cos 2\psi \rangle / 2 \equiv \langle D \rangle, \end{aligned} \right\} \quad (4)$$

where $P_2(\cos \theta)$ is a second Legendre polynomial. The translational order parameters $\tau_k = \langle \cos k\xi \rangle$ can be found from X-ray scattering data [6]. As the amplitudes of smectic harmonics for real smectic A phases with $k > 1$ are negligible according to the experiment [7] consideration can be restricted to $\tau_1 \equiv \tau$ [8]. Finally, orientational ordering in all known smectics requires the mixed order parameters

$$\sigma = \langle P_2 \cos \xi \rangle, \quad \kappa = \langle D \cos \xi \rangle$$

to be taken into account. From experimental information about some of the order parameters in equation (2) the best approximation for the real distribution function is the function $f(\Omega, z)$, which maximizes the informational entropy functional [9, 10]

$$\sum [f(\Omega, z)] = - \int f(\Omega, z) \ln f(\Omega, z) dz d\Omega, \quad (5)$$

taking into account equations (3) and (4). At known values of S , G , σ , κ and τ the maximum of the functional corresponds to

$$f(\Omega, z) = \exp[\lambda_P P_2 + \lambda_D D + \lambda_\sigma P_2 \cos \xi + \lambda_\kappa D \cos \xi + \lambda_\tau \cos \xi]/Z, \quad (6)$$

where the normalization factor Z is found from equation (3). The Lagrange multipliers λ_k are the solution of the system of equations

$$S = \frac{\partial \ln Z}{\partial \lambda_P}, \quad G = \frac{\partial \ln Z}{\partial \lambda_D}, \quad \sigma = \frac{\partial \ln Z}{\partial \lambda_\sigma}, \quad \kappa = \frac{\partial \ln Z}{\partial \lambda_\kappa}, \quad \tau = \frac{\partial \ln Z}{\partial \lambda_\tau}. \quad (7)$$

For uniaxial solute molecules at $G = \kappa = 0$ and $\lambda_D = \lambda_\kappa = 0$ equation (6) transfers to the one obtained before [1] and coincides with the trial function $f(\Omega, z)$ used in [11].

To characterize the statistical properties of orientational-translational molecular ordering and to describe the spectral properties of the solute besides the average values of the order parameters the following differences are important

$$\left. \begin{aligned} \Delta_P &= \langle P_2^2 \rangle - S^2, & \Delta_{PD} &= \langle P_2 D \rangle - SG, & \Delta_D &= \langle D^2 \rangle - G^2, \\ \Delta_{P\sigma} &= \sigma - S\tau, & \Delta_{P\kappa} &= \langle P_2 \cos \xi \rangle - S\sigma, & \Delta_{P\kappa} &= \langle P_2 D \cos \xi \rangle - S\kappa, \\ \Delta_{D\tau} &= \kappa - G\tau, & \Delta_{D\sigma} &= \langle P_2 D \cos \xi \rangle - G\sigma, & \Delta_{D\kappa} &= \langle D^2 \cos \xi \rangle - G\kappa, \end{aligned} \right\} \quad (8)$$

which can be presented as

$$\Delta_k = \frac{\partial^2 \ln Z}{\partial \lambda_k^2}, \quad \Delta_{kl} = \frac{\partial^2 \ln Z}{\partial \lambda_k \partial \lambda_l}, \quad (k, l = P, D, \sigma, \kappa, \tau) \quad (9)$$

using equations (2), (6) and (7).

Let us find the complete range of the changes in the parameters λ_k , Δ_k and Δ_{kl} . The orientational order parameter S of solute molecules in a solvent can change within the interval $0 \leq S < 1$; this corresponds to changing λ_P within the interval $0 \leq \lambda_P < \infty$. The parameter G characterizes the biaxiality of the tensor \hat{S} (cf. equation (1)) and is caused by the hindered rotation of solute molecules around their longitudinal axis z_1 . As $\text{Tr } \hat{S} = 0$, so in the frame $(S; G)$ with $S, G \geq 0$ all physically possible values of G are within the triangle [12–14] with the apex coordinates $(0; 0)$, $(0.25; 0.75)$ and $(1; 0)$. The abscissae corresponds to rod-like molecules. The line segment $G = 3S$ between the points $(0; 0)$ and $(0.25; 0.75)$ corresponds to disc-like molecules with $S_{z_1 z_1} = S_{x_1 x_1}$. This asymptote corresponds to the dependence $\kappa = 3\sigma$. The line segment $G = 1 - S$ between the points $(0.25; 0.75)$ and $(1; 0)$ corresponds to biaxial molecules with a common shape with $S_{y_1 y_1} = -1/2$ and rotation around the z_1 axis being absent. The values $G < 0$ are placed within the triangle made by the reflection of the one just considered relative to the axis of abscissae S .

These restrictions on G do not depend directly on the presence or absence of translational molecular ordering, which only modifies the trajectories $G(S)$ owing to the presence of the non-zero parameters λ_σ and λ_κ in equation (6) but does not influence the asymptotic value of λ_D/λ_P , which corresponds to the sides of the orientational triangle. So it is possible to determine this asymptotic value of λ_P/λ_D for the particular case of an uniaxial nematic matrix within the limit of large values of S and small values of G . Being restricted to the expansion terms, which are sufficient to determine the asymptote $G(S)$, from equation (6) we find

$$Z = \frac{4\pi}{3(\lambda_P^2 - \lambda_D^2)^{1/2}} \exp(\lambda_P). \quad (10)$$

Using equations (7) and (10) gives

$$S = 1 - \frac{\lambda_p}{\lambda_p^2 - \lambda_D^2}, \quad G = \frac{\lambda_D}{\lambda_p^2 - \lambda_D^2} \quad (11)$$

and

$$G = \frac{\lambda_D}{\lambda_p} (1 - S). \quad (12)$$

This means that the sign of G coincides with the sign of λ_D . At fixed S the maximum value $G = 1 - S$ corresponds to the side of the orientational triangle and agrees with equation (12) at $\lambda_D = \lambda_p$. So the physical possibility of changing λ_D for $G \geq 0$ is determined by the interval $0 \leq \lambda_D \leq \lambda_p$. It should be noted that the maximum entropy method cannot directly make any predictions for the inter-relations of the various λ_k in equation (6) [15]. Nevertheless, limiting values of the parameters λ_D and λ_x can be determined using the additional condition $\text{Tr } \hat{S} = 0$ and the dependences $G(S)$ on the sides of the orientational triangle (see the Appendix).

The difference Δ_p describes the non-uniformity of the angular distribution of longitudinal molecular axes in a sample relative to the director. The value

$$\Delta_p = \frac{1}{\lambda_p} (1 - S) \quad (13)$$

found from equations (9)–(12) does not depend on the sign of λ_D . The differences Δ_D and Δ_{pD} characterize the correlation between the angular distribution of the longitudinal molecular axes z_1 relative to the director and the angular distribution of the transverse axes x_1 and y_1 relative to the planes $z_1 \mathbf{r}$. From equations (9)–(12) we obtain the equality $\Delta_D = \Delta_p$, independent of the value of λ_D/λ_p . At $\lambda_D = \lambda_p$ this equality is valid within the region $0.25 \leq S \leq 1$ as it follows from equation (8) when $D = 1 - P_2$ is substituted into the equation for Δ_D . From equations (9)–(12) it also follows that

$$\Delta_{pD} = -\lambda_D \Delta_p / \lambda_p, \quad (14)$$

i.e. the sign of Δ_{pD} is opposite to the sign of λ_D and the asymptotic value $\lambda_D = \lambda_p$ corresponds to the equality $\Delta_{pD} = -\Delta_p$ being valid within the region $0.25 \leq S \leq 1$.

The remaining differences Δ_{kl} (cf. equation (8)) characterize correlations between non-uniformities of orientational and translational molecular distributions in a sample. At $0.25 \leq S \leq 1$ and $\lambda_D = \lambda_p$ substituting $D = 1 - P_2$ into equation (8) gives the following correlations

$$\left. \begin{aligned} \Delta_{D\tau} &= -\Delta_{p\tau}, & \Delta_{D\sigma} &= -\Delta_{p\sigma}, \\ \Delta_{p\kappa} &= \Delta_{p\tau} - \Delta_{p\sigma}, & \Delta_{D\kappa} &= -\Delta_{p\kappa}, \end{aligned} \right\} \quad (15)$$

and within this limit $\Delta_{p\tau}$ and $\Delta_{p\sigma}$ are the independent orientational-translational differences. Relative values and signs of $\Delta_{p\sigma}$ and $\Delta_{p\kappa}$ can be determined by neglecting the correlation of orientational and translational distributions in equation (9). Then $\Delta_{p\tau} = 0$ and at $\lambda_D = \lambda_p$ the correlations

$$\Delta_{p\sigma} = \Delta_{D\kappa} = \Delta_{p\tau}, \quad \Delta_{p\kappa} = \Delta_{D\sigma} = \Delta_{pD}\tau = -\Delta_{p\tau} \quad (16)$$

are valid. As the value of τ can be compared with unity, so at $\lambda_D = \lambda_p$ the values of $\Delta_{p\sigma}$ and $|\Delta_{p\kappa}|$ can be compared with Δ_p .

The connection of the parameters λ_k in equation (6) with solute and solvent molecular properties can only be determined within the framework of a molecular statistical theory of a smectic A phase with biaxial solute molecules.

3. The positional-orientational pseudopotential in a smectic A formed of biaxial molecules

A starting point of a molecular statistical theory is the choice of the form of the pair interaction potential $\mathcal{U}_{12}(\mathbf{r}_{12}, \Omega_{12})$ for molecules 1 and 2, which depends on the radius vector \mathbf{r}_{12} connecting the centres of mass of these molecules and the Euler angles $\Omega_{12}(\varphi_{12}, \theta_{12}, \psi_{12})$ determining the transition from the frame of molecule 2 to that of molecule 1. In the McMillan model [8] for a pure smectic A composed of uniaxial molecules the pair potential $\mathcal{U}_{12}(|\mathbf{r}_{12}|, \theta_{12})$ was assumed to have the form

$$\mathcal{U}_{12}(r_{12}, \theta_{12}) = -\frac{V_0}{nr_0^3\pi^{3/2}} \exp[-(r_{12}/r_0)^2][P_2(\cos \theta_{12}) + \delta], \quad (17)$$

where r_0 is the effective interaction radius having the value of order of the molecular aromatic core length, n is the molecular concentration in the sample. The parameter V_0 characterizes the strength of the anisotropic part of the intermolecular interaction and the parameter δ determines the relative contribution of its isotropic part. The molecular statistical theory developed on the basis of equation (17) with corresponding choice of the parameters gives a good qualitative and sometimes quantitative description of the behaviour of real smectics [7, 8, 16–18]. It shows that equation (17) reflects the main features of the interaction of uniaxial molecules in a smectic A phase.

However, real mesogenic or solute molecules are biaxial and the available experimental data [3, 19–21] make evident the correlation between translational ordering of biaxial molecules and their rotational mobility relative to the longitudinal axis z_1 . Thus a molecular biaxiality has to be reflected by the form of the potential \mathcal{U}_{12} . When the Maier–Saupe theory [22] developed for uniaxial nematics composed of uniaxial molecules is generalized to biaxial molecules [20, 23, 24], the change of the molecular shape is concerned with the change of the orientational dependence of the potential \mathcal{U}_{12} and the possible modification of its dependence $\mathcal{U}_{12}(r_{12})$ is not taken into account. The correlation of the theoretical and experimental dependencies $G(S)$ for solvent and solute biaxial molecules [3, 4, 5, 19, 23–26] verifies this supposition. So the possible generalization of equation (17) for biaxial molecules is the following

$$\mathcal{U}_{12}(r_{12}, \theta_{12}) = -\frac{1}{nr_0^3\pi^{3/2}} \exp[-(r_{12}/r_0)^2][\Phi(\Omega_{12}) + \delta']. \quad (18)$$

To start with we consider a pure smectic A when the parameter r_0 is the same for all pairs of molecules. The expansion of $\Phi(\Omega_{12})$ in a complete set of basis functions [27] is

$$\Phi(\Omega_{12}) = \sum_{Lpq} u_{Lpq} D_{pq}^L(\Omega_{12}), \quad (19)$$

where the expansion coefficients are

$$u_{Lpq} = \frac{2L+1}{8\pi^2} \int \Phi(\Omega_{12}) D_{pq}^{(L)*}(\Omega_{12}) d\Omega_{12}. \quad (20)$$

The summation in equation (19) is made for $L > 0$ and $-L \leq p, q \leq L$ and is restricted to even L for apolar mesophases. The restrictions on p and q indices are concerned with the symmetry of molecules 1 and 2. If both molecules have C_{2v} , D_2 or D_{2h} symmetry indices p and q take zero and even values only and the relations $u_{Lpq} = u_{L-pq} = u_{Lp-q} = u_{L-p-q}$ are valid.

To obtain the equation for the mean field potential \mathcal{U}_1 affecting molecule 1 we average equation (18) over positions and orientations of all surrounding molecules

$$\mathcal{U}_1(\mathbf{r}_1, \Omega_1) = \frac{N \int \mathcal{U}_{12}(\mathbf{r}_{12}, \Omega_{12}) f(\mathbf{r}_2, \Omega_2) d\mathbf{r}_2 d\Omega_2}{\int f(\mathbf{r}_2, \Omega_2) d\mathbf{r}_2 d\Omega_2}, \quad (21)$$

where N is the total number of molecules being averaged. The magnitudes r_i and Ω_i determine the position and the orientation of molecule i in the laboratory frame (xyz), the z axis is normal to the smectic layer planes and coincides with the director, $f(\mathbf{r}, \Omega)$ is the single particle distribution function of mesogenic molecules. Within a smectic layer, which is a two dimensional liquid, the function $f(\mathbf{r}, \Omega)$ does not depend on the xy coordinates. So averaging the spatially dependent part of the potential \mathcal{U}_{12} can be divided into two steps, first in the xy plane and then over the coordinate z_2 . To average within a layer we use the radial distribution function $g(r_\perp)$ of a molecule in the smectic layer xy plane with properties: $g(r_\perp) = 0$ if $r_\perp^2 = (x_{12}^2 + y_{12}^2) < a^2$ and $g(r_\perp) = 1$ if $r_\perp \geq a$ [28], where a is the order of magnitude of the average intermolecular distance within a layer. Averaging gives

$$\langle \exp(-r_\perp^2/r_0^2) \rangle_{xy} = \frac{\int_0^R 2\pi r_\perp g(r_\perp) \exp(-r_\perp^2/r_0^2) dr_\perp}{\int_0^R g(r_\perp) 2\pi r_\perp dr_\perp} = \frac{\pi r_0^2}{Q} \exp(-a^2/r_0^2), \quad (22)$$

where at $R \gg a$ the area $Q \approx \pi R^2$. For the integration over z_2 it is convenient to write $\exp(-z_{12}^2/r_0^2)$ in the Fourier integral form

$$\exp(-z_{12}^2/r_0^2) = r_0 \pi^{-1/2} \int_0^\infty \exp(-r_0^2 t^2/4) \cos(z_{12} t) dt. \quad (23)$$

For a smectic A phase with biaxial molecules the most general form of the distribution function $f(z, \Omega)$ is [2]

$$f(z, \Omega) = \sum_{L' nk} A_{L' nk} D_{0n}^{L'}(\Omega) \cos \frac{2\pi k}{d} z, \quad (24)$$

where the coefficients are

$$A_{L' nk} = \frac{2L' + 1}{(1 + \delta_{k0}) 4\pi^2 d} \left\langle D_{0n}^{(L')*}(\Omega) \cos \frac{2\pi k}{d} z \right\rangle. \quad (25)$$

The summation in equation (24) is made over even $L' \geq 0$, zero and even $|n| \leq L'$, and integer $k \geq 0$. To carry out the integration over angles Ω_2 we use in equation (19) [27]

$$D_{pq}^L(\Omega_{12}) = \sum_j D_{jp}^{(L)*}(\Omega_2) D_{jq}^L(\Omega_1). \quad (26)$$

Substituting equations (19), (22)–(24) and (26) into equation (18) and carrying out the integration over spatial and angular variables gives

$$\begin{aligned} \mathcal{U}_1(z_1, \Omega_1) = & -\frac{N}{nQ} \exp[-a^2/r_0^2] \sum_k \exp\{- (\pi r_0/d)^2 k^2\} \cdot \cos \frac{2\pi k}{d} z_1 \\ & \times \left[\sum_{L' pq} \frac{8\pi^2}{2L' + 1} A_{L' pk} u_{L' pq} D_{0q}^{L'}(\Omega_1) + 8\pi^2 \delta' A_{00k} \right]. \quad (27) \end{aligned}$$

Based on the arguments presented in section 2 the summation can be restricted to values $L' = 2$; $p, q = 0, \pm 2$; $k = 0, 1$. Then using equation (25) and taking into account $N = nQd$ and the requirement of self-consistency we find

$$\mathcal{U}(\theta, \psi, z) = -V_0[(S + \lambda_1 G)P_2 + \alpha(\sigma + \lambda_1 \kappa)P_2 \cos \xi + (\lambda'_1 S + \lambda_2 G)D + \alpha(\lambda'_1 \sigma + \lambda_2 \kappa)D \cos \xi + \alpha \delta \tau \cos \xi], \quad (28)$$

where the following definitions

$$\left. \begin{aligned} V_0 &= u_{200} \exp[-a^2/r_0^2], & \alpha &= 2 \exp[-(\pi r_0/d)^2], \\ \delta &= \frac{\delta'}{u_{200}}, & \lambda_1 &= \frac{2u_{220}}{\sqrt{6u_{200}}}, & \lambda'_1 &= \frac{2u_{202}}{\sqrt{6u_{200}}}, & \lambda_2 &= \frac{2u_{222}}{3u_{200}} \end{aligned} \right\} \quad (29)$$

are used. For uniaxial molecules $\lambda_1 = \lambda_2 = 0$ and at $a = 0$ equation (28) reduces to that obtained by McMillan [8]. With $\sigma = \kappa = \tau = 0$ equation (28) reduces to that obtained in [23, 24] for pure nematics with biaxial molecules.

The single particle distribution function $f(\theta, \psi, z)$ has the form

$$f(\theta, \psi, z) = \exp[-\mathcal{U}(\theta, \psi, z)/kT]/Z \quad (30)$$

and its dependence on the molecular coordinates coincides with that obtained within the framework of the other approach (cf. equation (6)). Comparison of equations (6) and (28)–(30) allows us to write for a pure smectic A

$$\left. \begin{aligned} \lambda_P &= \frac{V_0}{kT} (S + \lambda_1 G), & \lambda_D &= \frac{V_0}{kT} (\lambda'_1 S + \lambda_2 G), & \lambda_\tau &= \frac{V_0}{kT} \alpha \delta \tau, \\ \lambda_\sigma &= \frac{V_0}{kT} \alpha (\sigma + \lambda_1 \kappa), & \lambda_\kappa &= \frac{V_0}{kT} \alpha (\lambda'_1 \sigma + \lambda_2 \kappa), \end{aligned} \right\} \quad (31)$$

these determine the connection of the parameters λ_k (cf. equation (6)) with the molecular interaction parameters, order parameters and molecular characteristics.

A molecular biaxiality is manifested in the parameters u_{Lpq} (cf. equation (29)), which characterize anisotropic intermolecular interactions of rank L . For the important particular case of the factorization

$$u_{Lpq} = \alpha_{12} \gamma_1^{(2,q)} \gamma_2^{(2,p)}, \quad (32)$$

which is valid for anisotropic dispersion interactions [23, 24], the parameters u_{2pq} are expressed through the irreducible components $\gamma^{(2,m)}$ of the polarizabilities of the interacting molecules. For pure liquid crystals $\gamma_1 = \gamma_2 = \gamma$ and the correlations $\lambda_1 = \lambda'_1$, $\lambda_2 = \lambda_1^2$ and

$$\lambda_1 = \frac{1}{3} \frac{\gamma_{x_1 x_1} - \gamma_{y_1 y_1}}{\gamma_{z_1 z_1} - \bar{\gamma}} \quad (33)$$

are valid, where $\bar{\gamma} = (\gamma_{x_1 x_1} + \gamma_{y_1 y_1} + \gamma_{z_1 z_1})/3$ is the average value of the molecular polarizability. In this case we obtain $\lambda_D/\lambda_P = \lambda_\kappa/\lambda_\sigma = \lambda_1$. The largest value $\lambda_1 = 1$ corresponds to disc-like molecules with $\gamma_{x_1 x_1} = \gamma_{z_1 z_1}$ that agrees with the limiting values of the ratios λ_D/λ_P and $\lambda_\kappa/\lambda_\sigma$ obtained from the analysis of the orientational triangle. In the absence of correlations between orientational and translational ordering we obtain $\lambda_\sigma/\lambda_P = \lambda_\kappa/\lambda_D = \alpha\tau$. For pure liquid crystals the experimental dependences $G(S)$ correspond to the values $\lambda_1 \approx 0.1-0.2$ and $G \ll S$ [23, 25, 29, 30]. Moreover, $\alpha \leq 1$ and $\tau < 1$ are valid [8, 18]. So we can write the following chain of the probable inequalities $\lambda_P \gg \lambda_D \approx \lambda_\sigma \gg \lambda_\kappa$.

The molecular field pseudopotential for the solute in a smectic A at low solute concentrations can be found by analogy with the case of pure liquid crystals if we consider molecules 1 and 2 to be solute and solvent molecules, respectively. In this case the restrictions on the indices n and p in equations (24), (25) and (27) are determined by the solvent molecule symmetry and the restriction on the index q in equation (27) by the solute molecule symmetry. The parameter r_0^{S-M} in equation (18) now plays the role of the effective interaction radius between solute and matrix molecules. In the absence of interactions between solute molecules r_0^{S-M} can be taken as $(r_0 + r_{0s})/2$, where the parameters r_0 and r_{0s} have values of the order of aromatic core length for the solvent and solute molecules. Then for the solute the parameter α_{S-M} in equation (33) has the form

$$\alpha_{S-M} = 2 \exp [-(\pi r_0^{S-M}/d)^2] = 2(\alpha/2)^{(\alpha+1)/2}]^2, \quad (34)$$

where $t = r_{0s}/r_0$, and changes within the interval $0 \leq \alpha_{S-M} \leq 2^{3/4} \alpha^{1/4}$.

Let solute and solvent molecules have a symmetry not less than C_{2v} , D_2 or D_{2h} . Then using the same terms of the expansion (cf. equation (27)) and taking into account the self-consistency requirement we can obtain for the mean field potential of the solute subsystem in a smectic A matrix the expression

$$\begin{aligned} \mathcal{U}_S(\theta, \psi, z) = & -V_0[(S_M + \lambda_1 G_M)P_2 + \alpha_{S-M}(\sigma_M + \lambda_1 \kappa_M)P_2 \cos \xi \\ & + (\lambda'_1 S_M + \lambda_2 G_M)D + \alpha_{S-M}(\lambda'_1 \sigma_M + \lambda_2 \kappa_M)D \cos \xi + \alpha_{S-M} \delta_{S-M} \tau_M \cos \xi], \end{aligned} \quad (35)$$

where the index M indicates the corresponding order parameters of the matrix. Here the parameters λ_1 , λ'_1 and λ_2 are determined by equation (29), where the coefficients u_{Lpq} depend on the properties of the solvent and solute molecules. For the nematic phase equation (35) coincides with that obtained in [20]. In the smectic A phase at high values of S_M the inequalities $G_M \ll S_M$ and $\kappa_M \ll \sigma_M$ are valid with $\lambda_k < 1$ in equation (35). So the corresponding terms in equation (35) can be neglected and the expression $\mathcal{U}_S(\theta, \psi, z)$ reduces to that of biaxial solute molecules in a smectic A composed of uniaxial molecules

$$\begin{aligned} \mathcal{U}_S(\theta, \psi, z) = & -V_0[S_M P_2 + \alpha_{S-M} \sigma_M P_2 \cos \xi + \lambda'_1 S_M D \\ & + \alpha_{S-M} \lambda'_1 \sigma_M D \cos \xi + \alpha_{S-M} \delta_{S-M} \tau_M \cos \xi]. \end{aligned} \quad (36)$$

The single particle distribution function $f_S(\theta, \psi, z)$ for the solute has the form

$$f_S = \exp [-\mathcal{U}_S(\theta, \psi, z)/kT] / Z \quad (37)$$

and comparison with equation (6) gives

$$\left. \begin{aligned} \lambda_P = \frac{V_0}{kT} S_M, \quad \lambda_D = \frac{V_0}{kT} \lambda'_1 S_M, \quad \lambda_\tau = \frac{V_0}{kT} \alpha_{S-M} \delta_{S-M} \tau_M, \\ \lambda_\sigma = \frac{V_0}{kT} \alpha_{S-M} \sigma_M, \quad \lambda_\kappa = \frac{V_0}{kT} \alpha_{S-M} \lambda'_1 \sigma_M. \end{aligned} \right\} \quad (38)$$

In the absence of correlations between orientational and translational ordering of solvent molecules $\lambda_\sigma/\lambda_P = \lambda_\kappa/\lambda_D = \alpha_{S-M} \tau_M$. For the solute the parameter λ'_1 can take any value within the interval $0 \leq \lambda'_1 \leq 1$, where the maximum value corresponds to disc-like solute molecules.

The parameter δ_{s-M} characterizes the translational ordering tendency of solute molecules independent of their orientational ordering. For uniform aromatic solute molecules the inequality $\delta_{s-M} < \delta$ can be expected. On the other hand the parameter $\delta < 1$ corresponds to real smectics A [8, 17, 18], so it is possible to expect $\delta_{s-M} \ll 1$. Taking into account that $\alpha_{s-M} \lesssim 1$ [8, 18] and $\tau_M < 1$ we have $\lambda_s \ll 1$ in equation (38) and the last term in the brackets in equation (36) can be neglected. As a result we find

$$\mathcal{U}_s(\theta, \psi, z) = -V_0(S_M + \alpha_{s-M}\sigma_M \cos \xi)[P_2 + (2/3)^{1/2}\lambda D], \tag{39}$$

where the parameter $\lambda = (3/2)^{1/2}\lambda'_1$ defined in [19, 20, 24] is used. The dependences $G(S), \dots, \tau(S)$ and $\Delta_{ki}(S)$ calculated using equations (37) and (39) for values of the parameters S_M, σ_M, λ and α_{s-M} are presented in [31].

4. The static shift and splitting of polarized solute absorption bands in a smectic A

For low solute concentrations and solute absorption bands far from those of the solvent, the solute spectrum shift at the isotropic–liquid crystal transition is determined only by the static solute–solvent interaction. For a biaxial solute in a smectic A the static shift $\Delta v(\theta, \psi, z) = v_0(\theta, \psi, z) - v_i$ of the absorption band maximum relative to its position v_i in the isotropic phase depends on the orientational and translational coordinates of the solute molecule and can be expanded in a complete set of basis functions, which reflect the symmetry properties of the liquid crystal and solute molecules

$$\Delta v(\theta, \psi, z) = - \sum_{Lnk} \varepsilon_{Lnk} D_{0n}^L(\theta, \psi) \cos k\xi. \tag{40}$$

This summation is made over even values $L \geq 0$, even values $|n| \leq L$ and integer values $k \geq 0$, with the term $L = n = k = 0$ being included in v_i . To explore the features of the influence of molecular biaxiality on the solute’s spectral properties the summation in equation (40) can be restricted to terms with $L \leq 2$. The consideration of the translational ordering of the solute can be restricted to the value $k = 1$, with good accuracy. Then taking into account $\varepsilon_{22k} = \varepsilon_{2-2k}$ gives

$$v_0(\Omega, z) - v_i = -(\varepsilon_{200}P_2 + \frac{2}{\sqrt{6}}\varepsilon_{220}D + \varepsilon_{201}P_2 \cos \xi + \frac{2}{\sqrt{6}}\varepsilon_{221}D \cos \xi + \varepsilon_{001} \cos \xi). \tag{41}$$

The coefficients ε_{Lnk} in equation (41) depend on the matrix order parameters $\langle D_{0n}^L \cos k\xi \rangle_M$ and vanish at the transition to the isotropic liquid. As the orientational and translational ordering of solute molecules is a consequence of the corresponding ordering of solvent, so to a first approximation equation (41) can be written as

$$v_0(\Omega, z) = v_i - S_M(AP_2 + BD) - \sigma_M \cos \xi(CP_2 + ED) - \tau_M F \cos \xi, \tag{42}$$

where the coefficients A, \dots, F are weakly dependent on temperature [3].

The absorption band shape $D(v, \theta, \psi, z)$ of a solute molecule does not depend on the solvent phase to a first approximation, but the maximum position $v_0(\theta, \psi, z)$ of this band depends on it according to equation (42). The spectral distribution of the optical densities $\mathcal{D}_{\parallel, \perp}(v)$ in the solute band components polarized parallel and perpendicular to the director is given by [14, 32]

$$\mathcal{D}_{\parallel, \perp}(v) = k \frac{\rho f_{\parallel, \perp}^2}{3n_{\parallel, \perp}} \int \mathcal{D}(v, \Omega, z) \mathcal{J}_{\parallel, \perp}(\Omega) f(\Omega, z) d\Omega dz, \tag{43}$$

where k is a constant, ρ is the density, $n_{\parallel,\perp}$ and $f_{\parallel,\perp}$ are the background values of the refractive indices and the local field tensor components of the light wave within the absorption band studied; $\mathcal{J}(\Omega)$ is the solute absorption band intensity with components

$$\mathcal{J}_{\parallel} = 1 + 2P_2 S_{\beta} + \frac{2}{3} D G_{\beta\varphi}, \quad \mathcal{J}_{\perp} = 1 - P_2 S_{\beta} - \frac{1}{3} D G_{\beta\varphi}. \quad (44)$$

Here the designations $S_{\beta} = (3 \cos^2 \beta - 1)/2$, $G_{\beta\varphi} = (3 \sin^2 \beta \cos 2\varphi)/2$ are used, where β is the angle made by the electronic transition moment μ with the z_1 axis of the solute frame, φ is the angle made by the x_1 axis of this frame with the projection of μ onto the $x_1 y_1$ plane.

If the solute absorption band is far from that of the solvent, which gives the main contribution to the background values $n_{\parallel,\perp}$ and $f_{\parallel,\perp}$ at small solute concentration, the dispersion of these magnitudes can be neglected. So equations $d\mathcal{D}_{\parallel,\perp}(v)/dv = 0$, which determine the maximum positions $v_{\parallel,\perp}$ of the polarized components $\mathcal{D}_{\parallel,\perp}(v)$ of the solute band reduce to

$$\int \mathcal{D}'(v, \Omega, z) \mathcal{J}_{\parallel,\perp}(\Omega) f(\Omega, z) d\Omega dz = 0. \quad (45)$$

Expanding the derivative $\mathcal{D}'(v, \Omega, z)$ in a power series in $(v - v_0)$ near $v = v_0$ (cf. equation (42)) and using the linear approximation valid for uniaxial and biaxial solute molecules in a nematic [3, 33] the solution of equation (45) is found to be

$$\begin{aligned} v_{\perp} = v_0 &- S_M(AS + BG) - \sigma_M(C\sigma + E\kappa) - \tau_M F\tau \\ &+ \frac{S_{\beta}}{1 - SS_{\beta} - GG_{\beta\varphi}/3} [S_M(A\Delta_P + B\Delta_{PD}) + \sigma_M(C\Delta_{P\sigma} + E\Delta_{P\kappa}) + \tau_M F\Delta_{P\tau}] \\ &+ \frac{G_{\beta\varphi}/3}{1 - SS_{\beta} - GG_{\beta\varphi}/3} [S_M(A\Delta_{PD} + B\Delta_D) + \sigma_M(C\Delta_{D\sigma} + E\Delta_{D\kappa}) + \tau_M F\Delta_{D\tau}], \quad (46) \end{aligned}$$

with the result for v_{\parallel} being made by the substitution of $-2S_{\beta}$ and $-2G_{\beta\varphi}$ for S_{β} and $G_{\beta\varphi}$.

Thus the static anisotropic solute-solvent interaction results in a shift and splitting of the solute absorption polarized bands, which depend on the features of structural and statistical properties of the liquid crystal and the electronic structure of the solute molecules in different ways. The shift of the doublet centre of gravity is described by the first three terms in equation (46) and is determined by the solute and solvent order parameters but does not depend directly on the parameters S_{β} and $G_{\beta\varphi}$. The band splitting is described by the fractional terms in equation (46) and depends essentially both on the solute differences and the parameters S_{β} and $G_{\beta\varphi}$. For uniform orientational and translational ordering of solute molecules in a sample all of the differences vanish and the static splitting of the solute bands is absent independent of both the solvent and solute ordering and of the electronic structural features of the molecules. Thus the static band splitting is concerned with the specificity of a liquid-crystalline state as a partially ordered system. On the other hand for the transitions with $S_{\beta} = G_{\beta\varphi} = 0$ the band splitting is also absent independent of the features of the orientational-translational distribution of the solute.

In the absence of the correlation between orientational and translational ordering equation (46) reduces to

$$\begin{aligned}
 v_{\perp} = v_i - S_M[(A + C\tau_M\tau)S + (B + E\tau_M\tau)G] - F\tau_M\tau \\
 + \frac{S_M S_{\beta}}{1 - SS_{\beta} - GG_{\beta\phi}/3} [(A + C\tau_M\tau)\Delta_P + (B + E\tau_M\tau)\Delta_{PD}] \\
 + \frac{S_M G_{\beta\phi}/3}{1 - SS_{\beta} - GG_{\beta\phi}/3} [(A + C\tau_M\tau)\Delta_{PD} + (B + E\tau_M\tau)\Delta_D]. \tag{47}
 \end{aligned}$$

This equation differs from the analogous one for the nematic [14] only by the renormalization of the coefficients before Δ_P , Δ_D and Δ_{PD} and by the additional shift of the doublet centre of gravity in the smectic phase. For $A = C$, $B = E$ and the rest of the conditions being equal the splitting $\Delta v = v_{\parallel} - v_{\perp}$ of solute bands in nematic (Δv_N) and smectic (Δv_S) phases are connected by the relation

$$\Delta v_S = \Delta v_N(1 + \tau_M\tau). \tag{48}$$

By analogy we found

$$(v_i - \bar{v})_S = (v_i - \bar{v})_N(1 + \tau_M\tau) + F\tau_M\tau \tag{49}$$

for the shift $v_i - \bar{v}$ of the doublet centre of gravity \bar{v} . From here we can see, that the layering effect is small for typical thermotropic smectic values $\tau_M = \tau \approx 0.3$ [8] but it can become noticeable in specially prepared layered structures with high values of τ_M and τ , e.g. in Langmuir–Blodgett films [34, 35].

The absorption band splitting $\Delta v = v_{\parallel} - v_{\perp}$ calculated using equations (37), (39), (46) and (47). Δv —the calculation using equation (46); Δv_S —using equation (47); Δv_N —using equation (47) at $\tau_M = \tau = 0$. For all cases $S_M = 0.6$; $\tau_M = 0.3$; $\sigma_M = 0.18$; $\alpha_{S-M} = 0.415$; $A = C = F = 200 \text{ cm}^{-1}$; $B = E$.

$\beta/^\circ$	$\phi/^\circ$	λ	S	B/A	$\Delta v/\text{cm}^{-1}$	$\Delta v_S/\text{cm}^{-1}$	$\Delta v_N/\text{cm}^{-1}$
0	0	0.3	0.3	0.5	-62	-59	-58
			-0.5	-93	-90	-89	
		0.5	0.6	0.5	-47	-42	-40
			-0.5	-88	-83	-80	
		0.9	0.3	0.5	-50	-48	-47
			-0.5	-112	-109	-107	
	0.5	0.6	0.6	0.5	-44	-39	-36
			-0.5	-113	-110	-101	
		0.3	0.3	0.5	23	21	21
			-0.5	106	105	103	
		0.6	0.6	0.5	37	32	31
			-0.5	103	99	95	
90	0	0.3	0.3	0.5	34	33	32
			-0.5	118	117	115	
		0.9	0.6	0.5	43	39	36
			-0.5	121	118	109	

To obtain numerical estimates using equations (37), (39) and (46) we have to choose probable values for the available parameters. For π - π^* electronic transitions in planar molecules we should consider the two limiting cases of transitions polarized along the axes z_1 ($\beta=0^\circ$) and x_1 ($\beta=90^\circ$, $\varphi=0^\circ$). To illustrate the influence of molecular biaxiality on spectral properties the values $\lambda=0.5$ and $\lambda=0.9$ can be taken. The first of these is within the interval $\lambda=0.3$ – 0.7 and is valid for a biaxial solute of the anthracene type in nematic and smectic phases [3, 19]. The value $\lambda=0.9$ is interesting to see what the biaxiality growth may result in. At $S_M=0.6$; $\tau_M=0.3$; $\sigma_M=0.18$ being typical for smectic A phases the values $\alpha_{S-M}=0.415$; $S=0.6$ and 0.3 reflect the possible correlation of the orientational and translational ordering of solvent and solute for $r_{0s} \simeq r_0$ [3, 19, 21]. According to available experimental data for anthracene in different matrices [3, 36, 37] the ratio B/A changes on average from -0.5 to 0.5 with the typical value $A=200 \text{ cm}^{-1}$. To estimate the maximum contribution of the layering effect we take $A=C=F$ and $B=E$.

The results of the calculation using equations (37), (39), (46) and (47) are presented in the table. The values of the splitting correspond to those observed experimentally [3, 37]. The sign of $\Delta\nu$ is determined by the angle β . For $\beta=0^\circ$ $\Delta\nu < 0$ and for $\beta=90^\circ$ $\Delta\nu > 0$. For the same remaining conditions the values of $|\Delta\nu|$ for $\beta=0$ and 90° are close to one another. The sign of the parameter B influences the value of $\Delta\nu$ more strongly than the parameter λ . The correlation of the values of $\Delta\nu_S$ and $\Delta\nu_N$ presented in the table is described by equation (48); their difference is not more than 10 per cent. Taking into account orientational-translational correlations gives the additional increase of $\Delta\nu$ in comparison with $\Delta\nu_S$ and the general contribution of smectic ordering to the value of $\Delta\nu$ makes up 20 per cent, that is in quantitative agreement with the experimental data [3].

5. Conclusion

The structural and spectral aspects can be pointed out as a result of the present investigation. The former is concerned with the general problem of the structural description of partially ordered molecular media composed of molecules with arbitrary shape. Smectic A phases are a simple and common enough model for such media with two main ordering types: uniaxial orientational and unidimensional translational. The analysis of spectral properties of these shows, that to describe their structure it is necessary to use not only average values of the order parameters (cf. equation (8)), but also the uniform and mixed differences (cf. equation (9)). It is obvious, that these differences have also to be manifest in other physical properties of smectics, which depend on the non-uniformity of the orientational and translational molecular distribution and on the correlation of these ordering types. The spectral aspect is that the relative contribution of orientational and translational molecular ordering to spectral properties of the mixture as well as the role of the correlation between these ordering types have been solved. The orientational molecular ordering has been shown to make the dominant contribution to the static shift and to the splitting of the polarized bands of a solute electronic absorption, that is in agreement with the available experimental data.

Appendix

To obtain the asymptotic value $\lambda_\kappa/\lambda_\sigma$ corresponding to the orientational triangle sides the limit of weak orientational and translational ordering of the solute can be considered, when all the parameters λ_k in equation (6) are small. Expanding

the exponent in equation (6) and $\ln Z$ up to terms of order $\lambda_p^m \lambda_D^n \lambda_0^k \lambda_\kappa^l \lambda_\tau^q$ with $(m+n+k+l+q)=3$ and making the integration over angular and spatial variables we find the following approximate equations

$$S = \frac{1}{5}\lambda_p + \frac{1}{35}\lambda_p^2 - \frac{3}{35}\lambda_D^2 + \frac{1}{70}\lambda_\sigma^2 - \frac{3}{70}\lambda_\kappa^2 + \frac{1}{10}\lambda_\sigma\lambda_\tau,$$

$$G = \frac{3}{5}\lambda_D - \frac{6}{35}\lambda_p\lambda_D - \frac{3}{35}\lambda_\sigma\lambda_\kappa + \frac{3}{10}\lambda_\kappa\lambda_\tau,$$

$$\sigma = \frac{1}{10}\lambda_\sigma + \frac{1}{35}\lambda_p\lambda_\sigma - \frac{3}{35}\lambda_D\lambda_\kappa + \frac{1}{10}\lambda_p\lambda_\tau,$$

$$\kappa = \frac{3}{10}\lambda_\kappa - \frac{3}{35}\lambda_p\lambda_\kappa - \frac{3}{35}\lambda_D\lambda_\sigma + \frac{3}{10}\lambda_D\lambda_\tau,$$

$$\tau = \frac{1}{2}\lambda_\tau + \frac{1}{10}\lambda_p\lambda_\sigma + \frac{3}{10}\lambda_D\lambda_\kappa.$$

From the first pair of equations we can see that the asymptotic correlation $G=3S$ within the interval $0 \leq S \leq 0.25$ is valid only for $\lambda_p = \lambda_D$ and $\lambda_\sigma = \lambda_\kappa$. The same result can be obtained from the next pair of equations for the correlation $\kappa = 3\sigma$. So for $G \geq 0$ the parameter λ_κ changes within the interval $0 \leq \lambda_\kappa \leq \lambda_\sigma$. The correlation between the parameters λ_p and λ_σ can be only determined within the framework of a molecular statistical theory for a definite molecular model.

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