Friction model of Photo-induced Reorientation of Optical Axis in Photo-oriented Langmuir-Blodgett Films

S. Palto, Geoffroy Durand

Friction Model of Photo-induced Reorientation of Optical Axis in Photo-oriented Langmuir-Blodgett Films

S.P. Palto (*) and G. Durand

Laboratoire de Physique des Solides (LA2), Université de Paris-Sud, 91405 Orsay, France

Abstract. — A model of the Photo-induced Optical Anisotropy (POA) is proposed for molecular films consisting of ordered domains. The model describes the molecular motion in an anisotropic molecular field at different rates of collisions (friction) between, respectively, excited and ground state molecules and a substrate under polarized light illumination into a molecular absorption band. It is shown that if an angular distribution function of domain molecules has a non-zero width, the different friction coefficients would result in domain director rotation. At low light intensity, these different frictions could be due to three processes: i) change in molecular conformation, ii) change in molecular interaction and iii) local recrystallisation. The domain director rotation is considered as a result of the conservation of the angular momentum for the whole system, which includes the substrate. A new method, based on double illumination of photo-oriented films, is proposed to observe the light-induced optical axis rotation. Experimental results concerning photo-induced rotation of the optical axis in photo-oriented Langmuir-Blodgett films are presented and explained by the model. The angular dependence of the photo-induced angular torque is confirmed. The existence of an angular threshold for out-of-plane rotation (θ-rotation) is demonstrated and qualitatively explained by anchoring of molecular layers with the substrate.

1. Introduction

The effect of the Photo-induced Optical Anisotropy (POA) is a phenomenon that was observed in many molecular systems such as solutions [1,2], polycrystalline films [3], polymer films [4–6] and Langmuir-Blodgett (LB) films [7–12]. The essence of the POA effect is that, under illumination of a molecular system in its absorption band, an optical axis of a larger absorption and birefringence, which is perpendicular to the light polarization vector, is induced. The POA effect described in this paper is not related to irreversible photochemical reactions but due to a molecular reorientation. Usually the POA is explained by photochemical reactions of *trans-cis* isomerisation. Such interpretations are made in the assumption of an isotropic distribution of molecules before illumination and isotropic properties of matrices. The molecular reorientation

---

(*) Permanent and mail address: S.P. Palto, Institute of Crystallography, Academy of Science, 117 333 Moscow, Russia.

is explained by transitions of excited molecules to *cis*-form and successive relaxation to more stable *trans*-states but with different angular positions. It results in that, at random, the molecules (whose absorption oscillators are perpendicular to the light polarization vector) do not participate in the excitation process and conserve their angular position. In despite of the fact that this simple interpretation seems to be reasonable for viscous dye solutions [2] and diluted solutions of dyes in polymer matrices [5], there are problems of similar explanation of the POA in ordered LB films [8,10,12]. To our mind, the main limitation of all pure photochemical mechanisms based on the simple idea of the photochemical light selection is that they do not take into account molecular interactions with a crystalline molecular field, which exists in ordered systems. The problems of an explanation of the POA by pure photochemistry were already discussed and a model, which takes into account a molecular interaction within the frame of a mean field approximation, has been proposed [11, 12]. Nevertheless, in [11] the possible role of *trans-cis* reactions was not distinguished from the other physical processes, and the conservation of total angular momentum under the POA induction was not discussed either. Another mechanism, also based on a mean field approximation of the interaction of the excited dye molecules with the nematic host, has been proposed to explain anomalous optical reorientation in nematic guest-host systems [13]. We do not have a binary system as the "*guest-host*" and the results of [13] cannot be used in our case. Moreover we do not believe that the prediction of [13] about continuous but opposite rotations of dyes and nematic has much physical meaning. To get external rotation of the distribution function of the total system, as observed in dye molecular films [11,12], one needs to introduce from first principles an interaction with an external medium, for instance the solid substrate. We do put such an interaction in our model through different "frictions" between substrate and, respectively, excited and unexcited molecules. First we explain qualitatively how we can get the rotation of a molecular packet under the light excitation taking into account an interaction with the mean molecular field. Then we derive expressions which describe this rotation. We show that a torque arises. We interpret it in terms of a total balance of angular momentum for the system. Thus the angular momentum of the rotated molecular domain is just balanced by the angular momentum arisen as a reaction of the sample substrate. Three processes: i) change in molecular conformation, ii) change in molecular interaction and iii) local recrystallisation, which can be responsible for the POA effect are now discussed in our model. Recently, we proposed a new method to create by POA "bistable anchoring surfaces" for nematic liquid crystals [14]. This method is based on light induced domain axis rotation in photo-oriented films. In this paper we explain how we understand such rotation.

In the experimental part we show new results on photo-induced transformations in photo-oriented LB films. First we briefly describe a procedure of LB film preparation and an experimental set-up used to investigate the POA. Afterwards we propose a new method of creation of a molecular system for which the rotation of the optical axis can be observed. The method is based on second illumination of photo-oriented LB film. We show the data on optical axis rotation. On the one hand, we demonstrate problems of explanation of the data by pure *tranc-cis* photo-isomerisation mechanisms proposed for isotropic molecular systems. On the other hand, a satisfactory agreement of the observed results with the new model is shown.

2. Model

The main object described here is a molecular packet (domain). We consider this domain as consisting of linear rod-like molecules. We conceive that these molecules have higher polarizability along their long axes. Thus, below some temperature, due to an anisotropy of interaction, the molecules turn out to be aligned with their long axes along some direction **L**,

called the domain director. Such a behaviour is well known, for instance in the case of nematic liquid crystal molecules, and can be described in terms of a mean molecular field [15]. Therefore, we consider our molecular system as consisting of many microscopic domains somehow distributed in a film sample. In this section we describe the reorientation of a single domain under illumination into a molecular absorption band by linearly polarized light. Then, in the experimental part, we will show how to get a reasonable approximation of single domain rotation using multidomain Langmuir-Blodgett films.

First let us introduce the Cartesian system as shown in Figure 1. The **XY** axes are in the plane of a film substrate. We consider a domain with a director **L** at an angle ψ_0 with respect to the X-axis. We will describe the rotation of **L** under illumination with the polarization vector **e** oriented along the X-axis. From the symmetry, this rotation can only be in the **X − L** plane (the two-dimensional rotation) until we do not introduce some anchoring with a substrate. For
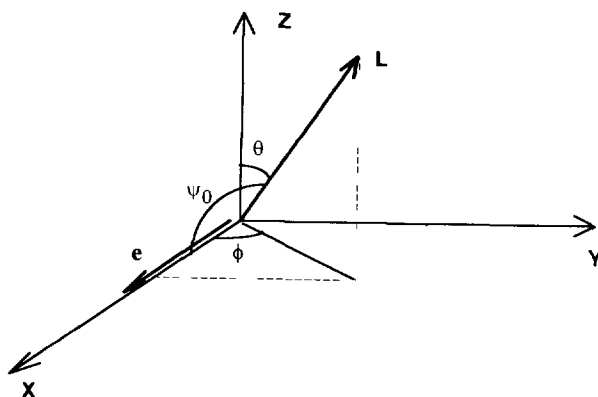

Fig 1. — The scheme of Cartesian system. The **X − Y** plane corresponds to the substrate plane, **e** is the light polarization vector. **L** is the domain director.

simplicity, we assume isotropic interaction of molecules with a substrate (attraction forces do not depend on the orientation of the molecule). Because of the two-dimensional description, the three-dimensional molecular distribution function will be considered as a projection onto the **X − L** plane. The rotation in the **X − L** plane can be decomposed into two rotations: ϕ-rotation (in the **X − Y** plane) and θ-rotation (in the **L − Z** plane). In view of the fact that the model described must explain experiments on the POA effect observed under illumination at rather low intensities, we will also neglect the interaction of the molecular polarizability with the electromagnetic field of the light.

2.1. QUALITATIVE EXPLANATION OF THE POA EFFECT. — A crucial point in the model described is that we introduce a "friction" between molecules and the substrate, which is different for excited molecules. Figure 2 explains the occurrence of rotation of a domain director under illumination by polarized light. At thermal equilibrium under the influence of the mean molecular field, the molecules in the domain are represented by the initial distribution function $f(\psi)$ (curve (1)) with a maximum corresponding to an arbitrary angle ψ_0 with respect to the light polarization vector. An interaction of the molecules with light produces excitations in the initial distribution function. Because the molecule chromophores behave like linear oscillators,
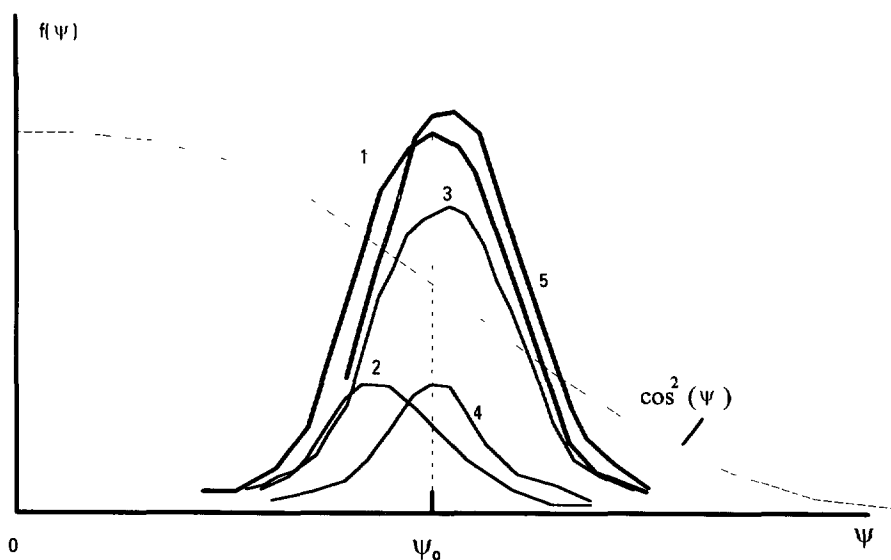
Fig. 2. — Demonstration of the director rotation for a molecular domain. (1) initial molecular distribution function; (2) shape for molecular excitations under polarized illumination (orientation of the light polarization vector is at $\psi = 0$); (3) distribution of unexcited part of molecules; (4) equilibrium distribution for excited molecules; (5) new distribution function (sum of curves (3) and (4)).

the shape of these excitations (curve (2)) is proportional to the product $f(\psi)\cos^2(\psi)$. It results in asymmetry in the distribution function of ground-state molecules (curve (3)). At the starting point the sum of curves (2) and (3) gives the initial distribution function (curve (1)). Because the excited molecules are in the molecular field, they are redistributed into the shape (curve (4)) defined by the interaction of the excited molecules with the molecular field. We assume that for the excited molecules the friction with the substrate is much less than for molecules in the ground state. The latter assumption is based on the fact that under excitation the molecule can change its conformation and the energy of the interaction with the mean molecular field. As a result, the rate of collisions with the substrate, which defines the friction, will be different for the excited molecules. Thus, during the time while the redistribution of excited molecules takes place (shift to the centre with minimum molecular potential, from curve (2) to curve (4)), the ground distribution (curve 3) remains unchanged. We can now see that the sum of curves (3) and (4) gives the new distribution function (curve (5)) shifted with respect to the initial one in the direction of higher ψ. The domain molecules "escape" the absorption of light. Because the maximum of the distribution function is shifted, the direction of the molecular field is shifted too, so that the redistribution of unexcited molecules takes place as well. At continuous illumination it gives the result of the domain director rotation.

2.2. CALCULATION OF THE LIGHT-INDUCED ANGULAR SHIFT OF A DISTRIBUTION FUNCTION.

— Here we are going to describe the molecular motion in the $X - L$ plane under light excitation into a molecular absorption band. In the description we make a series of simplifications. One of them, for instance, is related to the form of the mean molecular potential. This is done to get a simple analytical solution of the problem. As will be seen, despite the simplicity, the model predicts general trends observed in the experiment. It also makes predictions

which are not observed yet. The observed quantitative discrepancies are mainly due to other processes, some of them are discussed below and suggested for an additional study.

To calculate the shift of the molecular distribution function, let us take the angular part of the interaction energy W^* for excited molecules as follows:

$$W^* = \frac{1}{2} W_0^* (\psi - \psi_0)^2, \tag{1}$$

where W_0^* is the amplitude of the interaction energy. Equation 1 is written for small angular changes. (the superscript ($*$) anywhere will be related to an excited molecule and omitted for an unexcited one). In principle one can take any other form of the potential, which satisfies the symmetry of the molecules.

Between two collisions we write the angular acceleration for an excited molecule:

$$\ddot{\psi} = -\frac{1}{J^*} \frac{\partial W^*}{\partial \psi}, \tag{2}$$

where J^* is the molecular inertial moment in the excited state with respect to the axis perpendicular to the longitudinal molecular axis. Equation 2 is just the Newton law. We integrate (2) during the time between two collisions in the assumption that the angular change in the position of a molecule is small, so the torque from the mean field is still a constant:

$$\dot{\psi} = -\frac{1}{J^*} \frac{\partial W^*}{\partial \psi} \Delta t_i + C_i, \tag{3}$$

where Δt_i is the time between the collisions $i - 1$ and i, C_i is an integration constant, which is an initial angular velocity after the collision $i - 1$. Then we also assume that each molecule has many collisions during some time δt before its average angular position is changed significantly. Thus we average over δt:

$$< \dot{\psi}^* > = -\frac{1}{J^*} \frac{\partial W^*}{\partial \psi} < \Delta t_i > + < C_i > \equiv -\frac{1}{J^*} \frac{\partial W^*}{\partial \psi} \tau_c^* + < C_i > \tag{4}$$

Because after each collision a vector of the velocity is not defined (the molecule forgets its previous velocity), we can postulate $< C_i > = 0$. τ_c is the average collision time between molecules and between molecules and a substrate. Taking into account expression (1), we write the molecular angular velocity in the sense of the average value defined by (4) as:

$$\dot{\psi} = -\frac{\tau_c^*}{J^*} W_0^* (\psi - \psi_0) \tag{5}$$

Expression (5) is now a "friction law", giving a mean velocity proportional to the mean field. It reflects the rotation of the molecule under the friction towards the centre of the molecular distribution with a friction coefficient defined as:

$$\eta^* = \frac{J^*}{W_0^* \tau_c^*} \tag{6}$$

η^* has the dimension of time. A similar expression can also be written for an unexcited molecule. We assume that the shape of the potential for unexcited molecules is similar to equation (1) (we only omit the superscript ($*$)). Because we postulate a different friction, we have to use different collision time τ_c, interaction energy W and inertial moment J for the ground state molecule. The solution of equation (5) is an exponential decay of $\psi - \psi_0$ with a time constant η^*. On long time scale (much longer than δt) the value $< \psi - \psi_0 > = 0$.

Nevertheless the molecular distribution has a finite half-width $< (\psi - \psi_0)^2 > \neq 0$ at non-zero temperature. To see this let us write equation (2) for an unexcited molecule in the form:

$$J\dot{\psi}\frac{\partial\dot{\psi}}{\partial t} = -W_0\psi\dot{\psi} \tag{7}$$

In (7) we have multiplied two parts of (2) by $J\dot{\psi}$ and we have taken $\psi_0 = 0$ to simplify the calculations of $< (\psi - \psi_0)^2 > \equiv < \psi^2 >$. To start with, we consider one molecule oriented at $\psi = 0$. Suppose that at the moment t_0 it has a collision with another molecule. During the time $t_1 - t_0$ until the second collision takes place we integrate (7):

$$J\int_{\psi_0}^{\psi_1} \dot{\psi}\mathrm{d}\dot{\psi} = W_0 \int_{t_0}^{t_1} \psi\dot{\psi}\mathrm{d}t \equiv -W_0 \int_0^{\psi_1} \psi\mathrm{d}\psi \equiv -\frac{W_0}{2}\psi_1^2 \tag{8}$$

The left part in (8) presents the angular part of the change in the molecular kinetic energy between two collisions. Now we follow the molecule until it has N collisions. We make the sum of equations such as (8):

$$\frac{J}{2}\sum_{k=1}^{N}(\dot{\psi}_k^2 - \dot{\psi}_{k-1}^2) = -\frac{W_0}{2}\sum_{k=1}^{N}(\psi_k^2 - \psi_{k-1}^2) \equiv -\frac{W_0}{2}\psi_N^2 \tag{9}$$

After averaging over a long time at thermal equilibrium, the value of the left part in (9) must be equal $-kT/2$ (here k is the Bolzmann constant and T is the absolute temperature), so that we have:

$$< \psi_N^2 >= \frac{kT}{W_0} \propto \Delta^2 \tag{10}$$

where Δ reflects the width of the molecular distribution:

$$f(\psi) = \frac{1}{\Delta\sqrt{\pi}} \exp\left[-\frac{(\psi - \psi_0)^2}{\Delta^2}\right], \tag{11}$$

which is the stationary solution of the Bolzmann equation in the mean field W.

Now let us go back to (5) and make averaging over all molecules. The shift of the distribution function of the domain per unit of time coming only from one excited molecule is defined by simple division of (5) over the number of molecules N in the domain. To calculate the angular velocity for the total molecular packet, we make an average over all molecules. For simplicity we consider a two-dimensional monolayer domain to have the same intensity I of incident light for all molecules. We illuminate the domain by linearly polarized light with the polarization vector at $\psi = 0$. We also assume that the disturbance of the distribution function is small enough, so that we can use the shape (11) for the molecules in the ground state. The number of excited molecules in the angular segment $(\psi + \mathrm{d}\psi/2, \psi - \mathrm{d}\psi/2)$ is:

$$\mathrm{d}N^* = \frac{IS\sigma\tau_e}{h\nu A} \cos^2(\psi)f(\psi)\mathrm{d}\psi, \tag{12}$$

where S is the area occupied by all domain molecules, σ is the molecular cross section for the light polarized along the long molecular axis, τ_e is the molecular lifetime for the excited state, $h\nu$ is the photon energy and A is the area per molecule. We must understand that the process we are considering changes thermal equilibrium. Thus the molecular distribution function used in (12) in the form (11) is a reasonable approximation only when $N^* \ll N$.

The average angular shift per unit of time coming from all the molecules in the segment $d\psi$ is:

$$d\Omega = (\dot{\psi}^* dN^* + \dot{\psi}(N f(\psi) d\psi - dN^*))/N \tag{13}$$

The first term in (13) reflects the contribution from the excited molecules and the second one from the molecules in the ground state. Taking into account that $S/A = N$, from equation (5) and from a similar expression for unexcited molecules the integration over all ψ gives the angular velocity for the molecular packet as:

$$\Omega = \frac{I\sigma\tau_e}{h\nu}\left[\frac{1}{\eta^*} - \frac{1}{\eta}\right]\int_\psi (\psi - \psi_0)f(\psi)\cos^2(\psi)d\psi + \frac{1}{\eta}\int_\psi(\psi - \psi_0)f(\psi)d\psi \tag{14}$$

The first integral in (14) is the contribution from excited and unexcited molecules when the illumination is turned on. The second one is equal to zero in that it reflects the equilibrium state of the non illuminated molecular packet. We assume that the width of the distribution function is small in comparison with $\pi/2$ and we do the approximation for $\cos^2(\psi)$ in the vicinity of ψ_0 as:

$$\cos^2(\psi) = \cos^2(\psi_0) + \left[\frac{d(\cos^2(\psi))}{d\psi}\right]_{\psi_0}(\psi - \psi_0) \tag{15}$$

Now we find the integral (14) and we write the result in the form:

$$\Omega = -\frac{\tau_c}{J}\Gamma_a \tag{16}$$

where

$$\Gamma_a = \frac{I\sigma\tau_e}{2h\nu}W_0\left(1 - \frac{\eta}{\eta^*}\right)\sin(2\psi_0)\Delta^2 \tag{17}$$

Equation (17) defines an "apparent" torque Γ_a acting on the domain molecules. One can see that this torque is equal to zero if $\Delta = 0$ (perfect ordering of molecules in the domain). In real systems Δ is non-zero because of temperature. Moreover, in systems consisting of microdomains Δ is higher in the vicinity of domain walls. Thus, for systems with highly ordered domains the model predicts that the reorientation starts in the vicinity of domain walls.

The torque appears only if η and η^* are different. Its sign is related to the sign of $\eta^* - \eta$. For $\eta^* < \eta$, the molecules tend to "escape" from the light polarization orientation. For $\eta^* > \eta$, they would orient along the light polarization vector. In all cases, the rotation induced on molecules obeys the friction law defined by equation (16), which expresses that the mean angular velocity of the distribution is proportional to the apparent torque. The final stable equilibrium angle ψ is zero or 90°, depending on the sign of $\eta - \eta^*$.

Let us now discuss the reasons which can lead to non-zero value of $\eta - \eta^*$. According to equation (6) one can consider three cases: i) change in the moment of inertia; ii) change in the interaction energy; iii) change in collision time.

i) The moment of inertia can be changed, for instance, if the molecules can show the photochemical reactions of *trans-cis* isomerization. We can assume that in the *cis* form the molecular inertial moment is less than in the *trans*-state, so $\eta^* < \eta$. In this case we have a good sign in (17) to explain POA effect ($\Omega > 0$ means that ψ_0 increases and the director rotates to be perpendicular to the light polarization vector) observed for azocompounds.

ii) The change of interaction energy can take place if molecular parameters such as the polarizability and the dipole moment in the excited state are different from those in the ground state. It is known, for instance, that for some azocompound molecules showing the POA effect in LB films, the static dipole moment in the excited state is of about 4 D higher than in the ground state so $W^* > W$ [12]. Thus it can also be the reason of POA effect in azocompounds. iii) At low intensities there is no reason to expect any difference in the collision time if we are far from a phase transition (to nematic or isotropic phase, for instance). Nevertheless in multidomain films, the transition temperature can be lower in the vicinity of domain walls, where the molecular distribution has a higher disorder. In this case we can have a change in collision time as a result of a very small heating. To have an accurate description for this case our model should be developed for instance within the frame of the Landau-de Gennes theory [15]. We are going to do this in a separate publication. Qualitatively, the explanation of POA can be as follows: locally in some place of the domain, where we approach the phase transition, illumination puts some additional disorder in the system. So locally we have a "melting" effect. Because of the anisotropy of the absorption, we put more disorder for molecules which are oriented at a smaller angle with respect to the light polarization, Figure 2. A result of this can be recrystallisation, but in a new direction, which is defined by the molecular field of the main domain. It gives the same shift of the distribution function as was qualitatively explained in (2.1). So the torque law should be similar to equation (17).

At high intensities, when we are able to melt the total domain, the proposed model does not work, so the law of equation (17) is not obvious. In our experiments the intensity is so weak $(10^{-2}$ W/cm$^2)$, that for thin LB films (thickness of about 400 Å) on glass substrate the estimated change in the temperature is many orders of magnitude less than one degree. Thus, at least for the experimental results we are going to present, the effect due to the total melting of domains seems to be unreasonable.

2.3. ROLE OF THE SUBSTRATE. — In our model we have considered the process of the POA induction at thermal equilibrium. Clearly the substrate, in this case, plays the role of a thermostat. It is also important to understand the balance of angular momentum during the POA induction that is actually presented by equation (16). Indeed, linearly polarized light has no angular momentum. The torque Γ_a (Eq. (17)) has an internal origin and is applied to the surrounding matrix and finally to the film substrate. Thus for the balance of the total angular momentum, the rotation of a domain in one direction should be accompanied by the rotation of something else in the opposite direction. Finally this "something" is the substrate. The interaction with the substrate in the proposed simplest consideration is due to the molecular collision mechanism (anchoring is not taken into account).

3. Experimental

3.1. PREPARATION OF LANGMUIR-BLODGETT FILMS. — To prepare LB films we use the azocompound of structure formula shown in Figure 3a. This dye molecule has a linear molecular oscillator strongly absorbing light in the spectral region $400 - 520$ nm. The compound was synthesised at the Institute of Organic Intermediates & Dyes (Moscow, Russia).

The LB films are prepared using successive transfers of monomolecular layers from a water surface onto quartz substrates. The dye molecules form spontaneously crystallised ("solid") films on a water surface. For this reason we use the Langmuir-Schaefer method [16] to prepare multilayer films. The details of the preparation procedure for LB films of this compound are described in [14]. In this work we used LB films of 15 layers.
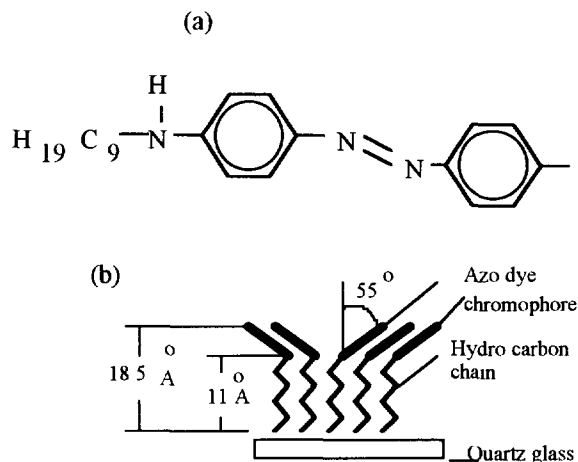
(a)

(b)

Fig. 3. — a) Structure of the azocompound molecule; b) An X-type structure of an azodye monolayer.

To characterise the films we use optical microscope observations as well as infrared and X-ray analysis. Microscope observations between crossed polarizers show the domain structure of the LB films. The domains are of about 0.5 microns in size and they have optical axes randomly distributed in the plane of the LB films. X-ray analyses have been done at the Institute of Crystallography, Moscow (group of Y. Lvov). A layered structure of period 18.5 Å is found, parallel to the substrate. Because of the preparation method we expect an X-type layer structure with hydrocarbon chains close to the normal of the plate. Taking into account the dye molecular model we can estimate the rigid azobenzene part to be tilted by an angle of about 55° with respect to the layer normal, Figure 3b. We have found nearly the same tilt ($\approx 55.7°$) from polarized absorption spectra measured at different incidence angles.

3.2. EXPERIMENTAL TECHNIQUE TO INDUCE FILM ANISOTROPY. — In this paper we skip the detailed description of the experimental set-up used to induce optical anisotropy because it is the same as was used in [14]. We only want to say that to measure the induced birefringence we use phase-sensitive registration of the modulated signal of He-Ne laser beam passed through the birefringent film perpendicular to the $X - Y$ plane. Using the phase-sensitive registration gives rise to a high sensitivity that allows accurate measurements of both maximum birefringence and angular position of the induced optical axis by rotation of the sample in the $X - Y$ plane. The position of the induced axis is defined from the value of the angle necessary to rotate the sample until a minimum signal is achieved. We use this ability during the second illumination, when the rotation of the induced optical axis is observed.

3.3. THE OBSERVATION OF THE INDUCED OPTICAL AXIS ROTATION. — The direct method to check the proposed model experimentally is to measure the rotation of the domain director. In principle, if the domain size is large in comparison with the wave length of light, it could be done by measuring a change of the domain axis position versus illumination time. As was said, the rotation of domain axis in the plane $X - L$ can be considered as rotations in two planes: $X - Y$ and $L - Z$, which can be measured experimentally. To measure ϕ-rotation one needs to measure the position of the optical axis in this plane during illumination. The θ-rotation in the $L - Z$ plane can be observed as a change in the maximum value of the measured birefringence if the quantity of molecules in the domain remains constant (no decomposition). Let us write

the expressions for ϕ- and θ-*rotation*.

It is useful to rewrite (16) as the following equation for the domain axis rotation:

$$\frac{d\psi_0}{dt} \equiv \Omega = CI \sin(2\psi_0), \tag{18}$$

where

$$C = \frac{\sigma \tau_e}{2h\nu} \left(\frac{1}{\eta^*} - \frac{1}{\eta} \right) \Delta^2 \tag{19}$$

The solution of (18) for the domain rotation in the $\mathbf{X} - \mathbf{L}$ plane is:

$$\psi_0(t) = \text{arctg}(\text{tg}(\psi_0(0)) \exp(2ICt)) \tag{20}$$

For the angle between the light polarization vector and the projection of the domain director onto $\mathbf{X} - \mathbf{Y}$ plane we have:

$$\phi(t) = \text{ArcCos} \left(\sqrt{\frac{1 + (\zeta)^2}{1 + \left(\frac{\zeta}{\cos(\psi_0(t))} \right)^2}} \right) \tag{21}$$

For the maximum birefringence one can get:

$$\Delta n(t) \propto (\sin(\theta(t)))^2 = 1 - \frac{(\sin(\psi_0(t)))^2}{1 + (\zeta)^2}, \tag{22}$$

where ζ is defined by z- and y-components of the normal vector $(0, n_\theta, n_\phi)$ to the $\mathbf{X} - \mathbf{L}$ plane as:

$$\zeta = -\frac{n_\phi}{n_\theta} \tag{23}$$

$$n_\phi = \frac{\sin\theta \sin\phi}{\sqrt{\cos^2\theta + \sin^2\theta \sin^2\phi}}, \tag{24}$$

$$n_\theta = \frac{\cos\theta}{\sqrt{\cos^2\theta + \sin^2\theta \sin^2\phi}} \tag{25}$$

We remind that θ is the the angle between domain director and $\mathbf{Z}$-axis.

The dependences (21) and (22) could be checked experimentally if we are able to observe a single domain. Actually because a typical size of one domain is of about one micron or less, performing such a kind of measurement is difficult. So we propose another method based on a layer structure of Langmuir-Blodgett film to have a good approximation of one domain rotation.

Figure 4 explains qualitatively the idea of the new method. We first illuminate by linearly polarized light the film with an isotropic distribution of domain optical axes in $\mathbf{X} - \mathbf{Y}$ plane, Figure 4a. The result is, that all the domain axes are oriented almost perpendicular with respect to the light polarization, Figure 4b. Because of the layer structure of the LB film the domain reorientation is quasi ϕ-*rotation* and on average the tilt angle of the molecular oscillators is not changed significantly. This property of POA in LB films can also be understood in the frame of the model proposed. Let us image a film consisting of many domains with directors randomly distributed in the plane of this film, so all domain directors are in the same plane, which is
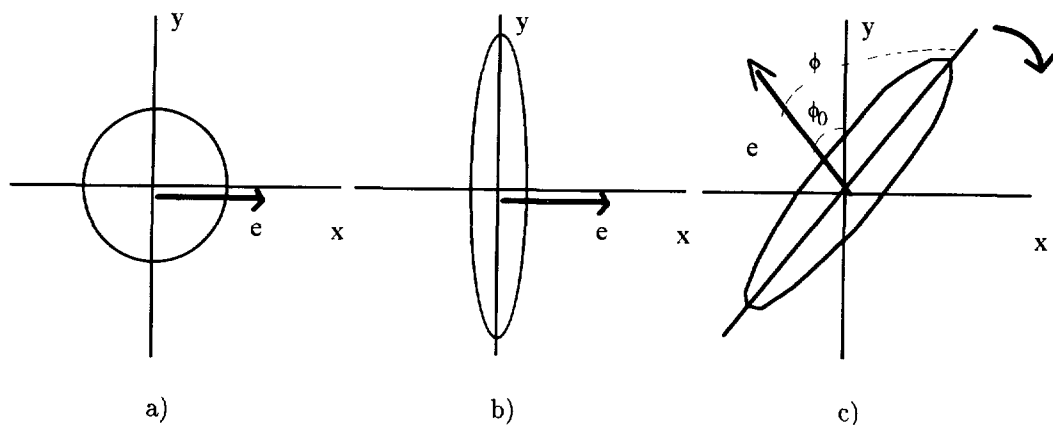
Fig. 4. — The scheme of two successive illuminations; **e** is the direction of the inducing light polariza-
tion; a) shows the domain distribution before the first illumination; b) the distribution of the domains
after the first illumination; c) the rotation of the optical axis during the second illumination.

$\mathbf{X} - \mathbf{Y}$. The light polarization vector is also in the film plane and oriented along the $\mathbf{X}$-axis.
According to the model, because the $\mathbf{X} - \mathbf{L}$ and $\mathbf{X} - \mathbf{Y}$ planes are coincident, the rotation of
each domain will be in the plane $\mathbf{X} - \mathbf{Y}$, so the domain rotation is pure ϕ-rotation. As was
shown, in real LB films the molecular oscillators are tilted with respect to the film plane. Thus,
if the polarization vector is in the film plane, we still have many distinctive planes $\mathbf{X} - \mathbf{L}_i$ for
each of ith-domain. Now according to the model we have not a pure ϕ-rotation. However,
because the initial tilt angle for molecular oscillators within each domain is the same (property
of LB films), the induction of the anisotropy can be characterised as a *quasi ϕ-rotation* in the
sense that for a majority of domains the tilt of oscillators is changed slightly. We will also see
proofs of this fact later. Thus, instead of observing a single domain, we propose to look at a
group of domains whose axes are oriented nearly the same way. Thus we can make the second
illumination with a new orientation of the light polarization vector at some angle from the
induced macroscopic optical axis, Figure 4c. Now the macroscopic optical axis can be rotated,
and the idea is to measure the new angular position of this optical axis in the plane of the film
and the corresponding maximum birefringence versus the time of illumination.

In the experiments we have used 15 layers LB films photo-oriented at the intensity of about
10 mW/cm^2 during half an hour. Under these conditions, after the first photo-orientation, the
value of the order parameter defined as:

$$S = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} \tag{26}$$

and measured by in-plane optical dichroism method is of about 0.8 ($D_{\parallel}, D_{\perp}$ are the absorptions
measured with the light polarization being parallel and perpendicular to the induced optical
axis respectively). After the first illumination the polarized absorption spectra show the in-
crease in the absorption for $\mathbf{Y}$-direction of the light polarization that is approximately equal
to the decrease for the $\mathbf{X}$-direction. It proves the assumption on the *quasi ϕ-rotation*. The
difference found of about 15% between the increase and decrease of the polarized absorption
is not due to molecular decomposition and points to the existence of a photoreorientation in
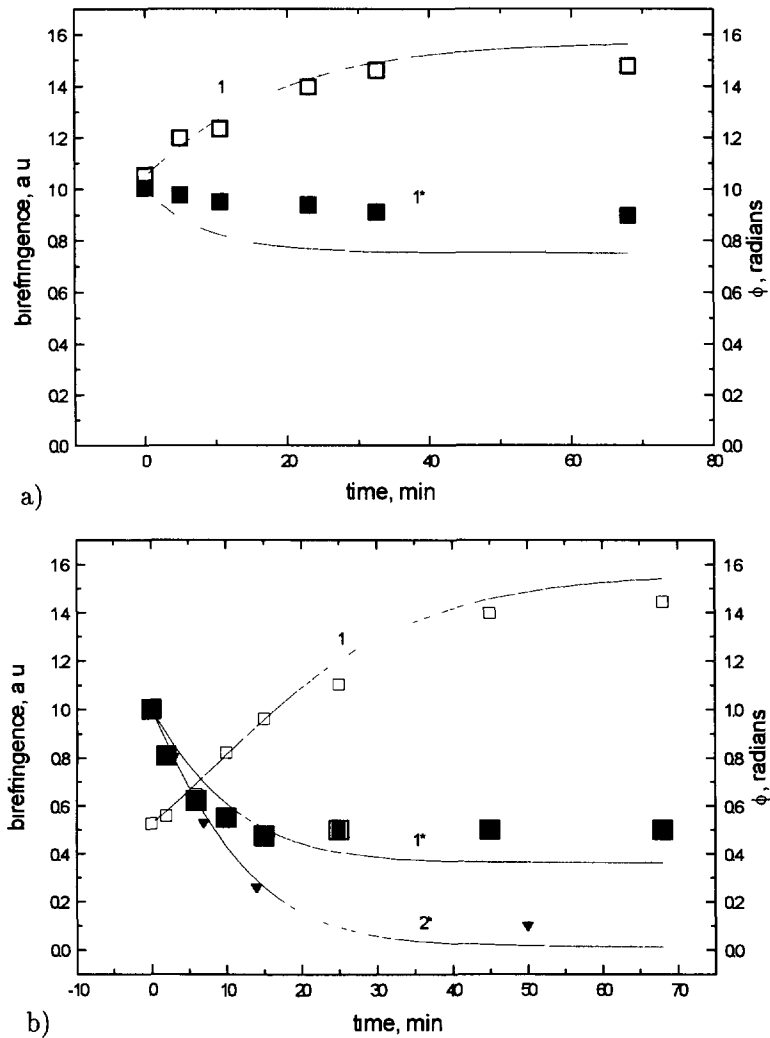direction of the film normal. The absence of decomposition was checked in a separate exper-

Fig. 5. — Experimental and theoretical dependences for the angular position ϕ of the induced optical axis and of the maximum of the birefringence versus time of second illumination. Experimental points are shown by scatters. a) 1, 1* are the calculated angle positions of the optical axis and birefringence *versus* illumination time for a domain with optical axis initially oriented at an angle of 60° with respect to the light polarization vector; b) 1, 1* are the calculated angle positions of the optical axis and birefringence *versus* illumination time for a domain with optical axis initially oriented at an angle of 30° with respect to the light polarization vector. 2* is the calculated birefringence *versus* illumination time for a domain with optical axis initially oriented at the angle of 5° with respect to the light polarization vector. The fitting constant in (21) and (22) is $IC = 0.03$ min^{-1}.

iment by measuring the out-of-plane optical dichroism, when the optical axis along the film normal was induced by unpolarized light of double intensity.

The experimental dependences of the maximum birefringence and the angle positions of the optical axis in the plane of the LB film *versus* time of second illumination are shown in Figure 5. We measured these dependences for different starting angles ϕ_0 between the light polarization

vector and induced axis.

If the starting angle between the light polarization vector and the induced optical axis is 60°, only a very small decrease of about 5% of maximum birefringence is observed (Fig. 5a) during the first 5 minutes of illumination. The result can be interpreted as a two-dimensional angular shift of the molecular distribution function when the value of the order parameter is preserved. The constant value of the order parameter during optical axis rotation cannot be explained by photochemical models based on simple absorption selection. It can be understood if the domain axes are really rotated and the rotation is mainly in the $\mathbf{X} - \mathbf{Y}$ plane.

If the second illumination is started at the angle of $\phi_0 = 30°$, we also observe the rotation of the induced optical axis, but at the same time we see the decrease by 2 times of the maximum birefringence, Figure 5b. For smaller initial angles ϕ_0 the decrease of the birefringence can be more then 10 times (Fig. 5b, curve (2*)). This extremely high decrease cannot be explained by the mentioned models of POA as well. According to the models based on a simple molecular selection under light excitation, when the excited molecule can occupy any angular position with a same probability, the birefringence decrease should not exceed 1/2 in the final state (saturation, when the optical axis is at 90° with respect to the light polarization vector).

To see if it is possible to understand these sets of observed results in the frame of our model we made fitting of the measured data by expressions (21) and (22) (solid curves in Fig. 5). We found that all data sets shown in Figure 5 can be fitted with the same value of $IC = 0.04$ min^{-1} ($C = 6.6 \times 10^{-6}$ W^{-1}m^{2}s^{-1}) taking the oscillator tilt angle of 55° with respect to the film normal. On average a better fitting is achieved when the tilt angle of the oscillators is taken to be equal to 40° and $IC = 0.03$ min^{-1}. Let us compare the value of C found with that estimated from Equation (19). Assuming $\eta^*/\eta = 0.9$ and taking $\tau_e = 10^{-10}$ s, $\sigma = 5 \times 10^{-21}$m^2, $h\nu = 2$ eV, $\tau_c^* = 10^{-13}$ s, $J^* = 10^{-42}$ kg m^2, $W_0^* = 0.2$ eV, $\Delta^2 \approx 0.1$, we estimate $C = 2.5 \times 10^{-5}$ W^{-1}m^{2}s^{-1}. which is of the same order as the measured value. Nevertheless, there are still significant discrepancies between the fittings and the data in the range of longer illumination times. The measured values of the birefringence are systematically higher than predicted by the model. These disagreements show that the photoreorientation is closer to ϕ-rotation than predicted. From the data in Figure 5 assuming the initial oscillators' tilt of 55° one can find that rotation in the $\mathbf{L} - \mathbf{Z}$ plane stops when the angle ψ_0 is of about 70°. This fact can be seen more clearly in Figure 6, where the measured data are presented as angular velocities of domain directors in the $\mathbf{X} - \mathbf{Y}$ (angle ϕ) and $\mathbf{L} - \mathbf{Z}$ (angle θ) planes versus their angle position ϕ during the induced rotation. According to equation (18), for the angular velocities of a director of a single domain one can write:

$$\frac{\partial \theta}{\partial t} = IC \sin(2\psi_0)n_\theta = 2IC \sin\theta \cos\phi\sqrt{1 - \sin^2\theta \cos^2\phi}\, n_\theta$$
$$\frac{\partial \phi}{\partial t} = IC \sin(2\psi_0)n_\phi = 2IC \sin\theta \cos\phi\sqrt{1 - \sin^2\theta \cos^2\phi}\, n_\phi \qquad (27)$$

The data shown in Figure 6 are measured for a starting angle ϕ_0 of 0.52 (30°). One can see that the rotation in θ-plane stops when ϕ is higher than 1 (60°) (corresponding θ is of about 40° − 30°). It does not agree with equation (27) showing that the velocity should not vanish until ϕ is equal to 90°. Obviously, to be in agreement with the experiment one needs to introduce some additional torque. We explain this result by the existence of an angle threshold for θ-rotation. In fact our model does not take into account anchoring of molecular layers with the surface of the substrate. To start with we have molecular layers, which are parallel to the substrate surface. The rotation in the $\mathbf{X} - \mathbf{L}$ plane must tilt the layer planes with respect to the $\mathbf{X} - \mathbf{Y}$ plane. It relates to some destruction of layers that needs producing an additional work
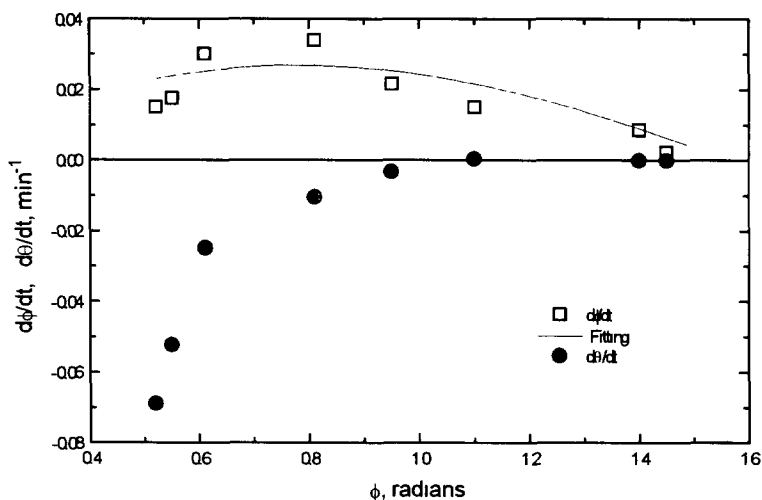
Fig. 6. — The ϕ- and θ-components of the angular velocity for domain directors during the second illumination versus angular position of the optical axis. Lowest value of ϕ corresponds to the start moment of the second illumination. The θ-component was calculated from data of maximum birefringence assuming the starting tilt of molecular oscillators to be of 55°. Solid curve shows calculated ϕ-component of the angular velocity at constant value of $\theta = 55°$ and $IC = 0\ 04\ \text{min}^{-1}$.

and could be the reason of the observed threshold. Another reason of the observed disagreement with the model can be related to some physical processes inside domain walls. At this stage we have no experimental data of any kind of these processes. This problem requires a separate theoretical consideration. The detailed investigation of this threshold will be addressed in future work. Is this angular threshold related to the intensity? It is also the question of the future work. Here we only want to emphasise that at high angles between light polarization and the induced axis the rotation can be pure ϕ-rotation. In the dependence of angular velocity upon ϕ there is a maximum at $\phi = 0.6 - 0.8$, Figure 6. The existence of this maximum is well explained by our model. In this case the value of ψ_0 is close to 45°, when the photo-induced torque has a maximum value, so the ϕ-component of the torque is the highest as well. The simplest fitting, when the θ-angle is assumed to be a constant and equal 55° is shown by a solid line in Figure 6. The fitting could be better if instead of one domain approximation, the multidomain distribution was used. The latter procedure needs additional information on the domain distribution function and was not used here specially to demonstrate that the simplest one domain approximation quite adequately describes the data. Nevertheless the model should be considered only as some step in understanding the POA effect. What is still not clear enough is the nature of the observed threshold. The experimental separation of *trans-cis* contribution from one due to the difference in the molecular interaction energies for excited and unexcited molecules will also be addressed in future work. To answer these questions one needs to find new molecules, which cannot show the reactions of *trans-cis* transitions but have high change of electrical parameters such as polarizability and dipole moment under excitation. One of such compounds has already been found and we hope that soon we will be able to present the experimental data on the role of a change in the interaction energy upon the light excitation

in POA effect. The last prediction of our model that is not yet checked is the change of sign of the axis rotation when the friction difference with the substrate between ground state and excited molecules also changes sign. Here also new compounds woud help to verify this point.

Finally, an interesting experiment associated with the new method of sample preparation used to observe the optical axis rotation, and similar to the effect of Einstein-de-Haas [17], can be proposed. In our photo-oriented system, because of the macroscopic rotation of the domains in the same direction, the reaction of substrate must take place. Our estimations show that at high intensities of illumination (huge laser pulse) the reaction of the substrate can be significant to be observed if no melting or decomposition will take place.

4. Conclusion

To conclude we proposed a model to explain the photo-induced optical rotation of photo-induced axis of dye molecular layers. The model is based on different friction coefficients for excited and unexcited molecules interacting with a substrate in mean molecular field. This difference in friction could be the result of change in either molecular conformation of the excited molecule or the interaction energy with a mean molecular field under light excitation. The POA effect is explained by the model as a continuous redistribution of ordered molecular packets when the molecular order is conserved by the mean molecular field but only the direction of the maximum of angular distribution is shifted. This rotation with respect to the substrate obeys the conservation of total angular momentum, where a photo-induced internal torque is just balanced by a reaction of the substrate. A new method based on second illumination of photo-oriented Langmuir-Blodgett films is proposed to observe the light-induced optical axis rotation. Experimental results concerning this photo-induced rotation of the optical axis in photo-oriented Langmuir-Blodgett films are presented and explained by the model. The angular dependence of the photo-induced angular torque is confirmed. The existence of angular threshold for out-of-plane rotation (θ-rotation) is observed and qualitatively explained by anchoring of molecular layers with the substrate.

Acknowledgments

References

[1] Neporent B.S. and Stolbova O.V., *Opt. Spektrosk.* **10** (1961) 294

[2] Makushenko A.M., Neporent B.S. and Stolbova O.V., *Opt. Spectrosk.* **31** (1971) 741.

[3] Wendorft J.H. and Eich M., *Mol. Cryst.* **169** (1989) 133

[4] Kvasnikov E.D , Kozenkov V.M. and Barachevsky V.A., *Dokl. Akad. Nauk SSSR* **273** (1977) 633.

[5] Dumont M. and Sekkat Z , SPIE Proceedings, San Diego, July 1992 (1992) p. 1774.

[6] Sekkat Z. and Dumont M , *Appl. Phys. B* **54** (1992) 486.

[7] Kozenkov V.M., Yudin S.G., Katyshev E G., Palto S.P., Lazareva V.T. and Barachevsky V.A., *Sov. Pys'ma Zh. Tekh. Fiz.* **12** (1986) 1267 (in Russian).

[8] Barnik M.I., Kozenkov V.M., Shtykov N.M., Palto S.P. and Yudin S.G., *J. Mol. Electron.* **5** (1989) 53.

[9] Seki T. and Ichimura K., *Thin Solid Films* **179** (1989) 77.

[10] Palto S.P., Shtykov N.M., Khavrichev V.A. and Yudin S.G., *Mol. Mat.* **1** (1992) 3.

[11] Palto S.P., Blinov L.M., Udal'yev A.A. and Yudin S.G., *Mol. Mat.* **2** (1992) 63.

[12] Palto S.P., Blinov L.M., Yudin S.G., Grewer G , Schönhoff M. and Lösche M., *Chem. Phys. Lett.* **202** (1993) 308.

[13] Janossy I , *Phys. Rev E.* **49**(N4) (1994) 2957.

[14] Palto S.P., Yudin S.G., Germain C. and Durand G , *J. Phys. II France* **5** (1995) 133.

[15] de Gennes P.-G., Physics of Liquid Crystals (Clarendon, Oxford, 1974).

[16] Langmuir I. and Schaefer V.J., *J. Am Chem. Soc* **60** (1938) 1351.

[17] Einstein A. and de Haas W.J., *Naturwissen.* **3** (1915) 237.