Orientation of 5CB Molecules on Aligning Substrates Studied by Angle Resolved X-ray Photoelectron Spectroscopy

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We studied alignment of 5CB molecules on several surfaces by Angle Resolved X-ray Photoelectron Spectroscopy. It was found that different surfaces orient 5CB molecules with different tilt while providing qualitatively the same type of the LC alignment in the bulk. In particular, quartz and PVA gave high tilt, while NaCl and glass gave very low tilt. At the same time all these surfaces provide degenerated quasi-planar alignment in LC bulk. These results point that the orientation of LC molecules in the bulk can strongly differ from the orientation of the first adsorbed monolayer and it is determined by integral anisotropic action of the surface and interface over interface region.

Keywords: alignment; anchoring; liquid crystal; tilt; XPS

1. INTRODUCTION

The orientation of liquid crystal (LC) molecules on aligning substrates and relationship of this orientation with orientation of the director in a LC bulk is a subject of undivided interest in last decade. Feller *et al*. [1], Barmentlo *et al*. [2], L. Marruchi *et al*. [3], Sakai *et al*. [4] and

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others demonstrated that the tilt angle in the bulk of nematic LC strongly correlates with the orientation of molecules in the adsorbed LC monolayer on polyimide surface. For rubbed polymers, it was shown that a short-range molecular interaction is responsible for the alignment of the first monolayer of liquid crystal molecules, which in turn aligns the LC bulk via epitaxy interaction. As a result, the tilt of the director in the bulk does not strongly differ from the orientation of the LC molecules onto the aligning surface. At the same time there are some exclusions from this rule. In particular, it was observed that the alignment of LC in the bulk may drastically differ from the orientation of LC molecules on the not-organic substrates [5–8]. Mullin *et al.* [5], Guyot-Sionnest *et al.* [6] and Barmentlo *et al.* [7] found that different silane-covered surfaces and bare glass molecules orient the adsorbed 8CB molecules with nearly the same tilt angle θ to the surface while providing qualitatively different type of the LC alignment in the bulk. For instance, bare glass and n-methyl-aminopropyltrimethoxysilane on glass give planar alignment, and octadecyltrichlorosilane on glass provides homeotropic alignment while the tilt of the 8CB molecules, $\theta \sim 33°$. Lately similar result was reported by Reznikov *et al.* [8]; it was established that 5CB molecules are oriented at the angle $\theta \sim 78°$ on the quartz surface while a planar alignment of 5CB is observed in the LC bulk.

In Refs. [1–8] the information about arrangement of the LC molecules on aligning surfaces was obtained by technique of optical-second harmonic generation which is sensitive to a polar order of the adsorbed molecules on the aligning surface, but which is not responsive to their not-polar arrangement. The orientation of the adsorbed molecules is calculated from the intensities of second harmonic signal measured for different polarisation of basic and second harmonics of light and following calculation of nonlinear optical susceptibility in the definite approximation of the angular orientation distribution of the adsorbed molecules. Here we report first studies of alignment of LC molecules adsorbed on several aligning surfaces by Angle Resolved X-ray Photoelectron Spectroscopy (XPS) [9] which allowed us to obtain *direct* information about orientation of the adsorbed molecules on the aligning surface by elemental and chemical analysis with a nanometer depth resolution.

2. EXPERIMENTS

We studied the orientation of pentyl-cyano-biphenyl (5CB) on four different aligning substrates: bare glass, polyvinylalcohol (PVA), NaCl plates and fused quartz. The LC was spin-coated on the substrates with a high speed (5000 rpm). In this case almost all 5CB was

spin-off the substrate and just the adsorbed molecules remained on the surface. The XPS spectra were acquired by Kratos AXIS Ultra photo-electron spectrometer. The samples were placed in the ultrahigh vacuum chamber with the base pressure $P = 2 \cdot 10^{-10}$ Torr, and operating pressure $P = 2 \cdot 10^{-9}$ Torr. The sample was then exposed to a low-energy, monochromatic X-ray Al Kα source operating at 300 W which causes the emission of photoelectrons from atomic shells of the elements present on the surface. To compensate for positive charge accumulated on the surface of the samples, they were exposed to low energy electron flooding. The kinetic energy E_k of the emitted photoelectron is determined by the known energy of the primary photon, hv, binding energy for the emitted photoelectron, E_b, and a work function which accounts for the additional energy required to remove an electron from the surface to the vacuum ϕ_ω

$$E_k = hv - E_b - \phi_\omega \tag{1}$$

The value ϕ_ω is a constant for spectrometer.

The emitted electrons possess an energy characteristic of the element and molecular orbital from which they are emitted. Formation of a chemical bond with another atom will change the energy of the ground state of the atom, which in turn will change the observed binding energy [9].

Ejected photoelectrons are directed into an electron energy analyzer, where they are separated according to energy and detected as a function of their kinetic energy, E_k. By counting the number of electrons detected at each energy value ($E_k < hv$), a spectrum of peaks corresponding to the elements on the surface is generated. The area under these peaks is a measure of the relative amounts of each element present, while the shape and position of the peaks reflect the chemical environment of each element.

The kinetic energies of the photoelectrons leaving the sample are so low that only those from the top 1–10 nm of the surface escape and arrive at the spectrometer. Electrons originating from far below the surface are reabsorbed or escape the surface with considerable energy loss. The information available from XPS is, therefore, highly specific to the surface of the material. In ARXPS, the effective sampling depth is varied by changing the angle of the sample with respect to the detector [9,10]. The actual depth sampled, d, is given by the equation:

$$d = 3\lambda \sin \Theta, \tag{2}$$

where λ is the effective attenuation length of the photoelectron and, Θ is the take-off angle between the sample surface and the analyzer

acceptance plane. By changing the incident angle one can vary the sampling depth, d, to increase the surface specificity of the analysis. By comparing the relative intensities of peaks at the same kinetic energy over several different take-off angles it is possible to calculate layer thickness [10,11]. Alternately, comparing relative intensities at low and high take-off angles indicates whether a species is enriched or depleted in the surface region. This allows for determination of the molecular orientation to the surface. For 5CB, comparison of total C and N elemental signals at different take-off angles will indicate whether the 5CB molecule is attached to the substrate by cyano group or alkyl tail, or it has no preferential orientation.

Substrates with no liquid crystal were analyzed at the same time as deposited samples. For each sample, a low energy resolution wide scan spectrum was acquired first, followed by high-resolution elemental spectra of C and N for all samples. The following take-off angles were selected for angle resolved studies: $\Theta = 90°, 60°, 45°, 30°,$ and $15°$. Data analysis and quantification were performed using the Vision software provided by the manufacturer. The results were averaged over 2–3 different samples using 3–4 areas per sample.

Figure 1a shows a low energy resolution wide scan spectrum of a 5CB monolayer deposited on a quartz substrate. Elements and the orbital from which electrons are ejected are marked on the figure. *O1s* and *Si2p* photopeaks from the quartz substrate are readily observed. Very little C contamination ($<2\%$) was detected for this substrate, so we can conclude that the *C1s* and *N1s* signals result from 5CB deposited on the sample. For all four substrates, signal from 5CB represents 10–20% of the total signal. Figures 1b and 1c show high energy resolution C and N spectra for $90°$ take-off angles acquired from a 5CB sample with thickness greater than the XPS sampling depth. Based on the molecular structure of 5CB, the high resolution *C1s* spectrum was curve-fitted using 4 peaks, corresponding to the following chemical components: aromatic carbon at 284.8 eV, aliphatic carbons CH_2–CH_3 at 285 eV, C–N species at 286.7 eV and some small amount of oxygen- and nitrogen-containing species at 288.2 eV due to oxygen contamination. Shake-up structure at 291.5 eV due to the aromatic structure is also identified. One type of N species results in the symmetrical *N1s* high resolution spectrum shown in Figure 1c. Figure 1d also shows the *C1s* spectrum at $15°$ take-off angle for the same sample. As can be seen, the curve fit results in the same types and amounts of carbon species, which means that no preferential orientation exists in the thick sample.

The orientation of 5CB molecule on different substrates was elucidated from the N/C ratio plotted as a function of take-off angle. At
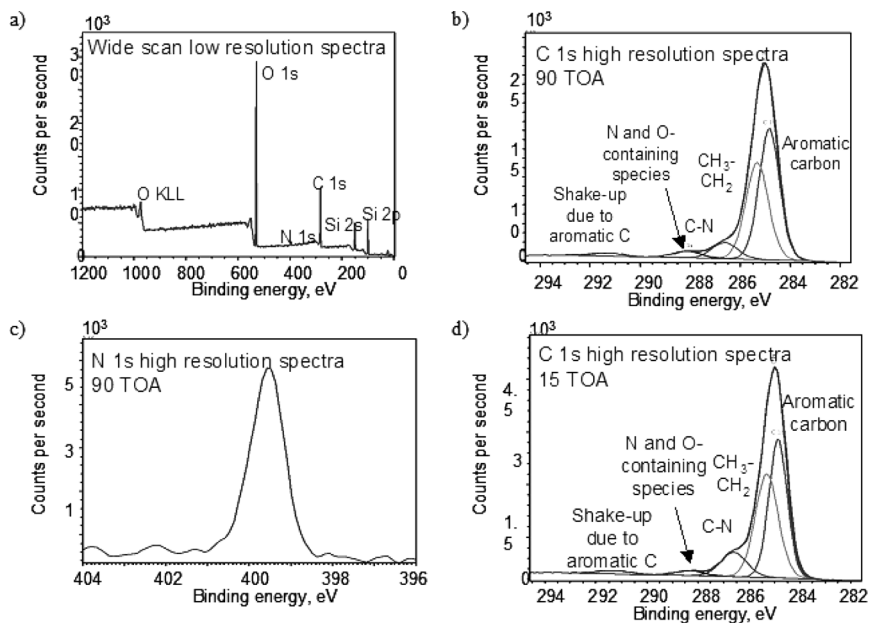
FIGURE 1 a) Wide scan survey spectrum of 5CB on quartz; b) C high resolution spectrum of thick 5CB at 90 TOA. Curve fit is shown; c) N high resolution spectrum of thick 5CB at 90 TOA and d) C high resolution spectrum of thick 5CB at 15 TOA. The same curve fit as in b) confirms no preferential orientation of thick 5CB.

$\Theta = 90°$, XPS has a sampling depth of 8–10 nm, while by decreasing the angle Θ down to 15°, shallower layers of approximately 2–3 nm are sampled. The increase of the N/C with decreasing Θ means that the molecule is oriented with cyano-group up and the alkyl chain towards the substrate, while a decrease of the N/C with decreasing take-off angle indicates the opposite molecular orientation – cyano-group attached to the substrate with alkyl chains at the shallower depths. The slope of the ratio plot indicates how significantly orientation of the molecule differs from the planar one.

Figure 2 shows plots of normalized N/C ratios for 4 substrates. A small change in N/C ratio with a change of take-off angle for NaCl and glass substrates indicates a low tilt of 5CB molecules on these substrates and a tendency to be oriented with cyano-groups towards the substrate. For the PVA substrate, XPS reveals evident enrichment of N-atoms near the substrate surface. This indicates that 5CB molecules are oriented with the polar cyano-groups down the substrate. This result is consistent with expectations, as the $C-OH$ groups of

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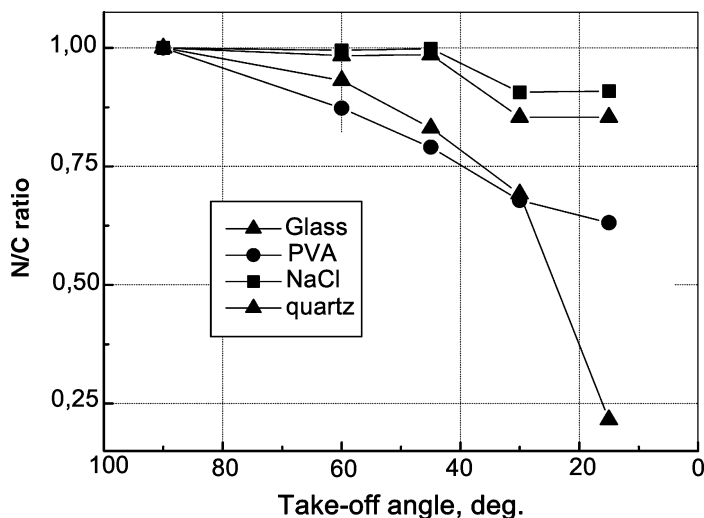
FIGURE 2 Normalized N/C ratio for different substrates.

PVA are very attractive for the polar cyano-fragment of 5CB. The highest slope of the change of N/C ratio with decreasing Θ is observed for the quartz sample. Almost no signal from N is observed at the shallowest $\Theta = 15°$, while at $\Theta = 90°$ the highest signal from N-atom is observed. This is reasonable due to strong interactions between cyano-groups and the polar quartz surface. One would expect to see similar results on glass, as its main constituent is silicon dioxide, but C detected on the clear glass substrate, indicated that the glass has a hydrocarbon contamination layer that decreases the polarity of the surface, influencing the interaction between the glass and 5CB molecules.

The thickness of the 5CB overlayer can be calculated from the ARXPS data and directly related to the tilt angle for molecules with known lengths, assuming that a single monolayer is deposited. For a substrate with deposited 5CB, the signal from elements in the substrate is attenuated by the overlayer. The thickness of the overlayer, t, thus, can be obtained from photoelectron intensities measured for element in the substrate, I_s^0, and in the overlayer, I_s^d as a function of take-off angle:

$$I_s^d = I_s^0 \lambda \exp\left(-\frac{t}{\lambda \cos \Theta}\right) \tag{3}$$

The parameter t/λ can be obtained as the slope of a plot of $\ln\left(I_s^d/I_s^0\right)$ versus $1/\cos \Theta$ [11]. For accurate thickness calculations, the effective

attenuation length, λ, of electrons travelling through the substrate and overlayer must be known. Any inaccuracy in λ estimation will cause erroneous thickness and tilt angles calculations [12]. Alternatively, a relative degree of signal attenuation (t/λ) can be used as a representation of relative tilt angles for different substrates. The degree of attenuation was compared for three substrates, i.e., quartz, PVA and salt plates. No calculations were made for 5CB on glass, as high C contamination results in erroneous quantitative results. For each type of substrate an element that is present only in the substrate was chosen, and the area of the peak for this element for pure substrate and substrate with 5CB deposited on it at all TOAs was used for calculating attenuation using Eq. (3). For quartz, PVA and salt plates, Si, O and Cl were chosen respectively. From these calculations, it is determined that the tilt angle of 5CB on quartz is 3 times larger than that on PVA and 13 times than that on salt plates.

Despite significant difference in the tilt of 5CB on the studied substrates, this liquid crystal reveals similar macroscopic alignment in LC cells. We assembled symmetrical cells using investigated materials as substrates. The thickness of each cell was about $20\,\mu m$. The cells were filled by liquid crystal via capillary effect at room temperature. Observations using polarizing microscope showed a degenerated quasi-planar alignment of 5CB in all cells. In particular, both quartz and PVA surfaces provided almost zero macroscopic tilt although ARXPS showed high-tilted orientation of 5CB on these surfaces. Previous studies showed that LC bulk does not strongly affect the orientation of adsorbed molecules on the substrates [1,6]. These data agrees with the results [8] where nearly high-tilted orientation of 5CB on a quartz substrate was observed by optical-second harmonic generation while a planar alignment was found in the LC bulk. NaCl and glass surfaces revealed small macroscopic tilt ($2°$–$6°$), which is correlated with the results of ARXPS measurements.

The previous studies of Shen's group [1,6] indicated that LC bulk does not strongly affect the orientation of adsorbed molecules on the substrates [1,6], while short-distance interactions are more significant for flat substrates. Therefore, our results confirm that bulk alignment of LC in a cell does not necessarily correlate with the orientation of LC molecules in the first surface layer. This statement reconciles with a microscopic model of the LC alignment in a cell described by Jerome in [13]. According to this model, a surface-induced positional ordering of LC molecules extended over the distance, ξ_{surf}, of several molecular layers near the surface. At the distance from the surface larger than this interface region, the director of LC takes a fixed orientation determined by integral anisotropic action of the surface and interface.

The orientation of the molecules over the distance ξ_{surf} near the surface has not to reproduce the orientation of the molecules in the first monolayer and is determined by specific parameters of intermolecular interaction. For example, the alkyl chains on the 5CB molecules of the first monolayers may provide an axially oriented "bed" on which the bulk molecules are planar aligned giving the homogeneously aligned LC in the cell. A planar alignment of 5CB molecules on a nearly normally aligned first monolayer is very reasonable because of the tendency of 5CB to form dimers whose lack of dipole moment would allow them to readily align on the aligned hydrophobic methylene chains at the top of the adsorbed layer [8].

The alternative explanation of the difference between "surface" and "bulk" orientation of LC molecules is the change of the orientation within the first monolayer in the presence of the LC bulk. This model does not have experimental proof so far and XPS technique cannot be readily applied for the studies of the "first" surface layer of a bulk sample. We believe that additional experiments using second harmonic spectroscopy which can give information about surface monolayer in a LC cell and computer simulation of the ordering of LC molecules over the distance ξ_{surf} can establish a relationship between surface and bulk alignment of LC in a cell.

3. CONCLUSIONS

Orientation of the adsorbed 5CB molecules on several aligning surfaces was directly obtianed from ARXPS studies. It was found that different surfaces (fused quartz, bare glass, NaCl, PVA) orient the adsorbed 5CB molecules with different tilt angles while providing qualitatively the same type of LC alignment in the bulk. In particular, quartz and PVA give high tilt, while NaCl and glass gave very low tilt. At the same time all these surfaces provide a quasi-planar alignment in LC bulk. Previous studies showed that LC bulk does not strongly affect the orientation of adsorbed molecules on the substrates [1,6]. Therefore, our results demonstrate that the orientation of LC molecules in the bulk can strongly differ from the orientation of the first adsorbed monolayer and it is determined by integral anisotropic action of the surface and interface over interface region.

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