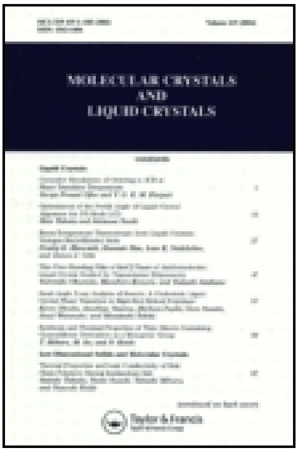

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STARK-SPECTROSCOPY AND DIPOLE ORDERING IN LANGMUIR-BLODGETT FILMS *

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Abstract An analogy between liquid crystals and Langmuir-Blodgett films is briefly discussed. The application of the Stark-spectroscopy technique to investigation of various phenomena in Langmuir-Blodgett films is demonstrated. It is very useful for determination of the orientational distribution function of molecular dipoles including the case of superlattices, for study of the photo-induced charge transfer and the dynamic of the photo-induced dipole reorientation, for measuring both the local fields from external sources and from dipolar layers. A possibility for application of the same technique to liquid crystalline materials is outlined.

Keywords: Langmuir-Blodgett films, monolayers, Stark-spectroscopy, absorbtion spectra

The paper has been presented as an invited lecture at the European Conference on Liquid Crystals in Courmayeur (Italy, 1991). The full text of it which is a rather comprehensive review of the authors' papers on the Stark-spectroscopy of Langmuir-Blodgett films will be published in the new journal *Molecular Materials* to be issued in the USSR[1]. Here we present a short version of the review which is, in fact, a summary of the basic application of the Stark-spectroscopy technique and can serve as a guide over the list of references.

ANALOGY BETWEEN LANGMUIR-BLODGETT FILMS AND LIQUID CRYSTALS

There is, perhaps not very deep, but still interesting analogy between the structure of Langmuir-Blodgett films and liquid crystals. Langmuir-Blodgett films are stacks of monomolecular layers transferred from the water surface onto a solid substrate[2-4]. To some extent they keep the structure of its precursor, a monolayer on water . The latter can be in a quasi two-dimensional liquid, liquid crystalline, or solid phase. During and after a transfer a process of recrystallization of a film takes place, thus, stricktly speaking, the final structure of a solid film differs from that of the precursor. In fact, the recrystallization occurs under specific conditions being restricted by the very two-dimensional nature of the transfer process. As a result, we have a quasi-equilibrium lamellar system reminding of the smectic B phase which, as it is well known, can be either a true three-dimensional crystal phase or the hexatic phase. However, from the symmetry point of view Langmuir-Blodgett films are polar systems because the two directions, upward of and downward to a substrate are different. Generally they posess a polar axis directed along the film normal. Only in a special case of the bilayered structure (Y-type transfer) the bulk of rather thick films may be considered to be non-polar.

On the macroscopic scale Langmuir-Blodgett films show a polycrystalline or polydomain structure. The azimuthal distribution of individual domains is, as a rule, isotropic though a few interesting examples of the in-plane anisotropy have been demonstrated[2,4]. Thus ordinary films are optically uniaxial with the unique axis directed along the film normal. In this respect they look like cylindrically symmetric smectic A liquid crystals though, in this case, the polar ones.

In order to characterize Langmuir-Blodgett films one can consider a density wave with the wavevector along the film normal. In contrast to smectics this wave is not sinusoidal, its higher harmonics are very well pronounced. One can also introduce the orientational distribution function for long molecular axes

$$f(\vartheta) = (1/2\pi)\sum (n+1/2)\, P_n\langle \cos\vartheta\rangle\, P_n(\cos\vartheta) \qquad (1)$$

where ϑ is an angle between the longitudinal molecular axis and the film normal. In contrast to non-polar liquid crystals (nematic, smectic A, B, C, etc.) this expansion contains not only even but odd Legendre polynomials P_n which include terms $\langle\cos^n\vartheta\rangle$ with odd numbers $n = 1, 3, \ldots$ Even parameters P_2 and P_4 are analogous to those for liquid crystals. For example,

$$P_2 = (1/2)(3\langle\cos^2\vartheta\rangle - 1) \qquad (2)$$

describes nematic ordering. The most important among odd parameters is $\langle\cos\vartheta\rangle$ which describes the polar ordering in the film and determines its macroscopic polarization.

It should be noted that P_n can not be considered as true order parameters as they can not be related to corresponding phase transitions. This is a fundamental difference between Langmuir-Blodgett films which are quasi-equilibrium systems and liquid crystals which are equilibrium phases.

The Stark-spectroscopy technique allows one to study structural features of Langmuir-Blodgett films, for example, to measure even and odd P_n parameters, to investigate the dynamics of the reorientation of molecules, to measure local electric fields in medium, to study charge transfer phenomena, etc. In future this technique may be used for investigation of liquid crystals, at least, polymeric ones. The crucial point is to have low conductivity of the medium.

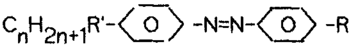
STARK-SPECTROSCOPY

The classical Stark-effect is splitting spectral lines of atoms, molecules, impurity centers, etc. in an electric field. In application to organic materials the term Stark-effect means any changes in optical (electronic or vibrational) spectra as a result of the *direct* interaction of an electric field with atoms and molecules composing the substance. Not only splitting but either broadening, shifts and even birth of new bands due to the field induced symmetry changes may be considered. However, we do not take into account such effects as field destruction of matter and electrochemical changes of spectra. We also skip the effects of the field reorientation of molecules (electrochromism)[6-8].

The term Stark-spectroscopy means a recording of the field induced changes in optical density $D(\lambda)$ of a substance in a certain wavelength range. The most important technical aspect is an application of an a.c. electric field to a sample and a subsequent lock-in detection of a relatively weak electro-optical modulation. After normalizing the modulation signal to the intensity of the transmitted light we have a spectrum of the field induced change in the optical density $\Delta D(\lambda, E)$ called the Stark-spectrum. The experimental technique is described in[9,10]. An alternative version is luminescent Stark-spectroscopy[11]. In the last decade, the *high resolution* Stark-spectroscopy has been developing which is based on field scanning over a spectral hole burnt by a laser in an optical band of an ensemble of organic molecules incorporated, as a rule, into a special matrix[12-14]. The latter experiments require cryogenic temperatures. In this paper we shall only discuss the results obtained by the Stark-spectroscopy technique for Langmuir-Blodgett films having rather broad optical bands.

DETERMINATION OF THE ORIENTATIONAL DISTRIBUTION FUNCTION FOR ROD-LIKE MOLECULES COMPOSING A LANGMUIR-BLODGETT FILM

Had one measured a number of P_n in Eqn.(1) the distribution function $f(\vartheta)$ is known. The problem is that each of P_n requires its own technique to be measured. The Stark-spectroscopy technique combined with the optical dichroism measurements allows us to determine the first four parameters P_n ($n = 1$-4) for the special case when molecules have the rod-like shape and both their optical oscillators and electric dipole moments are directed along longitudinal molecular axes. It is the case, e.g., for azo-compounds with various substitutients R and R':



(I)

Even in this simplest case one must use various versions of the optical and electro-optical technique[1,10].

The "nematic" orientational parameter P_2 , Eqn.(2), can be determined from the dichroism measurements. However, due to the cylindrical symmetry of a Langmuir-Blodgett film with respect to the film normal the sample is placed at a certain angle to the light beam of a monochromator and then the optical density is measured for various polarization vector of light. From the dichroic ratio parameters $\langle\cos^2\vartheta\rangle$ and P_2 are easily calculated as if we dealt with homeotropically oriented liquid crystal[15].

To find $\langle\cos\vartheta\rangle$ which determines the polarity of a film we measure the amplitude of the linear-in-field Stark-effect. Let us remind that the electric field induces a spectral shift of the molecular optical band

$$\Delta h\nu = \Delta\mu E + (1/2)\Delta\alpha E^2 \tag{3}$$

which includes linear and quadratic-in-field terms. The first of them depends on the difference $\Delta\mu = \mu_e - \mu_g$ of the dipole moments of an excited and the ground state and on the angle Ψ between vectors $\Delta\mu$ and E; the second term is proportional to the difference of the corresponding polarizabilities $\Delta\alpha = \alpha_e - \alpha_g$. When $\langle\cos\vartheta\rangle \neq 0$ there is a total shift of the band on the wavelength scale which is a measure of $\langle\cos\vartheta\rangle$[16]. In the opposite case we have only band broadening.

More detailed consideration of the problem[16,17] allows us to calculate $\langle\cos^3\vartheta\rangle$ from the dependence of the amplitude of the linear Stark-effect on light polarization. In fact, we use the "dichroism of the linear Stark-effect" which depends on both $\langle\cos\vartheta\rangle$ and $\langle\cos^3\vartheta\rangle$. In the framework of the same approach we can use the "dichroism of the quadratic Stark-effect" to calculate the term $\langle\cos^4\vartheta\rangle$ (for details see paper [18]).

The four parameters P_n measured this way allowed for the construction of the orientational distribution function for azo-compound multilayers[10,19].

A special case of great interest is a superlattice consisting of dipolar alternating monolayers composed of different molecules. Each of sub-lattices demonstrates its own Stark-effect in the corresponding spectral range. The measurements of the corresponding signs and amplitudes of the modulated signals result in determination of the structure of the superlattice[20,21].

DYNAMIC REORIENTATION OF MOLECULES

Recently a novel effect has been discovered, namely, a photo-induced reorientation of electronic oscillators of azo-compounds (I) in Langmuir-Blodgett films[22,23]. Photo-excitation of the molecules in their long-wave absorption band results in a change of the optical properties of a film. Optical density decreases in the direction of the light polarization vector (e.g.,x) and increases in the order two perpendicular directions (y and z). For the non-polarized exciting light nearly all oscillators are oriented in the z-direction (along the film normal). The questions arise whether the reorientation of oscillators is accompanied by reorientation of molecules as a whole and whether the polar properties of the film are changed. To study this problem one can again observe the linear Stark-effect in the spectral range of the same dye molecule absorption. The experiment showed[24] that after illumination of the film by the natural light the corresponding modulation amplitude changed dramatically: this points to the total reorientation process of the molecular skeletons (their overturning after excitation). The illumination of the same film by the x-polarized light results in reorientation of the other kind when molecules reorient along the cone surface to achieve the y-direction without overturning. Such experiments can give information on the shape of the potential barriers for molecular reorientation. The situation reminds of that for the anchoring of liquid crystalline molecules (directors) at the interface with a solid substrate when one can distinguish between rather small azimuthal and rather large polar anchoring energies[25].

INTERMOLECULAR CHARGE TRANSFER

When molecules forming a Langmuir-Blodgett film are non-polar, $\Delta\mu = 0$, Stark-spectroscopy allows one to study optical transitions accompanied by the intermolecular electron transfer[26]. Such optical transitions result in a dramatic change in a dipole moment of a light absorbing center (a pair of molecules, an impurity center in a lattice, a molecular cluster or associate, etc.), $\Delta\mu_{CT} \gg 0$. Even in the case when the oscillator strength of the corresponding CT-band is very weak the Stark-signal can be easily detected against the "inactive" background of the intramolecular absorption. The experiments were carried out on films of molecular crystals[27-29] and Langmuir-Blodgett films of porphyrazines[30]. In future, this technique may be useful to study charge generation and transport processes in metalloorganic, e.g., discotic liquid crystals showing the electronic conductivity and photoconductivity.

LOCAL FIELD MEASUREMENTS

Both the external and internal electric fields in a condensed phase may be measured by the Stark-spectroscopy tehnique. To this effect a special molecular (Stark) probe has to be used. In our experiments an amphiphilic anthraquinone dye with a rather high value of the difference in polarizabilities $\Delta\alpha = \alpha_e - \alpha_g \approx 20$ Å^3 was used. This dye forms non-polar bilayers during the Langmuir-Blodgett transfer process and the amplitude of the quadratic Stark-effect measured in the spectral range of the bilayer absorption is a measure of the local field in the place of its location.

For example, we were interested in a spatial distribution of an external electric field E_{loc}(ext) along the normal of a very thin sandwich structure SnO_2 (or AL) - stearic acid multilayer - Al[9,31]. A multilayer consisted of 10 monolayers of stearic acid. A probing anthraquinone bilayer was put in various positions between the stearic acid monolayers and the amplitude of the Stark-modulation at the double frequency of the applied field was measured as a function of its position (stearic acid does not absorb light in the visible range and does not show any Stark-effect). From this amplitude which is proportional to $[E_{loc}(\text{ext})]^2$ the local field was calculated. It appeared to be extremely non-uniform for asymmetric (SnO_2 - Al) pair of electrodes and more or less uniform for the symmetric (Al - Al) pair.

Another example of application of the Stark-spectroscopy technique is a measurement of the local internal field in the vicinity of a dipolar monolayer[32]. Once again the quadratic Stark-effect of the same anthraquinone bilayer was used. However, now the amplitude of the Stark-modulation was measured at the first harmonic of the applied field which is proportional to the cross term $E_{loc}(ext)\,E_{loc}(int)$. If $E_{loc}(ext)$ is known from the measurements of the signal at the second harmonic, the permanent internal field $E_{loc}(int)$ can be calculated.

The same technique may be applied to the investigation of the dynamic of the photo-induced molecular orientation. We already discussed a possibility to follow the reorientation using the linear Stark-effect on the intrinsic absorption band of the reoriented azo-dyes. Another possibility is to follow the local permanent field induced by the same dipolar dyes at the place of location of the probe (anthraquinone) molecules[33]. Both results agree with each other.

The measurements of local fields by the Stark-spectroscopy technique may be very useful for investigation of ferroelectric liquid crystals especially polymeric ones where local field effects are extremely important.

CONCLUSION

In conclusion, we have pointed to some analogies between Langmuir-Blodgett films and liquid crystals and showed how the Stark-spectroscopy technique could be applied to investigations of (a) orientational distribution of dipolar molecules; (b) dynamics of dipole reorientation; (c) photo-induced charge transfer effects; and (d) local fields in Langmuir-Blodgett films. In our opinion, in the nearest future the same technique may be applied to liquid crystalline compounds (ferroelectric, discotic, metalloorganic) and especially to polymeric mesophases.

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