Selective Light-Induced Desorption: the Mechanism of Photoalignment of Liquid Crystals at Adsorbing Solid Surfaces

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Abstract. – We demonstrate experimentally that bare solid surfaces with adsorbed organic molecules can orient liquid crystals after UV light irradiation. The detailed structure and behavior of the surface-adsorbed molecules are not important to the effect: just their UV light absorption should depend on their orientation. The only requirement to the solid substrates is their transparency to the UV light. The universal reason for the photoinduced anisotropy in such systems is that photons clean from the surface those molecules that absorb them most intensively. This is a kind of light rubbing resulting in the anisotropic ablation of the adsorbed material.

Introduction. – Applications of liquid crystals (LCs) imply a good homogeneous orientation of the director in a working cell. The orienting element of a LC cell is its surface whose orienting ability is associated with the anisotropic surface tension called anchoring. Nowadays the problem of surface alignment is no longer of a pure applied status as physics has become deeply involved in new technologies. The photoalignment method which has been in the focus of the LC research over the last decade [1,2] gives the most recent example of how poor understanding of the alignment mechanism prevents the area from giving the desired output: this attractive technique has not been utilized on a large commercial scale [1]. The method is based on the ability of some substrates to get anisotropic (photo-oriented) under a UV light irradiation. But what is this substrate anisotropy? Which surface properties are necessary and which can be avoided to simplify the technique and make it less expensive? The massive experimental data do not give a clear answer.

The problem is that, as a surface material, the photoaligner studies have utilized a very complex physical system, i.e., polymers, where UV light can simultaneously induce a variety of physical, rheological, and chemical processes that cannot be separated from each
other and studied individually. On the one hand, the widely accepted idea has been that, whatever these processes are, the photoaligning action of light consists in a reorientation of some degrees of freedom, available in the irradiated polymer surface layer, thus inducing an anisotropic order which interacts with the liquid crystal molecules in the proximity of the surface and manifests itself in the preferred director orientation. For instance, anisotropic (orientation-dependent) light absorption (ALA) can make a polymer anisotropic by inducing a cross linking [3–6] or anisotropic distribution of the photoreaction products [7]. Ion beams also produce a surface anisotropy as the ions can reorient chemical bonds of the surface polymer [8]. The orientational anisotropy in polymers can be induced by anisotropic ablation, e.g., by ALA [9,10] or by ions [8] removing some objects (bonds, rings, parts of the molecules, etc.). Thus, the chemical structure of polymers has been considered crucial to the photoalignment as it is connected to the orientational properties of their fragments [1,2]. A dye-doped polymer becomes anisotropic due to ALA by the dye molecules followed by their photodegradation or cis-trans isomerization [11–14]. In this case the specific orientational properties of azo dye molecules also come into play.

On the other hand, however, there are indications that a polymer surface might also play a less exclusive role. Stöhr et al. [8] showed that, for the purpose of photoalignment, the polymer bonds can be successfully substituted for those of amorphous materials. The photoalignment effect, revealed by Ouskova et al. for a polymer surface with adsorbed dye molecules or in contact with a dye-doped LC [15], can be explained by an adsorption and desorption of dyes [15–17] while the surface might play the role of just an adsorbent. For instance, the dye desorption under UV light irradiation is anisotropic which can result in surface anisotropy [15,16]. Moreover, it was found that a LC can be photoaligned by the same LC [18]: a layer of 5CB adsorbed onto a solid surface gets anisotropic under light irradiation and gives a planar alignment of bulk nematic 5CB. This information casted a doubt upon the exclusive role of the complex chemical structure of polymer surfaces. Indeed, the molecules of 5CB do not possess any fragments that can be light-reoriented, neither can they rotate as a whole in the adsorbed state. Basically, the system of adsorbed 5CB molecules is almost trivial as compared to the polymer-based surfaces described above: the only property common for the both systems is ALA. At last, very recently Kumar, Kim, and Shi [19] showed that anisotropy of a subnanoscale surface roughness can be responsible for the surface alignment after very different treatments such as mechanical rubbing and UV light irradiation of polymer surfaces.

Thus, the effect occurs when there is nothing on the surface that light can reorient. On the one hand, this prompts that presumably it is not only the specific property of a substrate material (such as free fragments, cis-trans transition, specific molecular and polymer structure, and so on) but also an intrinsic ability of a LC to respond to a modest anisotropy of any origin that is behind the azimuthal anchoring [20]. On the other hand, the surface anisotropy (even on polymer surfaces) can also be induced merely by anisotropic ablation of the surface material, provided this gives rise to a sufficient anisotropic roughness [19]. To find the simplest photoalignment methods that, at the same time, would allow one to get a clear idea of the physics behind the effect, it is natural to resort to the simplest system that possesses just the minimal set of the necessary properties. To this end, we studied bare solid surfaces with different adsorbed molecules (AM) whose only common property is ALA. As the substrate material can considerably reduce the number of photons adsorbed by the AM, we explored both transparent and nontransparent substrates. We demonstrate that: 1) a uniform orientation of a LC can be achieved by a UV irradiation of bare transparent solid substrates with AM that possess the property of ALA; 2) AM can be of essentially different types: mesogenic and non-mesogenic, with UV light-induced cis-trans isomerization and stable to the light action, anisotropic and with no shape anisotropy; 3) surface anisotropy for any of these types is due
Adsorbed materials which give the photoinduced alignment. The alignment direction is given relative to the polarization of the incident UV light.

<table>
<thead>
<tr>
<th>No</th>
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<th>Orientation Before irradiation</th>
<th>Orientation After irradiation</th>
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<tr>
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<td>Homogeneous planar (n ⊥ E)</td>
</tr>
<tr>
<td>VI</td>
<td><img src="image6" alt="Image" /></td>
<td>Homeotropic</td>
<td>Homogeneous planar (n ⊥ E)</td>
</tr>
</tbody>
</table>

Experimental results and discussion. – For the substrate materials we used a UV-light transparent fused quartz and sapphire, and nontransparent glass and quartz covered with a nontransparent ITO layer. The chemical structure of the AM is shown in table I. All the combinations substrate-AM were explored.

This AM selection represents the main peculiarities apparently relevant to the photoaligning effect and, in particular, the trans-cis isomerization and mesogenity. AM I and II represent standard but different LC materials known as 5CB and 8CB (EM Industries): 5CB has a nematic phase while 8CB has both nematic and smectic A phases. AM III and IV also have a LC behavior [21,22], but completely differ in their light-induced isomerization. AM III can be easily switched between its cis and trans forms even by a visible light, whereas AM IV is stable under the action of light. AM V and VI are typical fluorescent materials extremely stable to UV light. The adsorbed layers of V and VI can be studied by the fluorescence methods due to their high quantum yield. \( p,p'\)-di-n-heptylazobenzene (III) was synthesized at the Liquid Crystal Institute (Kent, OH); \( p,p'\)-di-n-heptylazoxybenzene (IV) and dyes V and VI were synthesized at Institute of Organic Chemistry (Kiev, Ukraine).
First, the substrate material was fused quartz. The fused-quartz substrates were ultrasonically cleaned in acetone for 30 min, then in a water/sulfuric acid solution of $\text{K}_2\text{Cr}_2\text{O}_7$ for another 30 min, and rinsed with deionized water. Then the substrates were dried at 200°C for an hour. A given substance was adsorbed onto the quartz surface by dipping it in a dilute solution of the substance in isopropyl alcohol (0.02% by weight) for 60 min (the solvents were from “Brenntag Export” (Netherlands) and had purity better than 99.9%). The substrates were then rinsed in the pure solvent for 5–15 s to remove nonadsorbed molecules, and then gently dried [18]. Thus obtained quartz substrates with the adsorbed layer were irradiated with polarized UV light from a Hg lamp (500 W), the average light intensity was about 10 mW/cm². Then the irradiated substrates were assembled and filled with 5CB LC in the isotropic phase. The cell thickness was 10 µm.

The alignment was studied using two types of LC cells. The first-type cells were combined of the reference (quartz covered with a rubbed polyimide layer) and test (quartz with irradiated layer of the adsorbed material) substrates [18]. The second-type cells consisted of two identical quartz plates with similar irradiated spots located exactly against each other. These cells were used for substrates with initially homeotropic orientation and in the pretilt measurements.

In spite of the significant difference in the AM on the quartz substrate, after a sufficiently long time $t$ of linearly polarized UV light irradiation all of these substrates gave a uniform planar alignment of the nematic LC 5CB normal to the light polarization.

Fig. 1 – Microphotographs of irradiated cells for different exposure times: 5 (a), 10 (b), 30 (c), and 60 (d) min. The pictures are taken in crossed polarizers.
The nonirradiated areas of the substrates with AM I-IV had a multidomain planar alignment with the director rotating in the plane of the cell. With increase of the exposure time the difference between the alignment directions in different domains diminished, and the alignments in the individual domains were gradually approaching the common direction normal to the light polarization. The uniform alignment was achieved after $\sim 10$ min exposure.

The substrates with AM V-VI induced a homeotropic alignment within the nonirradiated area. This initial orientation remained until for $t \sim 5$ min it broke into a planar one with no predominant direction, fig. 1a. A further exposure increase resulted in a behavior similar to that described above: the larger $t$ the closer the orientation in different domains to the direction normal to the light polarization. The cells became uniformly aligned for $t \sim 30$ min, fig. 1b-d. The deviation from the pure planar alignment in the cells thus obtained was smaller than the accuracy of the crystal rotation method ($< 1^\circ$). Thus, the picture of a photoalignment looks identical for all the AM, although some of them can be in the cis form whereas others in the trans form, some are mesogenic whereas some are not: the longer the time of the UV irradiation the better the uniformity of the planar alignment normal to the light polarization. The obvious common property of the investigated AM is the dipole type ALA of the UV light.

The orienting properties of the substrates can be destroyed by a long UV exposure and/or polarization direction. The polarization of incident light was changed by $90^\circ$ each 30 min. After the fourth change when the full $360^\circ$ circle was passed, we observed a multidomain planar structure (planar with no common easy axis) for all AM. In particular, for AM I-IV imposing planar alignment before the irradiation, there was no significant difference between the irradiated and nonirradiated areas. This shows that the induced anisotropy can hardly be due to any kind of orienting effect of light as in the latter case the orienting elements could have been reoriented, the photoalignment would have followed the last light polarization. Along with the fact that the effect is similar for the very different AM, this justifies our assumption that the light-induced reorientions, that should be specific for the chemical structure of AM,

![Fluorescence spectra](image)

Fig. 2 – Fluorescence spectra of non-irradiated spot (a) and spot UV irradiated for 5 min (b and c). The excitation light polarization is normal (b) and parallel (c) to the polarization of the UV light.
are minimized if not fully absent in our system, and can be excluded as a possible mechanism of the photoalignment. Therefore, the photoablation (desorption) resulting in anisotropy of roughness seems to be the only mechanism possible in our simple system and consistent with all the experimental data. The observed diminishing of the orientational properties of the irradiated surface after a sufficiently long $t$ (of order of two hours) points out that the number of desorbed molecules is proportional to the number of incident photons which in turn is proportional to $t$, therefore for a very large $t$ the number of the remained AM will be very small and the surface roughness weak.

The light-induced ablation mechanism received an additional confirmation by detecting changes that occur on some particular surfaces upon light irradiation. Since AM V and VI have a significant fluorescence, we measured fluorescence spectra for the irradiated and nonirradiated areas of the substrates with the adsorbed material VI, fig. 2. We see a sharp drop of the fluorescence intensity with the exposure time. After $t = 5\ \text{min}$ (just at the break of the homeotropic alignment, fig. 1, a) the fluorescence from the irradiated area was almost four times lower than the initial one. After $t = 30\ \text{min}$ it dropped by two orders of magnitude and could hardly be detected. This signal drop is not related to any photo-induced transformations of the AM as the position and form of the signal remained the same, i.e., without any peaks or deformation that could be attributed to decomposition of the AM. Therefore, it is the number of AM that decreases upon light irradiation. Moreover, whereas the fluorescence from the nonirradiated areas was polarization independent, that from the irradiated areas showed a pronounced polarization dependence. The fluorescence output for the light polarized in the direction of the irradiating UV light (curve c, fig. 2) was much lower than that for the normal direction (curve b). This shows that after irradiation the surface has less adsorbed molecules with the transition dipoles along the polarization of the irradiating UV light and more molecules with the dipole moments normal to this direction, the total number of adsorbed molecules being considerably smaller than its value before the irradiation.

The idea that the light cleans the surface from the adsorbed molecules implies that the incident photons must not be intercepted by the substrate material (adsorbent) whose molecular density is necessarily much higher than that of the AM. Then a nontransparent substrate can prevent the photoalignment. Our experiment confirmed this. With the substrates made of glass and quartz covered with a nontransparent ITO layer, the photoalignment was never achieved irrespective of the exposure time and of the AM. In contrast, photoalignment on the sapphire substrates was quite similar to that obtained on the quartz substrates: after a sufficient UV irradiation, the director was planar and normal to the light polarization for all of the AM I-VI.

**Conclusion.** – We have shown that simple bare solid substrates, that can adsorb organic molecules and are sufficiently transparent to UV light, can be made photo-oriented by this light. A similar photoalignment effect can be obtained on the same solid substrate with AM of a very different structure provided they have the ALA of the UV light. This can be naturally interpreted in terms of a selective desorption. A molecule that absorbed a UV photon leaves the surface, and such an evaporation is governed by the ALA rate. This rate is maximum for molecules with their dipoles along the light polarization and minimum for the normal direction. As a result, the relative excess of the latter molecules form grooves along this normal direction. This is a kind of light rubbing along this direction normal to the light polarization: the rubbing readily removes the molecules lying across the rubbing direction whereas those lying along this direction have less chances to get scratched away. The light with a rotating polarization cleans the surface from molecules with any orientation making no anisotropy in accord with our experiment. The picture of grooves produced by the light rubbing on surfaces is in line with the gen-
eral role roughness can play on the effects of surface anisotropy [19]. Notable is that the simple system considered here not only exhibits the in-plane photo-orientation, but also an anchoring transition from a homeotropic to a planar state. This transition is yet to be understood.

To conclude, we have demonstrated a very simple photoalignment method. Indeed, adsorption is a very common property of solid substrates, plus there is no need in special layer deposition thereupon. The ALA is quite a common property of organic molecules, too. The origin of the light rubbing mechanism of setting an easy direction in the proposed systems is also clear: in contrast to the light-induced orientation of chemical bonds, molecular fragments and so on, the evaporation is a simple process and implies only the ALA of molecules. Our result points to the possibility that the search for photoaligning surfaces can continue not only by studying the complicated combinations of substrate materials and coating, but also by a much simpler study of the light rubbing of transparent bare solid substrates with adsorbed molecules.

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REFERENCES

[20] A similar idea in the context of carbonaceous substrates was pointed out in [8].