Journal of Physics: Conference Series

PAPER

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To cite this article: A K Dadivanyan *et al* 2018 *J. Phys.: Conf. Ser.* **996** 012018

Theory of liquid crystal orientation under action of light wave field and aligning surfaces

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Abstract. Theoretical models developed in the MRSU group under leadership of Professor Artem Dadivanyan in area of the LC orientation and photo-induced effects are presented. Angular distribution functions of the dye and liquid crystal molecules under action of intensive light beam have been derived. The number of molecules in cluster is estimated. A model of dimers formation in the photoalignment dye is suggested that explains influence of the dye molecular structure on both polar and azimuthal anchoring energy.

1. Introduction

In this paper we review main results obtained in the MRSU group under leadership of Professor Artem Dadivanyan in area of the LC orientation and photo–induced effects:

- The effect of photoalignment of liquid crystals under the action of polarized light. This technology is applied for the alignment of liquid crystals in liquid crystal displays, lenses, optical films [1–4].
- Photoinduced effects in layers of the LC, dyes and polymers [5,6].
- Investigation of properties of liquid crystal nano–colloids [7–9].

2. Liquid crystal alignment parameters

In [10] this model was expanded for the total orientation angular range from 0 to 180º.

A formula (1) for the energy of the mesogens intermolecular interaction vs. molecules orientation angle as well as order parameter S is as follows:

$$E = 2\sum_{i,j,n}\left(\mathrm{A}\left(\frac{A_{i,j,n}(S)\cos^2\alpha + b(i,j,n)}{C_{i,j,n}(S)\cos^6\alpha + F_{i,j,n}(S)\cos^4\alpha + G_{i,j,n}(S)\cos^2\alpha + h(i,j,n)}\right)^2,\right. \tag{1}$$
$$\left. -\mathrm{B}\left(\frac{A_{i,j,n}(S)\cos^2\alpha + b(i,j,n)}{C_{i,j,n}(S)\cos^6\alpha + F_{i,j,n}(S)\cos^4\alpha + G_{i,j,n}(S)\cos^2\alpha + h(i,j,n)}\right)\right).$$

where

$$A_{i,j,n}(S)=\sum_{k=0}^{2}a_k(i,j,n)\cdot S^k\ ,\ G_{i,j,n}(S)=\sum_{k=0}^{2}g_k(i,j,n)\cdot S^k\ ,F_{i,j,n}(S)=\sum_{k=0}^{4}f_k(i,j,n)\cdot S^k\ ,$$

$$C_{i,j,n}(S)=\sum_{k=0}^{6}c_k(i,j,n)\cdot S^k\ ,$$

$a_k(i,j,n), b_k(i,j,n), c_k(i,j,n), f_k(i,j,n), g_k(i,j,n), h_k(i,j,n)$ are functions that characterize number of the interaction contacts between molecules of both upper and lower layers.

The dependence of the energy of the intermolecular interaction vs. molecules orientation angle at different values of the order parameter S is presented in Fig. 1.

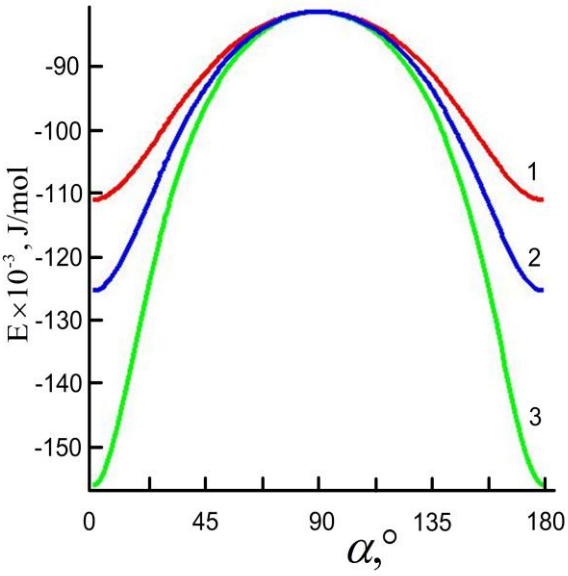

Figure 1. The dependence of the energy of the intermolecular interaction vs. molecules orientation angle at different values of the order parameter 1 – S=0.7; 2 – S=0.8; 3 – S=0.9.

If the angle α is replaced for the angle θ between the LC molecule and the normal to the XOY plane and review a case of α close to 90° (or θ close to 0) then this formula can be written in a view of Rapini–Papoular potential $E=w_1^{'}+w_2^{'}\sin^2\theta$ this formula can be written in a view of well–known Rapini–Papoular potential.

3. Distribution of dye and liquid crystal molecules orientation under action of the light wave field

In [11, 12] photoalignment properties of some azo dyes have been investigated and values of both polar and azimuthal anchoring parameters (W_θ and W_φ, accordingly).

In [11] a model of dimerization of some azo dyes molecules was developed that allows explanation of different values of the ratio W_θ/W_φ vs. dye chemical structure. When the dye molecule absorbs radiation, the nonradiative energy transition from the molecule in a triplet state to the molecule in a ground state takes place due to the exchange-resonance interaction. It occurs when electronic shells of excited and not excited molecule overlap and energy and electrons are transferred mutually [13, 14]. This interaction has an impact on the molecule structure. An assumption was made in [11] that dimers of the dye molecules are formed via hydrogen bonds between carboxyl–, hydroxyl– and CO groups, and the dimer formed has a nearly flat structure.

In [11] the following equation (2) for the variation of entropy has been derived:

$$\begin{aligned}\Delta S &= \frac{1}{2} N_A k \ln(2N^{d}_{trans}N^{d}_{or}) - 2N_A k \ln(2N^{m}_{trans}N^{m}_{or}) = \\ &= \frac{1}{2} R\left(\ln\frac{N^{d}_{trans}}{(N^{m}_{trans})^2} + \ln\frac{N^{d}_{or}}{(N^{m}_{or})^2} - \ln 2\right)\end{aligned} \tag{2}$$

where N_A is the Avogadro number, R is the gas constant.

The value of ΔS equal to 60 ± 10 J/mol·K, and the change of free enthalpy ΔG at the fusion temperature of CD–1≈ 600 K equal to –70 kJ/mol. These values indicate that the probability of the dye molecule to exist in the dimer form is by several factors higher than to be in the monomer form. Energy of dimerization for the dyes SD–1 and DR–23 was found using GAMESS software package [15], and equals to –107.5 kJ/mol and –49.5 kJ/mol, respectively. These values are approximately equal to the hydrogen bonds energy of the carboxylic and hydroxyl groups respectively. Calculated ΔS and ΔE allowed us to find the value of ΔG = –64 kJ/mol and –24 kJ/mol for SD–1 and DR–23 respectively. Consequently, these dyes must be in the dimer form, too.

For the dyes BY and CBY ΔE = –25 kJ/mol, that results in ΔG = +11 kJ/mol and the probability of forming the dimer is less than 10^{-3}.

Anchoring energy is proportional to the torque resistant to the molecule’s rotation. This torque is proportional to the particle (dimer or molecule) cross-section in the corresponding plane. Since the molecule orientation is planar, W_θ is proportional to the dimer cross–section σ_θ in the plane intersecting the easy rotation axes of both molecules, while W_φ is proportional to the section σ_φ in the plane orthogonal to easy rotation axes.

In [12] values of a $\cos^2\varphi$ parameter, which characterizes orientation order of both molecules and dimers, were obtained as well as energy of their orientation process. It is of order of $7\cdot 10^{-34}$ J per a molecule. Number of cooperatively oriented dye molecules was estimated. Therefore the number of cooperatively oriented molecules is of the order of 10^{13} at least.

The angles distribution functions for different dimers were found. The distribution function of the dimer in the electric field of the angle φ':

$$\rho(\varphi') = C\cdot e^{-\frac{NU(\varphi')}{kT}}, \text{ where } C = \frac{1}{\int_0^{2\pi} e^{-\frac{NU(\varphi')}{kT}}\,d\varphi'}.$$

Dipole electrical transition moments directed on angles close to 90º to the direction of maximal polarizability of dimers were revealed.

The transition dipole moments directions almost coincide with the direction of the highest polarizability of the molecule, while in the dimers one of the transition moments is directed nearly perpendicular. Consequently, when the dimers are oriented, certain transition dipole moments will form angles close to 90º with the polarization plane of the orienting radiation.

A consequence of the absorption mechanism of the photoalignment is that the photon absorption can result in dissociation of the hydrogen bonds between the molecules. For the CD–1 dye the dimerization energy is equal to $1.2\cdot 10^{-19}$ J (72 kJ/mol) that is of the same order as the energy of the photons used for the photoalignment (for the blue light with λ=450 nm the photons energy is $4.4\cdot 10^{-19}$ J (266 kJ/mol)). This fact must be taken into account considering the absorption mechanism of the photoalignment.

4. Conclusion

At the first time there were derived angular distribution functions of the dye and liquid crystal molecules under action of intensive light beam. This model results in values of the interaction energy of the molecule with the light wave electric field as well as molecules number in cluster. Both these directions are integrated with a model of dimers formation in a photoalignment dye that explains influence of the dye molecular structure on both polar and azimuthal anchoring energy.

5. Acknowledgement

The paper is prepared under partial support of Russian Foundation for Basic Researches (RFBR) (project No. 17-47-500752 and 17-47-500757 with Moscow Region Government).

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