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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Invited Lecture. Studies of liquid crystal monolayers and films by optical second harmonic generation

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To cite this Article Shen, Y. R.(1989) 'Invited Lecture. Studies of liquid crystal monolayers and films by optical second harmonic generation', Liquid Crystals, 5: 2, 635 — 643

To link to this Article: DOI: 10.1080/02678298908045414

URL: http://dx.doi.org/10.1080/02678298908045414

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Liquid Crystals, 1989, Vol. 5, No. 2, 635–643

Invited Lecture

Studies of liquid crystal monolayers and films by optical second harmonic generation

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It is shown that optical second harmonic generation can be used to probe a number of important properties of liquid crystals: second order non-linearity of liquid crystal molecules, polar ordering and orientation of liquid crystal monolayers at various interfaces, and bulk alignment of molecules in supported and freely suspended films. Surface effects on bulk alignment can also be investigated.

1. Introduction

Research in non-linear optics has two motives. One is to achieve a basic understanding of the non-linear interaction of light with matter and the other is to apply non-linear optics to other disciplines. Liquid crystals are extraordinary non-linear optical media. They can give rise to some very unique and most fascinating non-linear optical phenomena [1]. Their extremely high optical non-linearities make them potentially useful for optoelectronic devices. Non-linear optics can also be used to study liquid crystals. It offers some unusual opportunities to probe certain characteristic properties of the materials. For example, two-photon-excited luminescence allows the determination of higher rank orientational order parameters [2]. Laser-induced birefringence has been used to study the pretransitional behaviour of correlated molecular reorientation in the isotropic phase [3]. Both the critical divergence and the critical slowing down characteristics of the reorientation can be measured directly as the temperature is lowered towards the isotropic–nematic transition. With picosecond laser pulses we can also probe the uncorrelated reorientational dynamics of individual molecules [4]. It may even be possible to deduce from the measurements the effective moment of inertia for the director in the mesophase [5]. Here we review the problem of how we can use optical second harmonic generation to venture into some unexplored areas of liquid crystal research.

Optical second harmonic generation arises from radiation of dipoles oscillating at 2ω in a medium non-linearly induced by a laser field at frequency ω [6]. It has the following characteristic features. First, it is a coherent process and can be highly directional. Secondly, as a second order non-linear optical process, it is forbidden in a medium with inversion symmetry under the electric dipole approximation. Thirdly, it is sufficiently sensitive to be able to detect a submonolayer of molecules in a polar arrangement. These features have made second harmonic generation a most versatile probe for surface studies [7]. Applications of the technique to liquid crystals have also turned out to be very exciting.

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2. Second order non-linear polarizabilities

We discuss first how we can use second harmonic generation to measure the second order non-linear polarizabilities of liquid crystal molecules [8]. This is a topic of much current interest because of the need for organic non-linear optical materials for optoelectronic use [9]. Asymmetric liquid crystal molecules with strong electron delocalization are likely to be good candidates.

Consider a monolayer of liquid crystal molecules on a substrate. Second harmonic generation in the reflected direction from such an interface is given by [7]

$$S = \frac{32\pi \sec^2 \theta}{\hbar\omega^3} \,|\, L_{\hat{\mathbf{e}}}(2\omega)\hat{\mathbf{e}}_{2\omega} \cdot \boldsymbol{\chi}_s^{(2)} : \hat{\mathbf{e}}_\omega \hat{\mathbf{e}}_\omega L_{\hat{\mathbf{e}}}^2(\omega) \,|^2 I^2(\omega)\, AT \quad \text{photons pulse}^{-1} \qquad (1)$$

where θ is the angle of incidence, $\boldsymbol{\chi}_s^{(2)}$ is the surface non-linear susceptibility tensor, $\hat{\mathbf{e}}_\omega$ is the unit polarization vector at frequency ω, $L_{\hat{\mathbf{e}}}(\omega)$ is the appropriate Fresnel factor for the field at ω, and I, A and T are the laser intensity, beam cross-section at the surface and pulsewidth, respectively. In general, $\boldsymbol{\chi}_s^{(2)}$ is composed of three parts; one from the individual molecules, one from the substrate and one due to molecule–substrate interaction. In many cases, however, the molecular non-linearity dominates. This is actually the case for liquid crystal molecules on water or glass. Assuming that the interaction between molecules is negligible, we can then write

$$(\chi_s^{(2)})_{ijk} = N_s \langle G_{ijk}^{\xi\eta\zeta} \rangle \, \alpha_{\xi\eta\zeta}^{(2)}, \qquad (2)$$

where $\boldsymbol{\alpha}^{(2)}$ is the non-linear polarizability of the molecules, N_s is the surface density of molecules, $G_{ijk}^{\xi\eta\zeta}$ denotes a transformation from the molecular coordinates (ξ, η, ζ) to the laboratory coordinates (i, j, k), and the angle brackets refer to an orientational average over the molecules. Further simplifications result when we realize that many liquid crystal molecules are strongly anisotropic with $\boldsymbol{\alpha}^{(2)}$ dominated by a single element $\alpha_{\xi\xi\xi}^{(2)}$ along a molecular axis $\hat{\boldsymbol{\xi}}$ and in addition, they have a random distribution in the surface plane. Equation (2) then becomes

$$(\chi_s^{(2)})_{ijk} = N_s \langle (\hat{\mathbf{i}} \cdot \hat{\boldsymbol{\xi}})(\hat{\mathbf{j}} \cdot \hat{\boldsymbol{\xi}})(\hat{\mathbf{k}} \cdot \hat{\boldsymbol{\xi}}) \rangle \alpha_{\xi\xi\xi}^{(2)}, \qquad (3)$$

and the only non-vanishing components are

$$\begin{aligned} \chi_{s,zzz}^{(2)} &= N_s \langle \cos^3 \theta \rangle \alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{s,zxx}^{(2)} = \chi_{s,zyy}^{(2)} = \chi_{s,xzx}^{(2)} = \chi_{s,yzy}^{(2)} &= \tfrac{1}{2} N_s \langle \sin^2 \theta \cos \theta \rangle \alpha_{\xi\xi\xi}^{(2)}, \end{aligned} \qquad (4)$$

where $\hat{\mathbf{z}}$ is taken along the surface normal, and θ is the angle between $\hat{\mathbf{z}}$ and $\hat{\boldsymbol{\xi}}$. Using second harmonic generation to measure $\chi_{s,zzz}^{(2)}$ and $\chi_{s,zxx}^{(2)}$, and approximating the molecular orientational distribution with a δ-function, we can now deduce $\alpha_{\xi\xi\xi}^{(2)}$ and θ separately from equation (4).

We have used this technique to measure $\alpha_{\xi\xi\xi}^{(2)}$ and θ for a number of liquid crystal molecules spread on water (see figure 1). In this case the surface density of molecules N can be varied. As shown in figure 2, the second harmonic signal is directly proportional to N^2, or $\chi_s^{(2)} \propto N$, indicating that the local field effect is negligible, and θ is independent of the surface density. Equation (4) is then valid for our measurements. The results summarized in the table allow us to draw the following conclusions [8]. (*a*) The non-linearity has little dependence on the alkane chain length. (*b*) CN is a better electron acceptor than COOH. Its termination on a molecule results in a stronger charge transfer and hence a large non-linearity. (*c*) Insertion of N in the phenyl ring terminates the electron delocalization and therefore decreases the non-linearity.

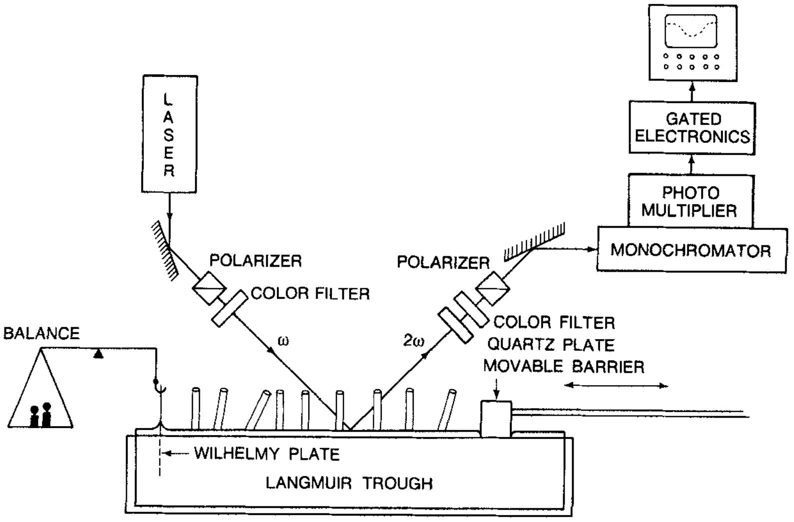


Figure 1. Schematic of the experimental set-up for second harmonic generation from a monolayer of molecules floating on water in a Langmuir trough.

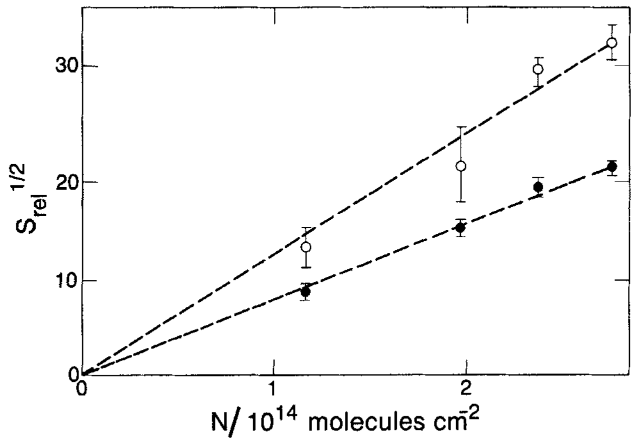


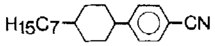
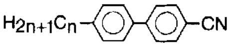
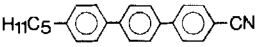
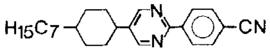
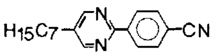
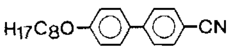
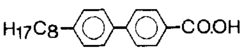
Figure 2. Square root of the relative second harmonic generation intensity $S_{rel}^{1/2}$ as a function of surface density of 4″-*n*-pentyl-4-cyano-*p*-terphenyl (5CT) spread on water. The input laser field was polarized at 45° to the plane of incidence, for which both the *s*-polarized (○) and *p*-polarized (●) second harmonic generation outputs were measured.

(*d*) Terphenyl molecules have a smaller non-linearity than the biphenyl, presumably because the former have their electron delocalization terminated by a twist between the rings. By improving the strength of the charge transfer and the length of electron delocalization, we can hope to find many liquid crystal molecules with unusually large non-linearities. For practical applications, however, there is still a further requirement that the crystals grown from such molecules should be sufficiently centro-asymmetric.

3. Interfacial molecular orientation

We now discuss how we can use second harmonic generation to probe the arrangement and orientation of liquid crystal molecules at various interfaces and in

Second order polarizabilities, $\alpha^{(2)}_{\xi\xi\xi}$, and average molecular tilt angles, θ, for a number of molecules deduced from second harmonic generation data obtained from monolayers spread on water.

		$\lvert\alpha^{(2)}_{\xi\xi\xi}\rvert$ at 2ω resonance/(10^{-30} esu)	θ/°
I		4	80 ± 10
II	 (n = 8–12)	25	71 ± 2
III		13	60 ± 2
IV		8	79 ± 3
V		8	82 ± 4
VI		40	78 ± 2
VII		6	63 ± 2

the bulk of a film [10, 11]. This problem is not only of fundamental interest but also of practical importance. The design and construction of many liquid crystal devices rely on the controlled alignment of the molecules. Although numerous methods based on surface treatment have been developed to yield the desired molecular alignment [12], it is still not understood very well how different surfaces can affect the bulk alignment differently. We are interested in the following questions. (*a*) How is a monolayer of liquid crystal molecules oriented on clean glass and on glass coated with different surfactants or polymers? (*b*) As more molecules are put on to a substrate to form a film, will the molecular orientation of the first monolayer be changed, and how does it affect the molecular orientation and arrangement of the inner layers? (*c*) What are the dominant physical mechanisms responsible for the bulk alignment? As we shall see, second harmonic generation measurements may help to answer some of the questions. They also allow us to learn how the top monolayer of liquid crystal molecules at the free surface (air–liquid crystal interface) of a liquid crystal film is oriented.

We use 4′-*n*-octyl-4-cyanobiphenyl (8CB) as a representative liquid crystal. It is known from the second harmonic generation experiment on an 8CB monolayer on water that the molecules are oriented with their hydrophilic CN head adsorbed on the water and their phenyl ring part tilted at about 70° from the surface normal [8]. Spreading a monolayer on glass and on DMOAP-coated glass yielded essentially the same result (with $\theta \sim 67°$) [10]. Thus, it is obvious that 8CB molecules also form a polar monolayer on these substrates and are more or less tilted the same way as on water. The large tilt angle may seem surprising since the DMOAP-coated surface is supposed to align the 8CB molecules homeotropically. However, when the same measurements were conducted for an 8CB monolayer on MAP-coated glass, rubbed or unrubbed, essentially the same results were again found, even though the MAP-coated surface is known to give preferential homogeneous alignment [13]. Such a monolayer arrangement can be understood if we realize that the molecular tilt could

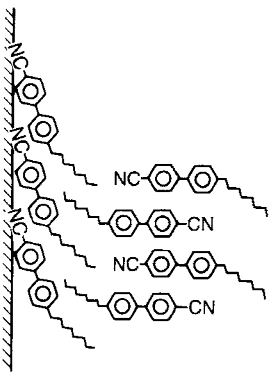


Figure 3. Model molecular arrangement of a multilayer 8CB film on glass in a homeotropic alignment.

greatly reduce the dipole–dipole interaction between the neighbouring polar-ordered molecules. We can then conclude that, in general, the molecular alignment in the bulk of a liquid crystal film is different from that of the first monolayer, and is not solely determined by the latter. Some other mechanism, presumably a long-range elastic interaction, must also be responsible for the bulk alignment [12].

By gradually increasing the number of 8CB molecules, N, on a DMOAP-coated substrate, the second harmonic signal first increased as N^2 and then quickly saturated at one full monolayer [10]. Further increase of N reduced the signal gradually; the signal reduction was appreciable only when N approached an equivalent number of about ten monolayers [13]. This immediately suggests that after the first monolayer, the molecules must be in a quadrupole-pair arrangement (see figure 3). The signal decreases with N because the molecules in a quadrupole pair have their heads facing each other so that the dipole layer contribution and the quadrupole pair contribution are of opposite signs. On the other hand, second harmonic generation from a free (air–liquid crystal) surface was smaller than that from a single monolayer on glass, indicating that no polar ordering of 8CB molecules was present at the free surface. For more quantitative results, the following experiments were performed [10, 11].

A homeotropically aligned 8CB film was deposited on DMOAP-coated glass. The film was sufficiently thick that second harmonic generation in reflection from one interface was not affected by second harmonic generation from the other interface, because the absorption length (about 0·1 μm) was much shorter than the film thickness (about 0·25 mm). Thus, second harmonic generation measurements from the two

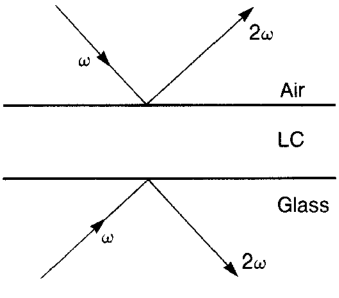


Figure 4. Schematic showing second harmonic generation from the air–liquid crystal and liquid crystal–glass interfaces of a homeotropic 8CB film on glass.

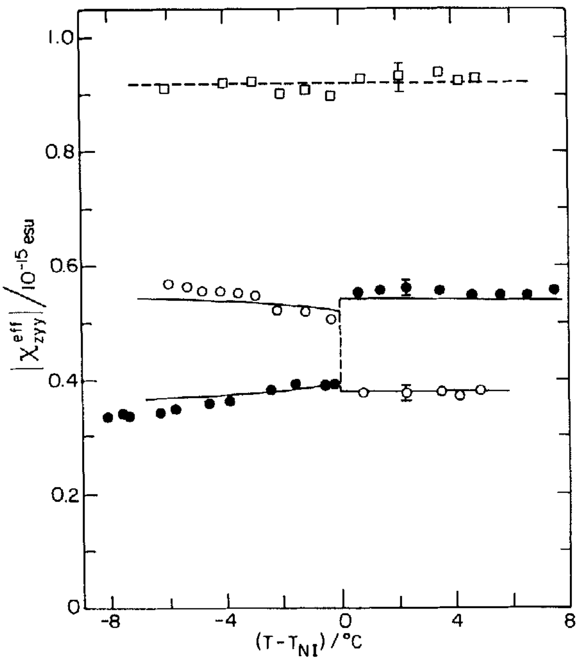


Figure 5. Effective non-linear susceptibility $|\chi^{\mathrm{eff}}_{zyy}|$ as a function of temperature for (*a*) (○) the 8CB free surface ($\chi^{\mathrm{eff}}_{zyy} = \chi^{(2)}_{\mathrm{AL},zyy}$), (*b*) (●) the 8CB-glass interface ($\chi^{\mathrm{eff}}_{zyy} = \chi^{(2)}_{\mathrm{LS},zyy}$) and (□) the algebraic sum of (*a*) and (*b*) ($\chi^{\mathrm{eff}}_{zyy} = \chi^{\mathrm{D}}_{\mathrm{s},zyy}/\eta_{\mathrm{s},zyy}$). The full curves are theoretical curves described by equations (5) and (6).

interfaces (air–liquid crystal and liquid crystal–substrate) separately (see figure 4) yielded two effective surface non-linear susceptibilities, $\chi^{(2)}_{\mathrm{AL}}$ and $\chi^{(2)}_{\mathrm{LS}}$, respectively. They are presented in figure 5 as a function of temperature. If there exists a polar-ordered surface layer at the liquid crystal–glass interface but none at the free surface, then it can be shown that

$$\begin{aligned} \chi^{(2)}_{\mathrm{AL},ijk} &= -\chi^{\mathrm{Q}}_{\mathrm{B},zijk}/\eta_{\mathrm{B},ijk}, \\ \chi^{(2)}_{\mathrm{LS},ijk} &= \chi^{\mathrm{D}}_{\mathrm{s},ijk}/\eta_{\mathrm{s},ijk} - \chi^{\mathrm{Q}}_{\mathrm{B},zijk}/\eta_{\mathrm{B},ijk}. \end{aligned} \tag{5}$$

Here $\chi^{\mathrm{D}}_{\mathrm{s}}$ and $\chi^{\mathrm{Q}}_{\mathrm{B}}$ refer to the surface non-linear susceptibility originating from the polar-ordered surface monolayer and the bulk quadrupole non-linear susceptibility resulting from the bulk molecules in a quadrupole-pair arrangement, respectively; η_{s} and η_{b} are dielectric screening factors which take into account the radiation efficiencies of the induced surface dipoles and bulk quadrupoles, respectively. The temperature dependence of $\chi^{\mathrm{Q}}_{\mathrm{B}}$ is determined from that of the bulk order parameters. Knowing that $\chi^{\mathrm{Q}}_{\mathrm{B}}$ comes from molecules in quadrupole pairs, we can write

$$\begin{aligned} \chi^{\mathrm{Q}}_{\mathrm{B},zijk} &= (N_{\mathrm{B}}/2)\langle \boldsymbol{\alpha}^{(2)}_{\mathrm{Q}} \rangle_{zijk} \\ &= (N_{\mathrm{B}}/2)\xi_0 \alpha^{(2)}_{\xi\xi\xi} \langle (\hat{\mathbf{z}}\cdot\hat{\boldsymbol{\xi}})(\hat{\mathbf{i}}\cdot\hat{\boldsymbol{\xi}})(\hat{\mathbf{j}}\cdot\hat{\boldsymbol{\xi}})(\hat{\mathbf{k}}\cdot\hat{\boldsymbol{\xi}}) \rangle \\ &= (N_{\mathrm{B}}/2)\xi_0 \alpha^{(2)}_{\xi\xi\xi} \tfrac{1}{15}[1 + \tfrac{5}{7}\langle P_2(\cos\theta)\rangle - \tfrac{12}{7}\langle P_4(\cos\theta)\rangle], \end{aligned} \tag{6}$$

where N_{B} is the density of liquid crystal molecules, ξ_0 is the longitudinal displacement of the two molecules in a quadrupole pair, P_n is the *n*th order Legendre polynomial, and $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are averages over the orientational distribution and are often known as order parameters. Since the order parameters should vanish suddenly as the liquid crystal bulk undergoes the nematic–isotropic transition, we should expect χ_B^Q, and hence both $\chi_{AL}^{(2)}$ and $\chi_{LS}^{(2)}$, to exhibit a sudden change at the transition. When $\chi_{AL}^{(2)}$ decreases, $\chi_{LS}^{(2)}$ increases correspondingly. This is indeed what the experimental data in figure 5 show.

Detailed analysis of the data led to the following conclusions. First, since

$$\chi_{AL}^{(2)} + \chi_{LS}^{(2)} = \chi_s^D/\eta_s,$$

it allows us to deduce χ_s^D from the data. We find $\chi_{s,yzy}^D = 1{\cdot}0 \times 10^{-15}\,\mathrm{esu\,cm^{-2}}$. As shown in figure 5, χ_s^D is essentially independent of temperature. These results are nearly the same as those obtained for a single monolayer on glass. They indicate therefore that the polar-ordered surface layer at the liquid crystal–glass interface must be a single full monolayer with a molecular orientation of θ about 67°. The molecular arrangement of this monolayer is not affected by the bulk ordering. Secondly, the free surface has no polar ordering. Thirdly, molecules in the bulk are in a quadrupole-pair arrangement. A theoretical plot using equation (5) and the experimental values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the literature [14] actually describe the data fairly well, as shown in figure 5. The value of $\chi_{B,zyzy}^Q$ $(T > T_{NI})$ is found to be $6 \times 10^{-16}\,\mathrm{esu\,cm^{-3}}$. From equation (5) we can deduce that ξ_0 is about 15 Å. This value may be too large, since we have neglected the local field correction factors in equation (6) [15].

The value of $\chi_{B,zyzy}^Q$ $(T < T_{NI}) \simeq 8 \times 10^{-16}\,\mathrm{esu\,cm^{-3}}$ obtained from figure 5 can be checked by an independent experiment using a freely suspended 8CB film in the smectic phase [11]. Such a film has its thickness quantized in terms of the number of molecular layers N. If all layers are equivalent, the second harmonic generation output from the film should be proportional to N^2. If not, then the surface layers must be different from those in the bulk. Such an experiment has been carried out and the data are shown in figure 6. For small N they are closely proportional to N^2, indicating that the former model of all the layers being equivalent is valid. As N increases, the data deviate increasingly from the N^2 dependence because boundary reflections and second harmonic absorption become increasingly important. The $\chi_{B,zyzy}^Q$ value deduced

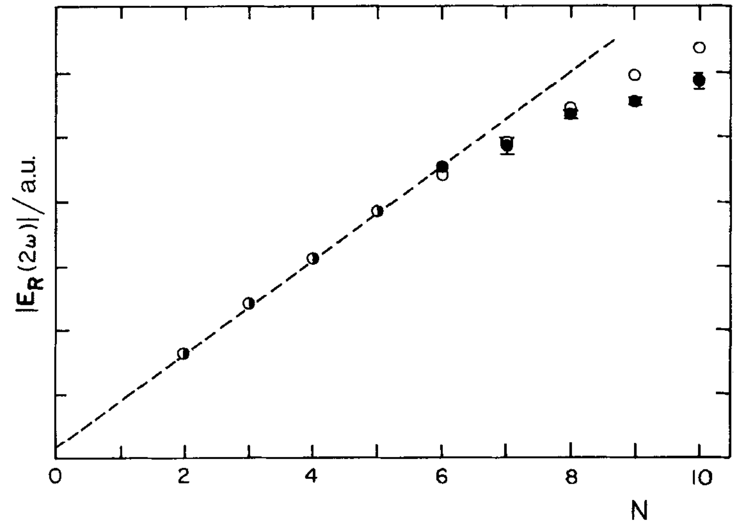


Figure 6. Amplitude of reflected second harmonic wave, $|E_R(2\omega)|$, as a function of the number of layers, N, in the freely suspended films. The incident excitation wave at frequency ω was s-polarized. ●, Experimental results; and ○, theoretical results.

from the experiment is also 8×10^{-16} esu cm^{-3}, which agrees well with that from figure 5 in the smectic phase.

Thus, we have obtained a fairly good understanding of the molecular arrangement in a freely suspended 8CB film and in a film deposited on DMOAP-coated glass or sandwiched between DMOAP-coated substrates. It may be found surprising that on a DMOAP-coated surface, the first 8CB molecular monolayer is tilted at 67° away from the surface normal, while the bulk has the homeotropic alignment. This can be understood if we realize that the ξ molecular axis actually refers to the biphenyl axis along which the molecular non-linearity is dominant [8]. Molecules in the first monolayer have their ξ axes inclined at $\theta = 67°$, but their alkane chains at 33°, knowing that the angle between the alkane chain and ξ of 8CB is 34°. The long alkane chains of the DMOAP molecules are along the surface normal, and they would align the next quadrupole-pair layer more towards the surface normal. This could be done with the arrangement shown in figure 3. Additional layers deposited on the surface are then aligned homeotropically in order to minimize the elastic energy.

The temperature independence of χ_s^D for the polar-ordered 8CB surface monolayer indicates that the ordering of the monolayer at the liquid crystal–substrate interface is governed by the short range molecule–substrate interaction. This short range surface ordering which acts as a boundary condition for the molecular arrangement may help in setting the direction of the bulk alignment, but the long range elastic interaction is perhaps more responsible for the actual bulk alignment. This is particularly evident in the case of 8CB films on rubbed MAP-coated glass. Since the first 8CB monlayer on that surface has the same molecular arrangement as on DMOAP-coated glass, the planar bulk alignment in the rubbing direction must result from the long range elastic interaction initiated by the surface topology.

We would like to know how an 8CB monolayer is oriented on many other surfaces and interfaces, for example, surfaces coated with other surfactants and different polymers. On surfaces that are hydrophobic, we should expect no polar-ordered 8CB monolayer. On strained hydrophilic surfaces, the polar-ordered surface monolayer may exhibit anisotropy in the surface plane. It is also interesting, and important for practical applications, to know how the molecular alignment gradually changes from that at the surface to that in the bulk in various cases. Studies of ferroelectric liquid crystals along the same line could be of special interest for surface stabilized ferroelectric liquid crystal devices. The possibility of having more than one polar-ordered monolayer in such systems is most intriguing.

In summary, we have demonstrated how we can use optical second harmonic generation to study non-linearities of liquid crystal molecules and the molecular arrangement at an interface and in the bulk of a film. The technique can be extended to different liquid crystals at different interfaces. It is belived that such a probe can lead to a better understanding of how a particular bulk liquid crystal alignment depends on the surface treatment.

Work described in this paper was carried out by G. Berkovic, P. Guyot-Sionnest, H. Hsiung and Th. Rasing in our laboratory. The author is indebted to them for their contributions. The major part of this work was supported by National Science Foundation—Solid State Chemistry—Grant DMR 8717137.

References

[1] See, for example, KHOO, I. C., and SHEN, Y. R., 1985, *Opt. Engng*, **24**, 579. TABIRYAN, N. V., SUKHOV, A. V., and ZEL'DOVICH, B. YA., 1986, *Molec. Crystals liq. Crystals*, **136**, 1.

[2] DURBIN, S. D., and SHEN, Y. R., 1984, *Phys. Rev.* A, **30**, 1419.

[3] WONG, G. K. L., and SHEN, Y. R., 1973, *Phys. Rev. Lett.*, **30**, 895.

[4] LALLANE, J. R., MARTIN, B., PONLIGNY, B., and KIELICH, S., 1977, *Molec. Crystals liq. Crystals*, **42**, 153. FLYTZANIS, C., and SHEN, Y. R., 1974, *Phys. Rev. Lett.*, **33**, 14.

[5] HSIUNG, H., SHI, L. P., and SHEN, Y. R., 1984, *Phys. Rev.* A, **30**, 1453.

[6] See, for example, SHEN, Y. R., 1984, *The Principles on Nonlinear Optics* (Wiley), Chap. 7.

[7] SHEN, Y. R., 1986, *New Laser and Optical Investigations of Chemistry and Structure at Interfaces*, edited by R. B. Hall and A. B. Ellis (Verlag Chemie), p. 151. SHEN, Y. R., 1986, *A. Rev. mater. Sci.*, **16**, 69.

[8] BERKOVIC, G., RASING, TH., and SHEN, Y. R., 1987, *J. opt. Soc. Am.* B, **4**, 945. BERKOVIC, G., SHEN, Y. R., and SCHADT, M., 1987, *Molec. Crystals liq. Crystals*, **150**, 607.

[9] See, for example, *J. opt. Soc. Am.*, **4** (June 1987; special issue on Nonlinear Organic Materials). CHEMLA, D. S., and ZYSS, J. (editors) 1987, *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press).

[10] GUYOT-SIONNEST, P., HSIUNG, H., and SHEN, Y. R., 1986, *Phys. Rev. Lett.*, **57**, 2963.

[11] HSIUNG, H., and SHEN, Y. R., 1986, *Phys. Rev.* A, **34**, 4303.

[12] See, for example, COGNARD, J., 1982, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon & Breach).

[13] MULLIN, C., GUYOT-SIONNEST, P., and SHEN, Y. R. (to be published).

[14] CONSTANT, M., and DECOSTER, D., 1982, *J. chem. Phys.*, **76**, 1708.

[15] Inserting the Lorenz–Lorentz local field correction factors in equation (6), we obtained for 8CB, $\xi_0 \sim 5$ Å, which is physically more reasonable.