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Local Field Anisotropy in Langmuir−Blodgett Films of Cadmium Arachidate

E. M. Aver'yanov

*Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50, Krasnoyarsk, 660036 Russia*
e-mail: aver@iph.krasn.ru
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Abstract—Lorentz tensor and local field tensor components for uniaxial Langmuir−Blodgett films of cadmium arachidate from 3 to 100 nm thick on silver, polymethyl methacrylate, and glass substrates have been experimentally determined using the data on the film refractive index dispersion in the visible range. The constraints from below on the mean value and anisotropy of the molecular polarizability caused by the intermolecular interactions in the film have been established.

Nanoscale Langmuir−Blodgett (LB) films are promising as elements of molecular electronics and optoelectronics [1−3]. Methods of linear optics and spectroscopy are efficient for studying their structure and properties [1−3]. Quantitative interpretation of data is based on the relation [4]

$$\varepsilon_j(\omega) = 1 + 4\pi N f_j(\omega)\gamma_j(\omega) \qquad (1)$$

between the permittivity components ε_j and the ensemble-averaged components γ_j of the molecule polarizability for light waves polarized along ($j = \|$) and across ($j = \perp$) the film optical axis $\mathbf{n}$ (N is the number of molecules per unit volume). The components $f_j = 1 + L_j(\varepsilon_j - 1)$ of the local field tensor relate the local field $E_j^{(\text{loc})}(\omega) = f_j(\omega)E_j(\omega)$ of the light wave acting on the molecule to the macroscopic field $E_j(\omega)$ of the light wave in a medium. In the film transparency range, $\varepsilon_j = n_j^2$, n_j are refractive indices, and L_j are Lorentz tensor components ($\text{Sp}\,L = 1$). Information on the orientational order of molecules and their properties is contained in components γ_j which are determined from relation (1) and depend on f_j and L_j. Therefore, to study LB films and to model their properties, the values of L_j should be experimentally determined, which is possible with the availability of the dependences $n_j(\lambda)$ of the film refractive indices on the light wavelength in the visible transparency range [5]. In this study, the aforementioned method is used to determine components L_j and f_j in LB films of cadmium arachidate (Cd−A) on various substrates and to determine constraints imposed by the formation of the LB film and intermolecular interactions in it on properties of the molecular polarizability tensor γ.

The optical axis $\mathbf{n}$ of Cd−A films is normal to the substrate surface, and the longitudinal axes $\mathbf{l}$ of [CH$_3$−(CH$_2$)$_{18}$−C(O)O$^-$]$_2$Cd^{++} molecules are preferentially oriented along $\mathbf{n}$ [2, 6−8]. For Cd−A molecules without aromatic fragments, the difference between polarizability densities for hydrophobic aliphatic chains and hydrophilic "heads" can be neglected, and the dependence of the components $\gamma_j(z)$, $\varepsilon_j(z)$, $L_j(z)$, and $f_j(z)$ on the coordinate $z \parallel \mathbf{n}$ within the molecular layer in formula (1) can also be ignored. A measure of the orientational order of molecules with respect to $\mathbf{n}$ is the quantity $S = \langle 3\cos^2\theta - 1\rangle/2$, where θ is the angle between $\mathbf{l}$ and $\mathbf{n}$ axes, and angle brackets $\langle...\rangle$ mean averaging over the molecular ensemble. For uniaxial Cd−A molecules, the tensor γ with longitudinal (γ_l) and transverse (γ_t) components is characterized by the mean value $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and anisotropy $\Delta\gamma = \gamma_l - \gamma_t$.

For LB films with $\Delta\gamma > 0$ and $\Delta\varepsilon = (\varepsilon_\| - \varepsilon_\perp) > 0$, the component $L_\perp$ ($L_\| = 1 - 2L_\perp$) is determined as follows. In the visible transparency range, we use the parameters $\bar{\varepsilon} = (\varepsilon_\| + 2\varepsilon_\perp)/3$, $Q = \Delta\varepsilon/(\bar{\varepsilon} - 1)$, and the quantities depending on them,

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0,$$

$$b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2. \qquad (2)$$

At a given film state characterized by the index T, these quantities are functions of T, and the desired

value of $L_\perp(T)$ is related to them by the expression [9]

$$L_\perp = L_{\perp k} - \frac{(\bar\varepsilon + 2)}{12(\bar\varepsilon - 1)} \tag{3}$$
$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}].$$

The sign of the anisotropy $\Delta f = f_\parallel - f_\perp$ is the same as the sign of b, and the value $L_{\perp k} = (3 + 2Q)/[3(3 + Q)]$ corresponds to the conditions $b = \Delta f = 0$. The function $b(\lambda, T)$ depends on the unknown $\bar\gamma$. If the values $n_j(\lambda_i, T)$ are known for a discrete set of values $\lambda_i (i = 1 - p)$ in the visible range, the function $b(\lambda, T)$ in the range $\lambda_1 - \lambda_p$ is approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \ldots + a_m(T)\lambda^m. \tag{4}$$

The value of $L_\perp(T)$ is independent of λ, and $m + 2$ unknowns $\{L_\perp^{(m)}, a_0 - a_m\}$ correspond to the state T. They are determined from the system of $m + 2 = p$ equations (3) each corresponding to one of values λ_i. The higher approximation in (4) implies the higher accuracy of values $n_j(\lambda, T)$; otherwise, the set of equations with respect to $\{L_\perp^{(m)}, a_0 - a_m\}$ can have no physical solutions. The criterion of adequacy of the approximation used in (4) is the accordance of the values $L_\perp^{(m)}$ with the values $\langle L_\perp^{(m-1)} \rangle$ averaged over the values $L_\perp^{(m-1)}$ corresponding to all possible combinations of $p - 1$ references λ_i from the set $\lambda_1 - \lambda_p$ [5]. In contrast to the known methods for determining the components L_j and f_j in uniaxial molecular media [4], this method is free of a priori assumptions on unobservable molecular parameters (sizes of molecules and anisotropy of their shape, properties of the tensor γ, oscillator strengths of molecular transitions).

For Cd–A films on various substrates, the dependences $n_j(\lambda)$ in the visible range are known [2, 6, 7]. For films on silver substrates, the table lists the values $n_j(\lambda)$ graphically presented in [6] and averaged over a set of samples with numbers of molecular layers from 1 to 12, which corresponds to the film thickness $d = 2.7$–32.3 nm [6]. For Cd–A films on polymethyl methacrylate (PMMA) and glass substrates, the table lists the values $n_j(\lambda)$ [7] averaged over samples with numbers of layers 29, 37, and 41 ($d = 77.7, 99.2,$ and 109.9 nm).

For the Cd–A film on silver, the values $n_j(\lambda_i)$ at six references λ_i yield identical values $L_\perp^{(4)} = 0.3570$ and $\langle L_\perp^{(3)} \rangle = 0.3571 \pm 0.0014$. For the film on PMMA (glass), the values $n_j(\lambda_i)$ at three references λ_i yield $L_\perp^{(1)} = 0.356$ and $\langle L_\perp^{(0)} \rangle = 0.352 \pm 0.002$ ($L_\perp^{(1)} = 0.365$

Parameters λ_i (µm) and the dependences of the indicated quantities on λ_i for Cd–A films on silver, polymethyl methacrylate, and glass substrates

Substrate	λ_i	$n_\parallel$	$n_\perp$	$-\Delta f$	σ
Ag	0.4416	1.5775	1.5344	0.058	0.429
	0.4579	1.5751	1.5314	0.057	0.414
	0.4880	1.5695	1.5269	0.057	0.424
	0.5145	1.5666	1.5238	0.056	0.415
	0.6041	1.5524	1.5100	0.054	0.397
	0.6328	1.5478	1.5048	0.052	0.379
PMMA	0.4579	1.589	1.544	0.053	0.384
	0.5145	1.571	1.533	0.058	0.485
	0.6328	1.550	1.517	0.059	0.563
Glass	0.4579	1.616	1.536	0.061	0.252
	0.5145	1.568	1.525	0.090	0.670
	0.6328	1.565	1.525	0.093	0.739

and $\langle L_\perp^{(0)} \rangle = 0.362 \pm 0.003$), which are in agreement within the accuracy of the $\langle L_\perp^{(0)} \rangle$ determination. In this case, the value $L_\perp^{(1)}(\text{Ag}) = 0.361$ corresponding to the values $n_j(\lambda_i)$ at the same references λ_i as for PMMA and glass substrates is identical to the average value $[L_\perp^{(1)}(\text{PMMA}) + L_\perp^{(1)}(\text{Glass})]/2$. Let us note high accuracy of values $\langle L_\perp^{(0)} \rangle$ for Cd–A films on PMMA and glass substrates at low accuracy (≈ 0.01) of values $n_j(\lambda_i)$ [7]. The weak dependence of $L_\perp$ on the film thickness is caused by the use of the values $n_j(\lambda_i)$ [6, 7] averaged over samples of various thicknesses. The difference of the values $n_j(\lambda_i)$ at identical λ_i for Cd–A films on various substrates appears at slightly different $L_\perp$.

The anisotropy Δf is more sensitive to these factors. For Cd–A films on silver, a weak decrease (a significant increase) in $|\Delta f|$ in the range $\lambda_1 - \lambda_p$ corresponds to the absence of the change $\Delta n = n_\parallel - n_\perp$ with increasing λ (decreasing Δn for films on PMMA and glass). The sign and value of Δf reflect the constraints imposed by intermolecular interactions on the values of $\bar\gamma$ and $\Delta\gamma$ during organization of molecules into an anisotropic ensemble [9]. Using the parameter

$$A = (L_\perp - 1/3)/(L_{\perp k} - 1/3), \tag{5}$$

the value quantity Δf and average value $\bar f = (f_\parallel + 2f_\perp)/3$ can be written as

$$\Delta f = Q(\bar\varepsilon - 1)(1 - A)/3,$$
$$\bar f = (\bar\varepsilon + 2)[1 - A(1 - r_0)]/3. \tag{6}$$

For Cd–A films on all substrates in the visible range, the experimental values of $L_\perp$ satisfy the inequalities $L_\perp > L_{\perp k} > 1/3$, $A > 1$, and $\Delta f < 0$. Taking into account $\Delta \gamma \Delta f < 0$ in the relation [4]

$$\bar{\varepsilon} - 1 = 4\pi N(\bar{\gamma}\bar{f} + 2S\Delta\gamma\Delta f/9) \tag{7}$$

we obtain the following constraints

$$\bar{\gamma} > \frac{\bar{\varepsilon} - 1}{4\pi N\bar{f}} > \frac{3(\bar{\varepsilon} - 1)}{4\pi N r_0(\bar{\varepsilon} + 2)}. \tag{8}$$

The quantity $S\Delta\gamma$ is given by the expression [5]

$$S\Delta\gamma = \bar{\gamma}Q(1 + \sigma), \tag{9}$$

where the correction σ to the anisotropy Δf is given by

$$\sigma = -\frac{\Delta f(9 - Q^2)(3 + 2Q)}{Q[3(3 + Q)(\bar{\varepsilon} + 2)r_0 + \Delta f(3 - Q)(3 + 2Q)]}. \tag{10}$$

The signs of σ and Δf are opposite; in the visible transparency range of Cd–A films on all substrates, $\sigma > 0$. The values of Δf and σ calculated by formulas (6) and (10) using the values $n_j(\lambda_i)$, components $L_\perp(\text{Ag}) = 0.357$, $L_\perp(\text{PMMA}) = 0.356$, and $L_\perp(\text{Glass}) = 0.365$, are listed in the table. We can see that despite small values of Δf, the values of σ are not small and are significant for determining the values of $\Delta\gamma S$ by formula (9). Taking into account (8) and (9), we obtain the constraints

$$S\Delta\gamma > \frac{\Delta\varepsilon}{4\pi N\bar{f}}(1 + \sigma) > \frac{3\Delta\varepsilon}{4\pi N r_0(\bar{\varepsilon} + 2)}. \tag{11}$$

Upper estimates of $\bar{\gamma}$ and $S\Delta\gamma$ in formulas (8) and (11) differ slightly from their exact values in (7) and (9).

The right-hand sides of formulas (8) and (11) correspond to the values of $\bar{\gamma}$ and $S\Delta\gamma$ at $\Delta f = 0$ and the isotropic tensor $f = \bar{f}$ ($A = 1$) = $(\bar{\varepsilon} + 2)r_0/3 < (\bar{\varepsilon} + 2)/3$. At given S controlled by LB film preparation conditions [1], constraints (8) and (11) reflect the effect of intermolecular interactions in the film on the components $\gamma_\| = \bar{\gamma} + 2S\Delta\gamma/3$ and $\gamma_\perp = \bar{\gamma} - S\Delta\gamma/3$ which vary mutually consistently with $n_j(\lambda)$, L_j, and f_j. This is important to understand and model properties of artificially organized anisotropic molecular ensembles, since it is generally accepted that molecular properties remain unchanged during the formation of such ensembles. The determination of the components L_j and f_j makes it possible to control properties of molecules during their structural organization.

For LB films whose molecules contain hydrophilic fragments such as large aromatic groups (chromophores, dyes [1]) with electronic structure and polarizability density significantly different from those of hydrophobic fragments, the used method for determining the components L_j and f_j is inapplicable. Separation of the film molecular layer into submonolayers formed by hydrophilic and hydrophobic molecular fragments results in modulation of the components $\gamma_j(z)$, $\varepsilon_j(z)$, $L_j(z)$, and $f_j(z)$ in the molecular layer and also requires the description of optical properties of such LB films as layered two-component composite materials.

Finally, we note that the studies of the dependences $n_j(\lambda)$ for LB films in a rather wide spectral range are rare so far [1–3, 6, 7]. The new possibilities of using these dependences to experimentally determine the components L_j, f_j, and the values of $\bar{\gamma}$, $S\Delta\gamma$ (at known density $\rho \propto N$) can stimulate the development of the methods for measuring $n_j(\lambda)$ for LB films in two directions: increasing the accuracy of n_j and extending the spectral range of λ.

REFERENCES

1. L. M. Blinov, Usp. Khim. **52**, 1263 (1983); L. M. Blinov, Sov. Phys.–Usp. **31** (7), 623 (1988).
2. J. D. Swalen, J. Mol. Electron. **2**, 155 (1986).
3. J. D. Swalen, Thin Solid Films **160**, 197 (1988).
4. E. M. Aver'yanov, *Local Field Effects in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999) [in Russian].
5. E. M. Aver'yanov, JETP **110** (4), 622 (2010).
6. I. Pockrand, J. D. Swalen, J. G. Gordon, and M. R. Philpott, Surf. Sci. **74**, 237 (1977).
7. J. D. Swalen, K. E. Rieckhoff, and M. Tacke, Opt. Commun. **24**, 146 (1978).
8. D. I. Allara and J. D. Swalen, J. Phys. Chem. **86**, 2700 (1982).
9. E. M. Aver'yanov, JETP **108** (1), 176 (2009).

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