

# Spectral investigations of surface ordering in ultrathin molecular films

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Surface molecular ordering in ultrathin molecular films is investigated. The optical transmission spectra of molecular films ranging in thickness from 2 to 13 smectic layers (6.7–43 nm) in the region of the electronic absorption bands in the smectic A phase of cyanobiphenyl CB9 are measured. The thickness and temperature dependences of the permittivity are determined. It is found that the orientational ordering of the molecules depends on the film thickness. The penetration depth of the surface molecular orientational order does not exceed two smectic layers (<7 nm). © 1999 American Institute of Physics. [S1063-7761(99)02205-2]

## 1. INTRODUCTION

A great deal of attention has been devoted in the last few years in both pure and applied investigations to the study of surface molecular layers. The difference of the interaction of molecules with the environment on the surface and in the interior can change the structure of the layer, change the collective and molecular dynamics, shift the phase transition temperatures, and induce new phases on the surface. Depending on the relative magnitude of various types of interatomic and intermolecular interactions, surface layers can melt at higher or lower temperatures compared with the interior of the sample. For example, investigations of the structures of SmA and SmO<sup>1,2</sup> have shown that cooling the isotropic phase produces layered smectic order on the surface at a temperature several degrees above the phase transition temperature in the interior. As the sample is cooled further, layer-by-layer phase transitions eventually cause the smectic phase to fill the entire sample.

Free-standing molecular films are convenient objects for investigating near-surface and dimensional effects in organic materials.<sup>3,4</sup> The two flat surfaces of these films are bounded by air, and the films themselves can be prepared with various (rigorously determined) numbers of molecular layers. Immediately after preparation a film can contain defects (dislocations, thickness nonuniformity, and so on). However, because of the comparatively high mobility of the molecules, the quality of the surface and of the film itself can be substantially improved by holding the film for several hours near the temperature of the transition to the isotropic or nematic phase. This makes it possible to obtain films ( $\sim 1 \text{ cm}^2$ ) that are uniform over their thickness and contain a definite number of smectic layers. The surface of such a film is a single, continuous smectic plane. This advantageously distinguishes the surface of a free-standing organic film from inorganic structures, where as a rule it is difficult to prepare perfect surfaces of adequate size. For this reason, molecular films, aside from their intrinsic interest, can also serve as model objects for investigating surfaces, two-dimensional structures, and phase transitions in finite-size samples. It has been shown that in molecular films, phase transitions accompa-

nied by a change in the structure of near-surface smectic layers<sup>5–9</sup> and transitions to a crystalline phase<sup>4,10,11</sup> occur at temperatures 10–30 °C above transitions occurring in the interior of the sample. Thin molecular films also melt at a higher temperature than bulk samples.<sup>12</sup>

Theoretical calculations have shown<sup>13–20</sup> that the influence of a surface on translational and orientational molecular ordering must be taken into account in a description of the structure and dynamics of thin films. At the same time, up to now there have been no direct experimental observations of the differences in orientational order of molecules on a surface and in the interior, and in consequence no direct observations of a dependence of the orientational ordering on film thickness. In the present work such investigations were performed using optical methods. The optical transmission spectra were measured in the region of the electronic absorption bands for films with various thickness. A smectic-A structure (Fig. 1), in which the “director”  $\mathbf{n}$  (the direction of the predominant orientation of the long axes of the molecules) is perpendicular to the plane of the layers and the film surface, was investigated. The measurements were performed in the UV region of the spectrum, where intense absorption bands of the molecules forming liquid-crystal structures are found. This made it possible to observe the electronic absorption in ultrathin samples (thickness down to  $\sim 7 \text{ nm}$ ) and to determine from the experimental spectra the imaginary part of the permittivity  $\epsilon_2(\omega)$  for films with various thicknesses. The quantity

$$E = \int \epsilon_2(\omega) d\omega,$$

where the integral extends over an electronic transition, is proportional to the squared projection of the dipole moment of the electronic transition on the direction of polarization of the light. The permittivity along the principal directions (parallel and perpendicular to the “director”) depends on the orientational order. This makes it possible to characterize the orientational ordering of a structure on the basis of the relative value of the permittivity.

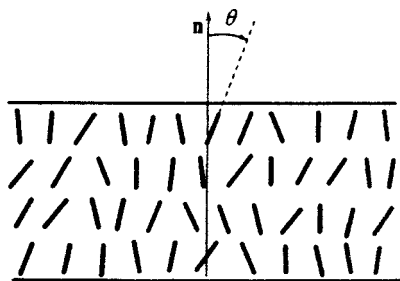


FIG. 1. Smectic-A film. The "director"  $\mathbf{n}$  is perpendicular to the surface;  $\theta$  is the disorientation angle of the long axes of the molecules relative to the "director."

## 2. EXPERIMENTAL RESULTS AND ANALYSIS

The measurements of the transmission spectra were performed on films of 4-cyano-4-n-alkylbiphenyl CB9 (nine is the number of carbon atoms in a chain). This substance forms a smectic-A phase with the smectic-A – nematic – isotropic-liquid phase transition temperatures 48 °C and 49.5 °C, respectively, in the interior of the sample. The films were placed in a 5-mm opening of a thin metal plate. Layer-by-layer thinning by heating a thick film above the temperature of the phase transition to the isotropic liquid in the interior was used to obtain thin films with the required number of molecular layers.<sup>12,21,22</sup> The transmission spectra were measured with the light polarized perpendicular to the "director." The spectra  $T(\omega) = I(\omega)/I_0(\omega)$  presented in this paper are the spectra  $I(\omega)$ , normalized to the lamp spectrum  $I_0(\omega)$ , of the light transmitted through a film. To take account of the reflection of light from the quartz windows of the heat-bath vessel, the spectrum  $I_0(\omega)$  was measured in the same geometry as  $I(\omega)$  without the film. To determine the film thickness (the number of smectic layers), the optical reflection was measured in the transmission region. The spectral dependence of reflection under normal incidence and "backward" reflection is given by<sup>23</sup>

$$\frac{I_r(\omega)}{I_0(\omega)} = \frac{(n^2 - 1)^2 \sin^2(2\pi n N d \omega)}{4n^2 + (n^2 - 1)^2 \sin^2(2\pi n N d \omega)}, \quad (1)$$

where  $N$  is the number of smectic layers in the film,  $d$  is the interplanar distance ( $\approx 3.3$  nm in the smectic-A phase of CB9),  $n$  is the index of refraction, and  $\omega = 1/\lambda$ . In thin films ( $N \leq 6$ ), the reflected intensity is proportional to the squared film thickness:

$$I_r(\omega)/I_0(\omega) \approx N^2 d^2 \pi^2 (n^2 - 1)^2 \omega^2. \quad (2)$$

In this case the number of smectic layers was determined according to the relative reflection intensities for films with various thicknesses.

Figure 2 shows the results of the measurements of the transmission spectra of films with thickness  $N=2, 3, 4, 5, 6$ , and 8 smectic layers. The spectra consist of two electronic bands  $F_a$  ( $\omega_a \approx 3.5 \times 10^4$  cm<sup>-1</sup>) and  $F_b$  ( $\omega_b \approx 4.6 \times 10^4$  cm<sup>-1</sup>). In cyanobiphenyls, the electronic transition dipole moment for the low-frequency band  $F_a$  is parallel to the long axis of the molecule. The transmission spectrum of a film with  $N=13$  layers for two temperatures 37.6 °C and 47 °C is shown in the top half of Fig. 3. The intensity of the spectrum

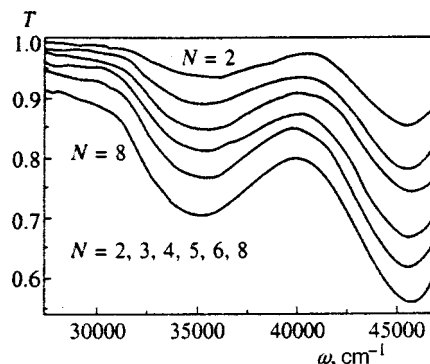


FIG. 2. Transmission spectra of films with thickness  $N=2, 3, 4, 5, 6$ , and 8 smectic layers at temperature  $T=47.7$  °C.

in the frequency range displayed in Figs. 2 and 3 is determined by electronic absorption and interference effects in the reflection of light by the film surface. Even in the transmission range the transmission spectrum exhibits a strong spectral dependence  $T(\omega) = [1 - I_r(\omega)/I_0(\omega)]$  [see the expression (1)]. This dependence is even more complicated in the vicinity of the absorption bands, since the absorption coefficient, the refractive index, and the change in phase of the light wave for transmission through a film depend on  $\omega$ . Interference effects make a large contribution to the intensity and frequency-dependence of the spectrum. Thus, the deviation of  $T(\omega)$  from 1 in the low-frequency part of the spectra is completely due to interference. On account of interference effects, the intensity of the light transmitted through a film in the absorption region does not follow the Lambert–Beer law, and the spectra must be analyzed taking account of energy dissipation in the film and interference.

The transmission spectrum and the response of the film<sup>21</sup> to a light wave are described by the permittivity  $\epsilon(\omega)$ , which depends on the orientational ordering of the molecules in the film. Even though the expressions relating the transmission spectrum of the absorbing film with  $\epsilon(\omega)$  were derived comparatively long ago and are presented in the classic monographs (see, for example, Refs. 24 and 25), thus far the optical spectra of the ultrathin films have not been analyzed using these expressions because of the lack of experimental data.

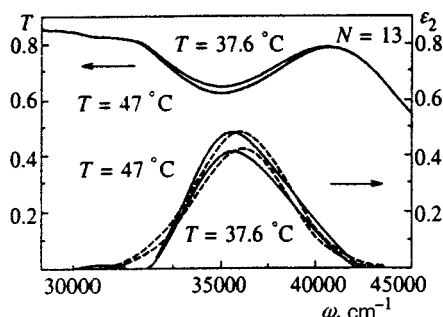


FIG. 3. Transmission spectra of a film with thickness  $N=13$  smectic layers at temperatures  $T=37.6$  °C and 47 °C (top half of the figure). The bottom half of the figure shows the imaginary part of the permittivity, obtained using Gaussian (dashed curves) and arbitrary (solid curves) forms for the spectral curves  $\epsilon_2(\omega)$ .

For an absorbing medium the light transmission coefficient  $T(\omega)$  of a film is given by the expression<sup>24,25</sup>

$$T(\omega) = \frac{16(n^2 + \kappa^2)\exp(-4\pi d\kappa\omega)}{[(n+1)^2 + \kappa^2]^2[1 - 2\rho\exp(-4\pi d\kappa\omega)\cos[2(\beta + 2\pi dn\omega)] + \rho^2\exp(-8\pi d\kappa\omega)]}, \quad (3)$$

where

$$\rho = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (4)$$

is the light reflection coefficient of the surface of a semi-infinite medium, and

$$\beta = \tan^{-1} \frac{2\kappa}{n^2 - 1 + \kappa^2} \quad (5)$$

is the phase delay due to energy dissipation in the absorbing film. It is well known that the absorption coefficient  $\kappa(\omega)$  and the refractive index  $n(\omega)$  can be expressed in terms of the real and imaginary parts of the permittivity  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ :

$$n = \frac{1}{\sqrt{2}} [(\epsilon_1^2 + \epsilon_2^2)^{1/2} + \epsilon_1]^{1/2}, \quad (6)$$

$$\kappa = \frac{1}{\sqrt{2}} [(\epsilon_1^2 + \epsilon_2^2)^{1/2} - \epsilon_1]^{1/2}. \quad (7)$$

Dipole electronic excitations bands are often described using for the permittivity the simple "classical dispersion" form

$$\epsilon(\omega) = \epsilon_0 - \frac{f/2\omega}{\omega - \omega_0 - i\gamma}, \quad (8)$$

where  $f$  is a parameter characterizing the oscillator strength of the electronic transition,  $\omega_0$  is the resonance frequency,  $\gamma$  is a decay constant, and  $\epsilon_0$  is the permittivity due to all other electronic states. This representation of  $\epsilon(\omega)$  greatly simplifies the calculations, since the imaginary and real parts of  $\epsilon(\omega)$  are given by analytic expressions that depend on the same parameters. We have attempted to describe the experimental transmission spectra (Figs. 2 and 3) using the permittivity for both transitions in the form (8). The quantities  $\epsilon_0$ ,  $f$ ,  $\omega_0$ , and  $\gamma$  served as adjustable parameters in the calculation of the transmission spectra. However, we were not able to obtain a satisfactory description of the experimental spectra. In the region of the absorption bands the transmission spectrum decreases much more rapidly than Lorentzian curves. This is due to the fact that, strictly speaking, the expression (8) is applicable for an isolated electronic-excitation band. Intrinsic absorption bands in the condensed state are, as a rule, a superposition of a large number of vibronic transitions with participation of intramolecular vibrations. Individual vibronic transitions are broadened because of structural disordering and temperature, forming a wide structureless band. The absorption bands  $F_a$  and  $F_b$  are a superposition of such vibronic transitions. In this case the permittivity  $\epsilon(\omega)$  in the form (8) can be used to describe the spectrum when the structureless contour formed by a super-

position of vibronic transitions accidentally happens to be close to a Lorentzian curve. For this reason, the calculations of the transmission spectrum were performed with a more general form of  $\epsilon(\omega)$  for each band. In this case, first, the form of only the imaginary part  $\epsilon_2(\omega)$  of the permittivity was given and  $\epsilon_1(\omega)$  was calculated on the basis of the analytic properties of the function  $\epsilon(\omega)$ . The imaginary and real parts of the permittivity are related by the Kramers–Kronig relation. This makes it possible to determine  $\epsilon_1(\omega)$  from the given function  $\epsilon_2(\omega)$  as<sup>24</sup>

$$\epsilon_1(\omega) = \epsilon_0 + \frac{2}{\pi} \int \frac{x\epsilon_2(x)}{x^2 - \omega^2} dx, \quad (9)$$

where we take the Cauchy principal value of the integral. The spectral dependence  $\epsilon_1(\omega)$  was calculated by numerically integrating of Eq. (9) for two transitions  $F_a$  and  $F_b$ . Much better agreement with experiment was obtained by using Gaussians for  $\epsilon_2(\omega)$ . On the basis of this analysis, the calculation of the optical transmission spectra of films with various thicknesses and the determination of  $\epsilon_2(\omega)$  from the experimental spectrum were performed in two steps according to the following scheme.

First,  $\epsilon_2(\omega)$  was approximated by a sum of two Gaussians:

$$\epsilon_2(\omega) = \sum H_i \exp \left[ -\ln 2 \left( \frac{\omega - \omega_i}{c_i} \right)^2 \right]. \quad (10)$$

The initial values of the adjustable parameters  $H_{a,b}$ ,  $c_{a,b}$ , and  $\omega_{a,b}$  were fixed, and the spectral dependence  $\epsilon_1(\omega)$  was determined from the Kramers–Kronig relation (9) by numerical integration. The permittivity  $\epsilon_0$  served as another adjustable parameter. The functions  $\epsilon_2(\omega)$  and  $\epsilon_1(\omega)$  obtained in this manner were used to calculate  $n(\omega)$  and  $\kappa(\omega)$  [Eqs. (6) and (7)] as well as the transmission spectrum (9). The optimal values of the parameters of the Gaussians and  $\epsilon_0$  were obtained by a least-squares fit of the computed curves (3) to the experimental spectra (Figs. 2 and 3). In Fig. 4 the experimental spectra (dots) are compared with the computed spectra (dashed curves) for films with  $N=3$  and  $N=8$ . The total intensity of the transmission spectrum and the decrease in intensity with increasing film thickness can be described satisfactorily in the absorption and transmission regions of the film. However, the differences in the position of the peaks and in the shape of the low-frequency band  $F_a$  cannot be eliminated by using Gaussians to describe  $\epsilon_2(\omega)$ .

In the second step of the calculations, the spectral dependence  $\epsilon_2(\omega)$  for the band  $F_a$  was not approximated by an analytic expression. To work with arbitrary curves the imaginary part of the permittivity was given by cubic spline interpolation over a set of discrete values  $\epsilon_2(\omega_i)$  ( $1 \leq i \leq 15$ ). This number of points was sufficient to describe the form of  $\epsilon_2(\omega)$ . The real part of the permittivity  $\epsilon_1(\omega)$  was calculated

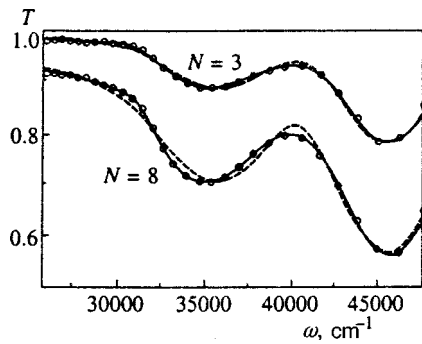


FIG. 4. Comparison of the experimental spectra (dots) with the computed spectra for films with  $N=3$  and  $N=8$  smectic layers. Dashed curves — calculation with  $\epsilon_2(\omega)$  given by a Gaussian. Solid lines — calculation with an arbitrary form of  $\epsilon_2(\omega)$ .

from the Kramers–Kronig relation (9). In the second step of the calculations the ordinates  $\epsilon_2(\omega_i)$  served as adjustable parameters. Next,  $T(\omega)$  [the expression (3)] was fit to the experimental spectrum using the same scheme as in the first step of the calculations. The spectra obtained are presented in Fig. 4 (solid lines). It follows from this figure that this method makes it is possible to obtain in the region of the  $F_a$  band a computed spectrum that is essentially identical to the experimental spectrum. Figures 5 and 6 display  $E = \int \epsilon_2(\omega) d\omega$  and  $E_d = d \int \epsilon_2(\omega) d\omega$  as a function of  $N$ . Figure 7 shows the temperature variation of  $E = \int \epsilon_2(\omega) d\omega$  for a film with 13 smectic layers. The figure also shows for comparison the results obtained in the first computational step, where  $\epsilon_2(\omega_i)$  was described by a Gaussian. One can see from Fig. 3 that the spectral dependence  $\epsilon_2(\omega_i)$  obtained in the second computational step is appreciably different from a Gaussian. However, the integrated intensities do not differ much (Fig. 7) and they show the same temperature variation.

### 3. DISCUSSION

A characteristic feature of the behavior of  $E = \int \epsilon_2(\omega) d\omega$  as a function of film thickness is that in ultrathin films  $E$  decreases (the fact that the straight line drawn through  $E_d$  in Fig. 6 does not pass through zero is due to this effect). As already mentioned,  $E = \int \epsilon_2(\omega) d\omega$  characterizes the orientational ordering of the molecules. Since the dipole moment of an optical transition for the  $F_a$  band is parallel to the long axis of a molecule, lower values of  $E$  correspond to lower values of the angle  $\bar{\theta}$  of disorientation of the molecules

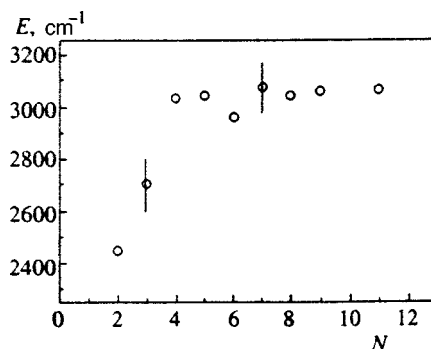


FIG. 5. Total intensity  $E = \int \epsilon_2(\omega) d\omega$  versus film thickness  $N$ .

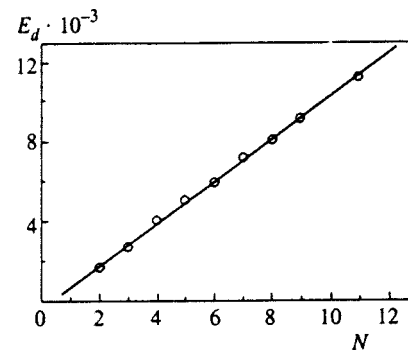


FIG. 6.  $E_d = d \int \epsilon_2(\omega) d\omega$  versus film thickness  $N$ .

relative to the “director”  $\mathbf{n}$  (Fig. 1) and therefore a higher degree of orientational ordering. As temperature decreases,  $E$  decreases (Fig. 7,  $N=13$ ), i.e., the orientational order of the molecules in the film increases. The temperature behavior of the orientational order in a film is similar to the change in the ordering in bulk samples in the smectic and nematic phases.<sup>26,27</sup> The fact that the molecules in a film become ordered on cooling can also be seen qualitatively by comparing the transmission spectra directly (Fig. 3). The decrease in the intensity of the  $F_a$  band on cooling is due to the increase in orientational order.

The quantity  $P_2 = (1/2)(3\langle \cos^2 \theta \rangle - 1)$ , called the degree of orientational ordering,<sup>26</sup> can be used to characterize the orientational order of molecules in bulk samples. In our case (the electronic transition dipole moment is parallel to the long axis of the molecules) the dependence of  $P_2$  on  $E$  has the simple form

$$P_2 = (1 - 3E/E^\parallel), \quad (11)$$

where  $E^\parallel = \int \epsilon_2^\parallel(\omega) d\omega$  and  $\epsilon_2^\parallel(\omega)$  is the permittivity in a direction parallel to the “director”  $\mathbf{n}$  in a completely ordered structure, i.e., with  $P_2 = 1$ . In thick films  $P_2$  should correspond to its value in the interior. For  $P_2$  of the order of 0.65 in films with  $N \geq 8$ , the relative variation of the orientational ordering  $P_2$  in ultrathin films ( $N=2,3$ ) can be estimated using Eq. (11) and the values of  $E$  for  $N=2, 3$  and  $N \geq 8$ . The degree of orientational ordering obtained in this manner is  $P_2 \approx 0.72$  ( $N=2$ ) and  $P_2 \approx 0.69$  ( $N=3$ ). The sharp depen-

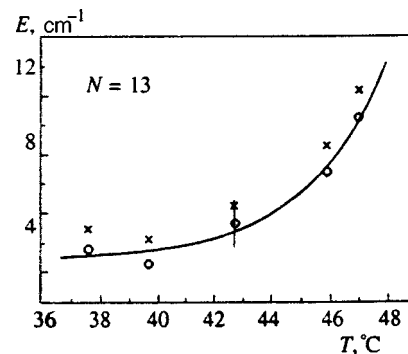


FIG. 7.  $E = \int \epsilon_2(\omega) d\omega$  versus temperature for a film with  $N=13$  smectic layers (O) and the values of  $E = \int \epsilon_2(\omega) d\omega$  obtained at the first step of the calculations where  $\epsilon_2(\omega)$  was given by a Gaussian (x).

dence  $E(N)$  for  $N \leq 4$  (Fig. 5) shows that the effect of the surface is limited to a thin near-surface layer of the order of one or two smectic planes.

A number of models have been proposed to describe the layer and orientational order of molecules near a surface. Rosenblatt and Ronis<sup>13,14</sup> were the first to use a lattice model to study the effect of a surface on the structure of and phase transitions in films. The material parameters of the bulk samples were used in the numerical calculations. A fundamentally important result of these works is that the order parameter near a surface is different from its value in the interior, and the thickness-averaged orientational order parameter in thin films is larger than in the interior. Surface ordering is often interpreted in terms of the wetting of the interface between media by various phases.<sup>16–18</sup> It has been shown that near the phase transition temperature in the interior this process can occur by continuous and layer-by-layer increase in the number of smectic layers near the surface.<sup>17,18</sup> In the mean-field model (the analog of the McMillan theory<sup>28</sup> for bulk samples) the influence of the surface was also taken into account by introducing an effective orienting field acting on a molecule at the surface

$$W_s(\theta) = -\frac{W_s}{2}(3\cos^2(\theta) - 1).$$

The absolute value of  $P_2$  on the surface depends on the ratio  $W_s/W_0$ , where  $W_0$  is the intermolecular interaction constant. The large arbitrariness in the choice of these quantities precludes a quantitative comparison of the experimental and computed values of  $P_2$  at a surface. More important is the theoretical dependence of  $P_2$  on the distance from the surface. The change in  $P_2$  from its value at the surface to its value in the interior occurs mainly at the transition from the first (surface) to the second molecular layer,<sup>20</sup> in agreement with our data.

The change of the collective and molecular dynamics at the surface makes a large contribution to the ordering of the molecules. The amplitude of the fluctuations of the smectic layers in the interior of a film is  $\sim 0.45$  nm. Surface tension suppresses collective (long-wavelength) fluctuations, decreasing their amplitude by 0.1–0.2 nm relative to the amplitude of the fluctuations in the interior of the film.<sup>19</sup> Precise measurements of the surface tension have been performed on thin films.<sup>29</sup> According to these data the surface tension does not depend on the film thickness, right down to two molecular layers, i.e., the mechanism responsible for surface tension is localized in a layer near the surface.<sup>29</sup> According to the calculations in Ref. 19 the amplitude of the surface fluctuations depends weakly on the film thickness. The bulk of the change in the amplitude of the fluctuations occurs at the surface over one or two molecular layers. Our results on the effect of a surface on orientational ordering agree with this model.

In summary, a spectral method for investigating surface orientational ordering was proposed in this paper. The first measurements of the transmission spectra of thin, free-standing, molecular films in the region of electronic absorption bands were performed.<sup>1)</sup> The degree of orientational order in ultrathin films ( $N=2,3$ ) is greater than in thick films.

Our results on the thickness dependence of the transmission spectra and permittivity show that the effect of a surface on the orientational structure is localized in one or two smectic layers near the surface.

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<sup>1)</sup>The electronic spectra of molecules forming liquid crystals are investigated, as a rule, in solutions. The intrinsic absorption spectrum in the liquid-crystal state is difficult to measure by the conventional method, i.e., when the substance is in a cell, because of the virtually complete absorption even in thin samples  $\sim 1 \mu\text{m}$ . Free-standing films make it possible to perform such measurements and can be used to investigate intrinsic electronic and vibronic absorption.

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