Orientation of Amphiphilic Molecules on Polar Substrates

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A microscopic model based on the intermolecular interactions between adsorbates and substrates is developed to calculate the orientations of amphiphilic molecules on various polar substrates. The calculated orientations of a homologous series of alkyl-cyanobiphenyl molecules on solid polar substrates and at the air-water interface and their dependence on the alkyl chain length are in good agreement with the experimental values measured by optical second harmonic generation.

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The orientation assumed by molecules adsorbed at surfaces and interfaces has far reaching consequences on a variety of surface related phenomena and techniques, including adhesion, lubrication, coating, catalysis, etc. The effect further extends to biological systems where the orientational ordering of organic molecules at liquid interfaces plays an important role. Accordingly, much effort has been exerted to characterize and understand molecular orientation at interfaces. Various experimental techniques, such as x-ray diffraction [1], neutron scattering [2], infrared spectroscopy [3], scanning tunneling microscopy [4], and more recently optical second harmonic generation (SHG) [5,6] and sum-frequency generation [7], have been developed for such studies. Theoretical calculations using molecular dynamics [8], Monte Carlo simulation [9], and other methods have also been made to predict molecular orientations based on assumed interactions between molecules and substrates. However, to our knowledge, no systematic study of the problem leading to quantitative agreement between theory and experiment has ever been reported.

In this paper, we report a recent theoretical and experimental investigation on molecular orientations of a homologous series of cyanobiphenyl molecules on a number of substrates. The molecular orientations were experimentally measured with the SHG technique and theoretically calculated with a microscopic model based on simple molecular interactions between adsorbates and substrates. The results show very good agreement between theory and experiment, suggesting that the assumed interactions indeed play the dominant role in determining molecular orientations on dielectric substrates.

The molecules under study were alkyl-cyanobiphenyls (nCB with $n = 1$–12), which are composed of a polar cyano group, a biphenyl chromophore, and an alkyl chain containing n methylene/methyl groups. Their chemical formula is $CN(C_6H_4)_2(C_nH_{2n+1})$. We are interested in these molecules because nCB with $n = 5$–12 are representative liquid crystal (LC) materials. It has been shown that molecular orientation of surface LC monolayers can dictate the overall bulk alignment of an LC film [10]. Understanding how a surface LC monolayer is oriented by a substrate is therefore of great importance in the de-

sign of LC displays and devices. The substrates we used were fused silica, poly-n-hexyl-pyromellitic imide (P6), and water. They are known as polar substrates for the presence of strong dipole groups at the surfaces, such as the hydroxyl OH in the case of water and fused silica or the carbonyl $C = O$ in the case of the polyimide. Cyanobiphenyl molecules adsorbed on these substrates appear to be polar oriented with the CN group facing the substrates. Such a molecular monolayer yields a large SHG signal which allows an accurate determination of the average molecular orientation.

The SHG technique and its underlying theory used to determine molecular orientation have been described in detail elsewhere [6] and will only be briefly summarized here. For a rodlike molecule like nCB, the second-order polarizability is dominated by a single element $\alpha^{(2)}_{\zeta\zeta\zeta}$ along the long axis ζ of the biphenyl chromophore [11]. A monolayer of such molecules polar oriented on a surface has a nonlinear susceptibility tensor

$$\chi^{(2)}_{ijk} = N\alpha^{(2)}_{\zeta\zeta\zeta}\langle(\zeta \cdot \hat{\mathbf{i}})(\zeta \cdot \hat{\mathbf{j}})(\zeta \cdot \hat{\mathbf{k}})\rangle_f, \tag{1}$$

where $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ are unit vectors along the lab coordinate axes $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$, respectively, N is the number of molecules per unit area, and $\langle \rangle_f$ denotes the orientational average weighted by a distribution function f. If the distribution has a mirror plane perpendicular to the surface, f can be approximated by

$$f = Ae^{-[(\theta-\theta_0)/\sigma]^2}(1 + d_1\cos\varphi + d_2\cos2\varphi + d_3\cos3\varphi). \tag{2}$$

In this expression, A is a normalization constant, and θ and φ are polar and azimuthal angles from the surface normal $\hat{\mathbf{z}}$ and the mirror plane, respectively. θ_0 and σ are parameters describing the average molecular tilt from $\hat{\mathbf{z}}$ and its spread, respectively, and d_1, d_2, and d_3 are parameters describing the azimuthal anisotropy. For azimuthally isotropic substrates, such as fused silica, unrubbed polyimide, and water, symmetry allows only two independent nonvanishing elements in $\overset{\leftrightarrow}{\chi}^{(2)}$: $\chi^{(2)}_{zzz} = N\alpha^{(2)}_{\zeta\zeta\zeta}\langle\cos^3\theta\rangle$ and $\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy} = \chi^{(2)}_{xzx} = \chi^{(2)}_{yzy} = \frac{1}{2}N\alpha^{(2)}_{\zeta\zeta\zeta}\langle\cos\theta\sin^2\theta\rangle$. From the ratio $\chi^{(2)}_{zzz}/\chi^{(2)}_{xxz}$, θ_0 can be determined if σ is known. Note that in this case all d_i parameters vanish.

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For an anisotropic surface that leads to an anisotropic distribution function described by Eq. (2), $\chi_{ijk}^{(2)}$ can have six independent nonvanishing elements from which all the five parameters appearing in Eq. (2) can be determined. The $\chi_{ijk}^{(2)}$ elements can be measured by SHG in reflection with different input/output polarization combinations while rotating the sample about its surface normal. We have performed the measurement on our samples with a frequency-doubled Q-switched mode-locked Nd:YAG laser at 532 nm. The incidence angle of 67° was chosen to optimize the accuracy in the determination of θ_0.

Monolayers of nCB on solid substrates were deposited by solution spreading or evaporation methods. On water, they were spread as Langmuir films if $n \geq 3$. For $n < 3$, molecules are soluble in water. However, we could still obtain a relatively rich monolayer of 1CB or 2CB at the air/water interface by saturating the bulk water with such molecules. The parameters of orientational distributions deduced from SHG measurements in various cases are shown in Figs. 1 and 2. On a P6 surface that had been rubbed along one direction, the orientational distribution of nCB was anisotropic as described by Eq. (2). We found that, as shown in Figs. 1 and 2, both the average polar angle θ_0 and the azimuthal anisotropy parameters d_1 and d_2 increase substantially with the alkyl chain length n. The parameter d_3 is virtually zero in all cases. On unrubbed P6 the distribution is azimuthally isotropic. The measurement yielded the same θ_0 vs n as in the rubbed P6 case. This indicates that the polar orientation of the molecules is insensitive to rubbing and is decoupled from the azimuthal orientation. On fused silica, the distribution is also azimuthally isotropic. With σ taken to be the same as in the P6 case, the dependence of θ_0 on n was found to be very similar to the case of P6. For nCB on water, however, θ_0 appears to be independent of n, equal to 72° if σ is assumed to be zero.

We have developed a molecular model to explain the observed polar orientations of nCB on azimuthally isotropic substrates. In this model, adsorbate-adsorbate
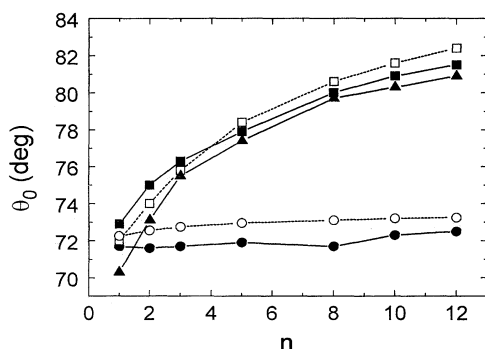
FIG. 1. Average polar angle θ_0 of nCB molecules vs alkyl chain length n obtained by SHG measurement (solid symbols) and by theoretical calculations (open symbols). Squares, triangles, and circles refer to P6 substrates, fused silica substrates, and air-water interface, respectively.
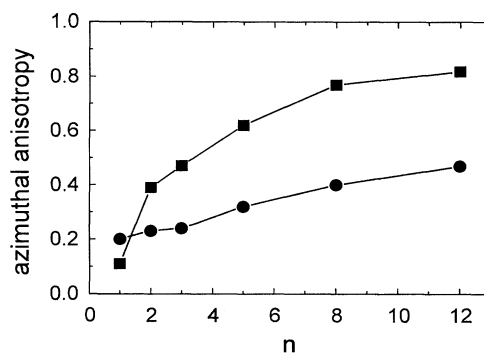
FIG. 2. Measured azimuthal anisotropic parameters d_1 and d_2 of nCB molecules on rubbed P6 vs alkyl chain length n. Circles are for d_1 and squares are for d_2.

interactions are neglected. This assumption finds justification in Ref. [12] where the orientation of adsorbates is shown to be independent of their surface density. We allow 4 degrees of freedom for each nCB molecule: 3 are external, namely, θ, ψ, and l, for the tilt of ζ from $\hat{z}$, the angle of molecular rotation around ζ, and the distance of the nitrogen atom from the surface, respectively, and 1 is internal, i.e., the rotation angle ϕ of the alkyl chain around ζ. It is assumed that the internal energy of the molecules is independent of ϕ. For simplification, we also assume that for a given θ the molecule takes its minimum energy $U(\theta)$ in the subspace of $\{\psi, l, \phi\}$. The average tilt θ_0 is then given by

$$\theta_0 = \int_0^{\pi/2} \theta g(\theta) \sin\theta \, d\theta \Big/ \int_0^{\pi/2} g(\theta) \sin\theta \, d\theta, \quad (3)$$

where $g(\theta) = \exp[-U(\theta)/k_B T]$ is the Boltzmann distribution function. To calculate $U(\theta)$, we further adopt the pseudoatom picture to model nCB molecules. In this picture, the CH groups in the phenyl ring and the CH_2 and CH_3 groups in the alkyl chain are treated as pseudoatoms, in addition to the other atoms in nCB. The potential energy of the molecule can be calculated by summing the potentials seen by individual pseudoatoms. In this work, we neglect many-body effects and assume interactions to be pairwise additive.

The dominant interaction between nCB molecules and solid substrates, such as P6 and fused silica, is the van der Waals force. Since the cyano moiety of nCB molecules is polar, one expects that its electrostatic interaction with the surface polar groups of the substrate may also be significant. However, although the magnitude of this interaction is large (about $3k_B T$, with $T = 300$ K), its anisotropy is very weak due to the large atomic dimensions with respect to bond lengths of these polar groups. Therefore, we can approximate this interaction as isotropic but strong enough to keep the nitrogen atom of nCB close to the surface, i.e., $l \approx 0$. This means that the nCB molecule is hinged to the surface on the nitrogen atom. All pseudoatoms are then subject only to the van der Waals interaction, which can be described by a

9-3 Lennard-Jones (LJ) potential [13]

$$U_i = C_{9,i}/z_i^9 - C_{3,i}/z_i^3 \qquad (4)$$

if we ignore the molecular structure of the substrate and treat it as a continuous semi-infinite dielectric medium of zero interfacial width. In Eq. (4), i is the index of the pseudoatom, and $C_{9,i}$ and $C_{3,i}$ are the LJ coefficients.

Numerical calculations have been carried out for nCB on P6, where the substrate is also composed mainly of hydrogen and carbon atoms. Considering that the differences in LJ coefficients between different hydrocarbon pseudoatoms are not larger than the spread of their values reported in the literature for the same pseudoatom, we have neglected the difference between pseudoatoms C, CH, CH$_2$, and CH$_3$ in nCB and given them a common set of coefficients $C_{9,i} = 1.2 \times 10^4 k_B T$ Å^9 and $C_{3,i} = 23 k_B T$ Å^3, obtained from a careful average over the existing literature values, taking into account the density and composition of P6 [13,14]. Using these coefficients and Eq. (4), we have calculated $U(\theta)$ of nCB. The result is shown in Fig. 3(a). We see that as the alkyl chain becomes shorter, the well of $U(\theta)$ becomes shallower, and broader on the low θ side. More importantly, this occurs in the energy range where thermal population of the system is appreciable. Therefore, the probability of finding molecules at lower θ is expected to be significantly higher for nCB with shorter chains. This leads to a smaller average tilt angle θ_0 for shorter molecules, as seen by the experiment. The calculated θ_0 vs n using Eq. (3) and $U(\theta)$ in Fig. 3(a) agrees very well with the measured results as depicted in Fig. 1. The similarity between the measured polar orientations of nCB on fused silica and on P6 suggests that the van der Waals interactions between hydrocarbon pseudoatoms and the two substrates should have similar strengths. The LJ coefficients between hydrocarbon and fused silica deduced from both adsorption measurements and polarizability calculations [15] confirm our speculation. Knowing that the van der Waals interaction between a molecule and a surface can be regarded as dispersion interaction between the molecule and its dielectric image, we could expect the similarity between fused silica and P6 from the fact that their dielectric constants in the optical region are not very different.

We now consider the case of the air-water interface. Water is very different from the solid substrates. First, its surface is penetrable by nCB molecules. Therefore, in the analysis, the density profile of the interface is important. We define the normalized profile as

$$\rho(z) = 1/(1 + e^{6z/\delta}), \qquad (5)$$

where $\delta = 3.6$ Å is the thickness for a 90% of density change [16]. Second, the interaction of an nCB molecule with water is more complicated than with a solid. The potential seen by pseudoatom i can be written as

$$U_i = U_{\text{vdW},i} = U_{h,i}. \qquad (6)$$

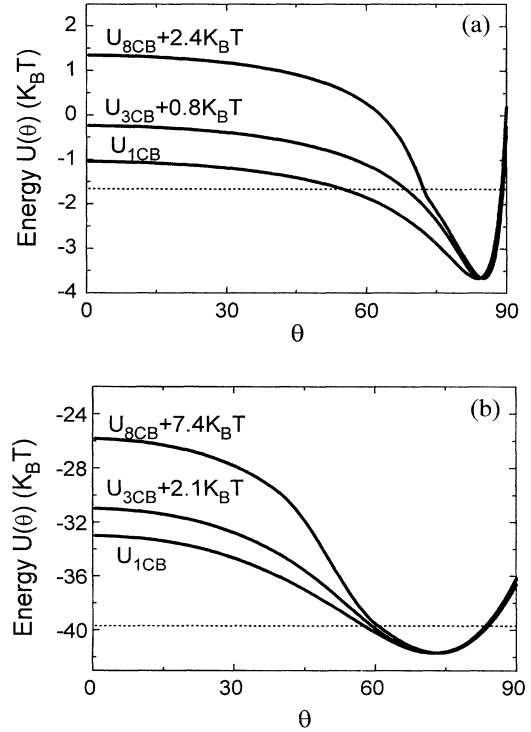The first term in Eq. (6) comes from van der Waals interaction. It consists of two parts:

FIG. 3. Potential energy U experienced by an nCB molecule as a function of its polar angle θ. Only three representative cases, $n = 1, 3,$ and 8, are shown. Dotted line is at $2k_B T$ above the minimum of the potential wells. (a) On solid substrates and (b) at air-water interface.

$$U_{\text{vdW},i} = U_{\text{dir},i} + U_{\text{rep},i}. \qquad (7)$$

$U_{\text{dir},i}$ refers to the direct van der Waals interaction between the pseudoatom and surrounding water molecules and is given by

$$U_{\text{dir},i}(\mathbf{r}_i) = \int V(\mathbf{r}_i - \mathbf{r}) n_0 \rho(\mathbf{r}) \, d\mathbf{r}, \qquad (8)$$

where n_0 is the number density of water molecules in the bulk and

$$V(\mathbf{r}) = \begin{cases} -\frac{C_i}{r^6} & \text{for } r > R_i + R_w, \\ \infty & \text{for } r < R_i + R_w \end{cases} \qquad (9)$$

is the van der Waals interaction between pseudoatom i and a water molecule at a distance r away. In Eq. (9), R_i and R_w are the radii of the pseudoatom and water molecule, respectively, and $C_i = 1400 k_B T$ Å^6 can be used for all pseudoatoms [13,14]. The $U_{\text{rep},i}$ term in Eq. (7) is related to moving those water molecules that have been replaced by the pseudoatom into bulk water and is given by

$$U_{\text{rep},i}(\mathbf{r}_i) = -n_i(\mathbf{r}_i)[U_w(\mathbf{r}_i) - U_w(z = -\infty)], \qquad (10)$$

where $n_i(\mathbf{r}_i)$ is the number of water molecules replaced by pseudoatom i and $U_w(\mathbf{r}_i)$ is the van der Waals interaction between a water molecule at $\mathbf{r}_i$ and its surrounding water molecules. We can calculate $U_w(\mathbf{r})$ using

Eqs. (8) and (9) with subindex i replaced by w and $C_w = 3400k_BT$ Å^6 [13]. The van der Waals interaction is clearly not the only type of interaction involved in the nCB/water system. Hydrogen bonding between molecules is also important. Immersing a pseudoatom in water may cause the surrounding water molecules to rearrange themselves and form a new net of hydrogen bonds. Unfortunately, the details are unknown. Therefore we have to take a phenomenological approach. We simply define the energy from such interaction between pseudoatom i and the surrounding water molecules as $U_{h,i}$, and assume

$$U_{h,i}(\mathbf{r}_i) = E_{h,i}\rho(\mathbf{r}_i) \tag{11}$$

with $E_{h,i} = U_i(-\infty) - U_{\text{vdW},i}(-\infty)$ from Eq. (6). $U_{\text{vdW},i}(-\infty)$ can be calculated, and $U_i(-\infty)$ is known from the literature [$-20k_BT$, $1.2k_BT$, and $2.0k_BT$ for immersing a CN, a CH in the biphenyl ring, and a CH$_2$ (or CH$_3$) group into bulk water, respectively [13,16]]. With Eqs. (5)–(11), we can then calculate the total energy $U(\theta)$ of an nCB molecule at the water surface. As shown in Fig. 3(b), contrary to the case of solid substrates, the potential curves for all nCB's nearly overlap in the energy range where thermal excitation is appreciable. This indicates that the average polar angle θ_0 should be essentially independent of alkyl chain length n. As seen in Fig. 1, the calculated θ_0 indeed agrees well with the measured values. It is worth noting that the alkyl chain affects the molecular orientation mostly through its van der Waals interaction with the substrate. Unlike in the solid substrate cases where the nCB molecule is relatively free to rotate about its nitrogen hinge, in the water case, part of the molecule's chromophore is buried in water with a preferential orientation dictated by its short-range interactions with water. Since the chain/water van der Waals interaction is weak compared to these short-range interactions, the molecular orientation of nCB molecules on water is therefore expected to be nearly independent of their alkyl chain length.

Finally, we need to explain the observed azimuthal anisotropic distribution of nCB on rubbed polyimide, as shown in Fig. 2. Physically, rubbing stretches the polyimide chains on the surface along a certain direction and breaks the azimuthal isotropy [6]; the interaction between the chains and the adsorbed nCB molecules then leads to the azimuthal anisotropy in nCB's orientational distribution. The results in Fig. 2, showing increase of the anisotropic parameters d_1 and d_2 with the alkyl chain length of nCB, indicate that the alkyl chain–polyimide chain interaction must have been increased with the alkyl chain length. This gives an important clue for the proper design of liquid crystal displays that requires certain bulk LC alignment, because, as we mentioned earlier, the bulk alignment is often dictated by the surface monolayer orientation. A more quantitative discussion to elucidate the aligning mechanism will also involve a detailed calculation of interactions between an nCB molecule and the anisotropic substrate. Since the structure of the latter

is not clearly known at the molecular level, we shall not dwell on it further.

In summary, we have applied optical second harmonic generation to measure the molecular orientation of a homologous family of alkyl-cyanobiphenyls with various chain lengths on different polar substrates. The mechanisms that determine the orientation are elucidated by a microscopic model incorporating the intermolecular interactions between adsorbate and substrate. For the first time, the theoretical predictions of the adsorbate orientation show a systematic and quantitative agreement with the experimental observations. In particular, we have found that the orientation assumed by alkyl-cyanobiphenyl molecules depends substantially on the nature of the substrate, as well as the length of their alkyl chains.

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