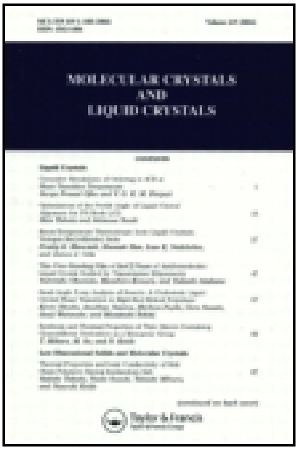

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Aritada Hatta [a]
[a] Laboratory of Interface Science of metals, faculty of Engineering, Tohoku University, Aramaki Aoba, Sendai, 980, Japan

Version of record first published: 14 Oct 2011.

To cite this article: Aritada Hatta (1981): Application of Infrared ATR Spectroscopy to Liquid Crystals. V. Orientation of 5CB Molecules in the Boundary Region of a Twisted Nematic Cell and Reorientation by a DC Electric Field, Molecular Crystals and Liquid Crystals, 74:1, 195-207

To link to this article: http://dx.doi.org/10.1080/00268948108073705

Mol. Cryst. Liq. Cryst., 1981, Vol. 74, pp. 195–207
0026-8941/81/7404-0195/$06.50/0

Application of Infrared ATR Spectroscopy to Liquid Crystals. V. Orientation of 5CB Molecules in the Boundary Region of a Twisted Nematic Cell and Reorientation by a DC Electric Field†

ARITADA HATTA

Laboratory of Interface Science of Metals, Faculty of Engineering,
Tohoku University, Aramaki Aoba, Sendai 980, Japan

(*Received December 1, 1980; in final form February 17, 1981*)

Infrared ATR measurements have been performed on a 90° twisted nematic 4-*n*-pentyl-4′-cyanobiphenyl (5CB) under an externally applied DC electric field. Analysis of polarized reflection absorbances for the C≡N stretching band at 2225 cm^{-1} allows the characterization of the anisotropic structure of a boundary layer about 3000 Å thick at the cell electrode surface. For instance, anisotropic absorption coefficients derived from the measured reflection absorbances at zero electric field confirm that molecular alignment at the boundary is substantially uniaxial. On the other hand, it is found from changes in the absorption coefficients with applied electric field that the threshold voltage for producing field-induced molecular reorientation is 5 V. The average direction of the cyano dipole with respect to the field direction is also obtained as a function of applied field strength.

1 INTRODUCTION

The anchoring properties of liquid crystal molecules have recently become of particular technological interest because they play a dominant role in determining the performance of electro-optical displays. Actually this practical problem has spurred a few investigators to get some insight into the mechanism of surface-induced alignment of liquid crystal molecules[1] or to look at the very posture of liquid crystal molecules at solid surfaces.[2] Nevertheless,

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†Presented in part at the Eighth International Liquid Crystal Conference, June 30–July 4, 1980, Kyoto (Japan).

methods to measure directly the anchoring of the molecules at electrode surfaces remain very limited. A related problem of importance is the response of the boundary molecules to a perturbation by an electric field, but information in this connection has not yet been obtained.

In this series of papers the author and others have shown some important possibilities of infrared ATR spectroscopy for the study of the orientational structure of liquid crystals adjacent to electrodes.[3,4] The present paper is concerned with an application of this technique to the observation of the molecular reorientation of 4-*n*-pentyl-4′-cyanobiphenyl (5CB)[5] near a 90° twist cell electrode under the combined influences of anchoring forces and an applied DC electric field.

2 EXPERIMENTAL

ATR spectra were taken on a JASCO IR-G grating spectrophotometer in conjunction with double-beam ATR optics[6] and with a polarizer consisting of six AgCl plates. Effort was made to adjust the alignments of mirrors on the optics to obtain the best fit in energy between a sample and reference beam. To form a "field effect" cell a nematic 5CB film 14 μm thick was sandwiched between a Si ATR prism for a single reflection and a Si plate, both served as the electrodes. The infrared radiation was incident on the totally reflecting Si prism/liquid crystal interface at a fixed angle of 40° from the normal. A DC electric field was applied normal to the liquid film, the Si prism electrode being made positive.

To produce a 90° twist of homogeneous orientation in the cell, SiO films were previously deposited under 6×10^{-5} torr onto the electrodes by a well-known oblique evaporation technique.[7] The electrodes were positioned approximately 20 cm from the SiO source placed in an alumina-coated tungsten wire basket. The evaporation angle was 60° relative to each electrode surface normal. The thicknesses of the SiO films were estimated from the mass changes of the electrodes after SiO deposition by a micro-balance with a minimum scale graduation of 5 μg. The density of the SiO films was taken as being equal to the bulk density of 2.24 $\mathrm{g \cdot cm^{-3}}$.

The sample of 5CB having a clearing point of 35.2°C was provided by Chisso Co. ATR measurements were made on the nematic phase super-cooled at 20°C as well as on the isotropic phase at 40°C.

3 RESULTS AND DISCUSSION

3.1 Transmission spectra of 5CB

To establish the transition moment direction of the normal modes of 5CB vibration, a transmission analysis with polarized radiation was performed on a

5CB thin film about 2 μm thick between two KBr windows whose inner surfaces were rubbed in one direction with a buff. The results are shown in Figure 1. In the figure, the solid and dotted lines refer to the electric vector of radiation polarized parallel and perpendicular, respectively, to the direction of rubbing. The bands at 2930 and 2860 cm^{-1} are due to the asymmetric and symmetric CH_2 stretching respectively and a sharp band at 2225 cm^{-1} is attributed to the C≡N stretching vibration. The 1607 and 1498 cm^{-1} bands are assigned to the phenyl ring modes which primarily involve C—C stretchings. Gray and Mosley have assigned most of the vibrational modes observed in the Raman spectra of 5CB and its deuterated species (5CB-d_{11}).[8] The absorption band at 812 cm^{-1} probably corresponds to a Raman band at 806 cm^{-1} which has been assigned by them as due to the phenyl ring breathing. The main contribution of this vibration is believed to be the in-phase wagging of the two adjacent hydrogens.[9] The vibrational assignments above are entirely compatible with the results of infrared dichroism observed as well as with the basic assumption that the long axes of the molecules are oriented uniaxially around the rubbing direction.

Assuming that the optical axis of the film coincides with the rubbing direc-

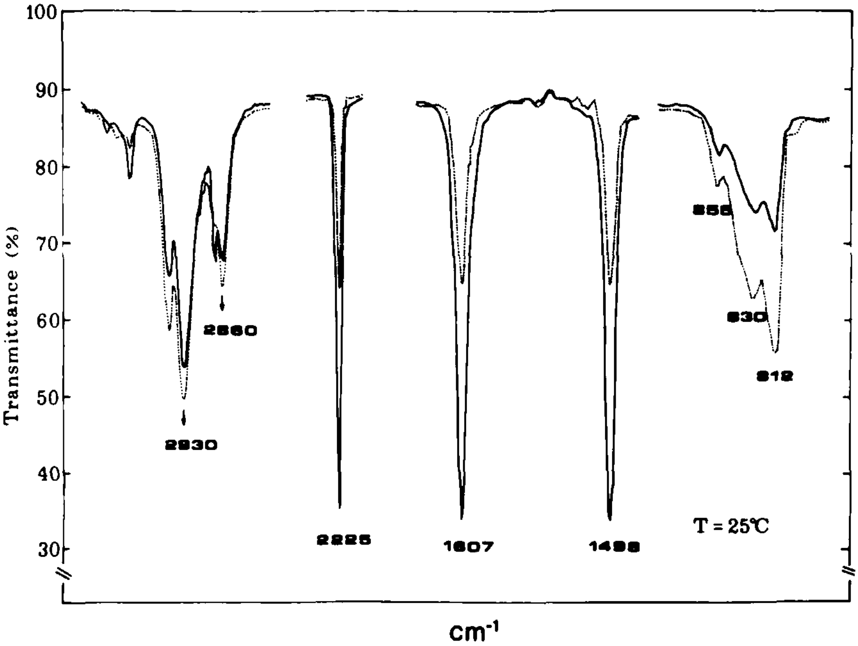

FIGURE 1 Polarized transmission spectra of a homogeneously oriented 5CB liquid crystal. The solid and dotted lines refer to the electric vector of radiation polarized parallel and perpendicular to the optical axis, respectively.

tion, the relationship between the dichroic ratio d and the orientational order parameter S is[10]

$$S = \left(\frac{d-1}{d+2}\right) / S_\beta \tag{1}$$

where $S_\beta = (3\cos^2\beta - 1)/2$ and β is the angle between the molecular long axis and the direction of transition moment. Furthermore, d is given by $A_\parallel / A_\perp$ where $A_\parallel$ and $A_\perp$ are the absorbances measured in radiation polarized parallel and perpendicular, respectively, to the optical axis. The values of dichroic ratio derived from Figure 1 are given in Table I, together with the assignments of the observed frequencies. It is evident from Table I that the 812 cm^{-1} has the lowest d value. If one assumes that the transition moment of the 812 cm^{-1} band is perpendicular to the long axis of the molecule, *i.e.*, $\beta = 90°$, then the S value is obtained to be 0.46. Obviously, this value is the minimum permissible value. Values of β for the remainder of the vibrational bands were then calculated on the basis of the same S value. A summary of the results is given in the last column in Table I.

3.2 ATR analysis for a 90° twisted cell

Polarized ATR spectra versus applied DC electric field measurements were performed on a 90° twisted cell,[11] as shown schematically in Figure 2. The 5CB molecules were aligned in such a way that the orientation axis of the molecules at the Si prism side is parallel to the y-axis. The SiO films deposited on the Si electrodes were about 1800 Å thick; they were prepared by slow evaporation (deposition rate ~200 Å/min) and, therefore, their optical properties may more or less be different from those of true SiO.[12] However, since the SiO thickness mentioned above remains very small compared to the wave-

TABLE I

Vibrational assignments and dichoric data for 5CB

Wavenumber	Assignment	Dichroic ratio	β^a
2930	CH_2 asym. str.	0.87	58.8°
2860	CH_2 sym. str.	0.86	59.2°
2225	C≡N str.	2.83	20.0°
1607	phenyl ring str.	3.06	16.1°
1498	phenyl ring str.	3.09	15.5°
855	pentyl chain[b]	0.57	72.5°
830	pentyl chain[b]	0.50	78.0°
812	phenyl CH wag.	0.44	90.0°[c]

[a] The angle between the transition moment direction and the long axis of the molecule.
[b] Ref. 8.
[c] Assumed.

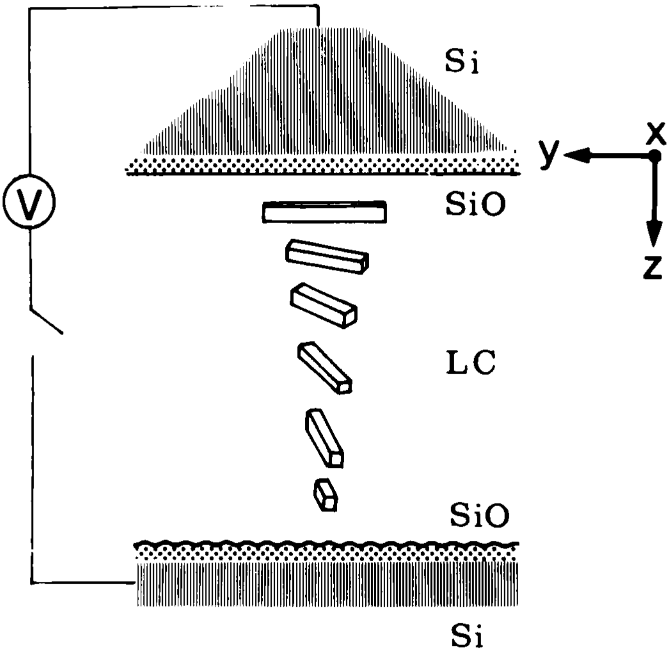

FIGURE 2 Schematic drawing of the molecular orientation in a 90° twisted cell and definition of the coordinate system for the present ATR analysis.

length of incident radiation, it is assumed that electric fields of evanescent wave at the SiO/5CB interface are still defined by the Si/5CB indices of refraction. This is equivalent to assuming that the SiO film is regarded as a medium which contributes only to a reduction of the depth of the evanescent wave penetration into the liquid crystal.

The reflection absorbance to be determined by ATR measurements is given by

$$\ln\,(R_{\perp}^{0}/R_{\perp}) = p\cdot k_{x} \tag{2}$$

for radiation polarized perpendicular to the plane of incidence (*yz* plane) and

$$\ln\,(R_{\parallel}^{0}/R_{\parallel}) = q\cdot k_{y} + r\cdot k_{z} \tag{3}$$

for radiation polarized parallel to that plane.[13] In these equations, $R_{\parallel}$ and $R_{\perp}$ are the reflectivities measured with radiation polarized parallel and perpendicular, respectively, to the plane of incidence, $R_{\parallel}^{0}$ and $R_{\perp}^{0}$ being the background reflectivities. Furthermore, k_x, k_y, and k_z are the components of the absorption coefficient along the x, y, and z axes and p, q, and r are functions of three factors, the refractive index of Si, the refractive indices of 5CB, and the angle of incidence. Provided the refractive indices of 5CB are equally replaced by an average index of 1.59 in the visible region,[14] the coefficients in Eqs. (2)

and (3) are calculated to be $p = 1.903$, $q = 1.310$, and $r = 2.747$ for the radiation incident on the Si/5CB interface at an angle of 40° from the normal. Another important variable that determines reflection absorbances mentioned above is the penetration depth of evanescent wave; the value is proportional to the wavelength of incident radiation.[15] In the present study, the C≡N stretching band was chosen as an indicator of the average amount of 5CB orientational order, because this vibration band is of strong intensity and is well isolated. In addition, it is obvious that the electric field exerts an orienting influence upon the molecules mainly through their C≡N dipoles. Under the present measuring conditions, the penetration depth of evanescent wave responsible for absorption of the C≡N stretching can be estimated to be about one-tenth the wavelength of radiation, *i.e.*, 0.45 μm. If the thickness of SiO film on the Si prism is taken into consideration, information to be derived from the C≡N stretching band may be related to the boundary layer about 2700 Å thick at the SiO/5CB interface.

In Figure 3 is shown a selection of ATR spectra of the C≡N stretching measured as a function of applied DC voltage. The upper and lower spectra refer to the electric vector of radiation polarized parallel and perpendicular, respectively, to the plane of incidence. The broken lines represent the spectra obtained for the isotropic liquid at 40°C. In order to mark a small change in reflectivity the ordinate scale was mangified 5 times on a chart recorder. The reflection absorbances obtained for the isotropic liquid are $\ln(R_{\parallel}^{0}/R_{\parallel}) = 0.107$ and $\ln(R_{\perp}^{0}/R_{\perp}) = 0.049$; these data lead to $D = 2.18$ where D is the "dichroic ratio" defined by $\ln(R_{\parallel}^{0}/R_{\parallel})/\ln(R_{\perp}^{0}/R_{\perp})$. The D value obtained above is in good agreement with the predicted value of 2.13 for a completely isotropic liquid, *i.e.*, $k_x = k_y = k_z$. As is shown in Figure 3, when the isotropic liquid was gradually cooled to 20° C the reflectivity $R_{\perp}$ increased, while the reflectivity $R_{\parallel}$ remained almost unchanged. Quantitatively, the following values were obtained for the nematic phase: $\ln(R_{\parallel}^{0}/R_{\parallel}) = 0.107$ and $\ln(R_{\perp}^{0}/R_{\perp}) = 0.032$. These data yield $D = 3.34$; the magnitude indicates that the molecules were aligned with their long axes parallel to the y-axis, as was prescribed. It should be mentioned here that a slight twist of the unique axis about the z-axis can be disregarded, because the thickness sampled by the evanescent wave is estimated to be of the order of 2% of the actual cell thickness. For the above texture, one finds $k_x = k_z$ and then obtains $k_y/k_x = 2.76$. If one notices that k_y/k_x exactly fits d in Eq. (1) and taking the value as 20.0° for the C≡N stretching, the S value is calculated to be 0.45. Obviously, the magnitude of the anisotropy is rather low. Possibly, this is a reflection of the detailed nature of the substrate, *viz.*, the geometry and size of the mountain-valley structure of the SiO film surface created by a self-shadowing mechanism. The thickness of the SiO film which is as large as 1800 Å in the present case may be responsible for the imperfect orientation observed above. Moreover, the influence of a lami-

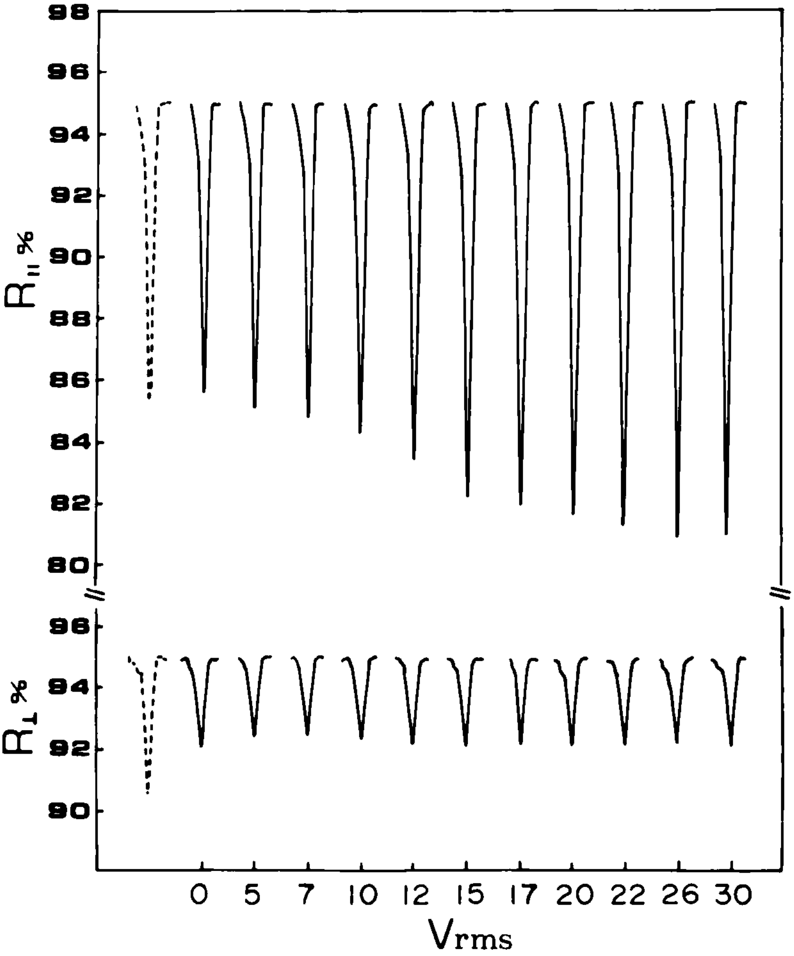

FIGURE 3 Polarized ATR spectra of the C≡N stretching of a nematic 5CB liquid at 20° C as a function of the strength of DC electric field applied. The broken lines represent the spectra of the isotropic liquid at 40° C.

nar flow which is thought to dominate under weak anchoring conditions may also be significant because it can act on the surface alignment.

As can be seen from Figure 3, on applying a DC electric field, $R_{\parallel}$ decreased with increasing field strength, whereas $R_{\perp}$ was virtually invariant. The former fact is considered as a consequence of both the decrease in k_y and the increase in k_z, owing to the positive dielectric anisotropy of the molecules.[5] The latter fact, on the other hand, indicates that the orientation of the transition moment of the C≡N stretching with respect to the yz plane remained unaltered during the course of molecular reorientation by the field. A schematic model de-

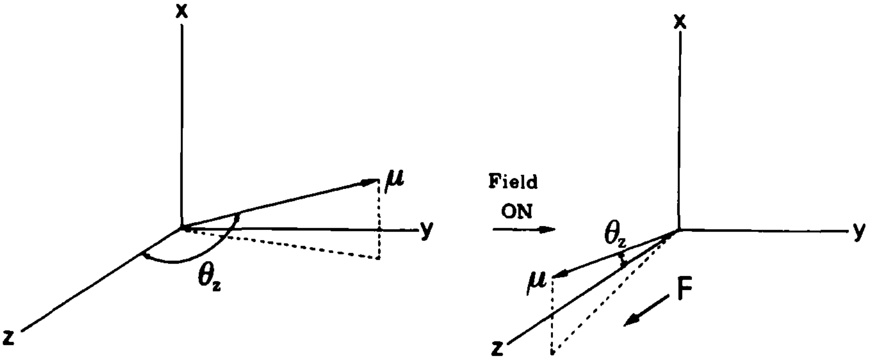

FIGURE 4 Schematic representation of the effect of a DC electric field of sufficient strength on the cyano dipole shown at the left.

scribing these observations is presented in Figure 4. In the figure μ represents the transition moment of the C≡N stretching which also describes the C≡N dipolar axis. θ_z designates the angle between the C≡N axis and the z-axis or the field direction. The variation of θ_z with rise of DC voltage will be described later.

Measurements were also made with decreasing electric field though spectra are not shown here for the sake of space. In this case the observed change in $R_{\parallel}$ was not reversible even though the initial value before field application was attained. In addition, no significant change in $R_{\perp}$ was observed. The D values derived from the reflection absorbances were plotted as a function of applied field strength in Figure 5. The open and full circles represent the experimental points obtained in the cases of increasing and decreasing electric field, respectively. As one can see, the variation of D with increasing field is not sharp on the whole and so the threshold voltage for reorientation cannot be defined accurately; the quantitative details must await the analysis of the absorption coefficents as will be treated later.

It is apparent from the discussion above that the measured amount of D can generally be related to the anisotropy. In the absence of any specific relation between k_y and k_z, however, the D value alone is not sufficient in order to specify the molecular orientation completely, because the experimental quantity, ln $(R^0_{\parallel}/R_{\parallel})$, reflects merely a sum of the terms of k_y and k_z. In what follows, therefore, we shall describe a convenient approach to separate these quantities and thereby obtain the complete set of anisotropic absorption coefficients. Implicit in this method is the assumption that the absorption coefficient k independent of molecular orientation remains unaltered at the transition from the isotropic to the nematic phase. In this connection, it should be noted that the absorption coefficient k is proportional to the square of the transition moment which is invariant to the choice of axes, *i.e.*, $k \propto \mu^2$ where $\mu^2 = \mu_x^2 + \mu_y^2$

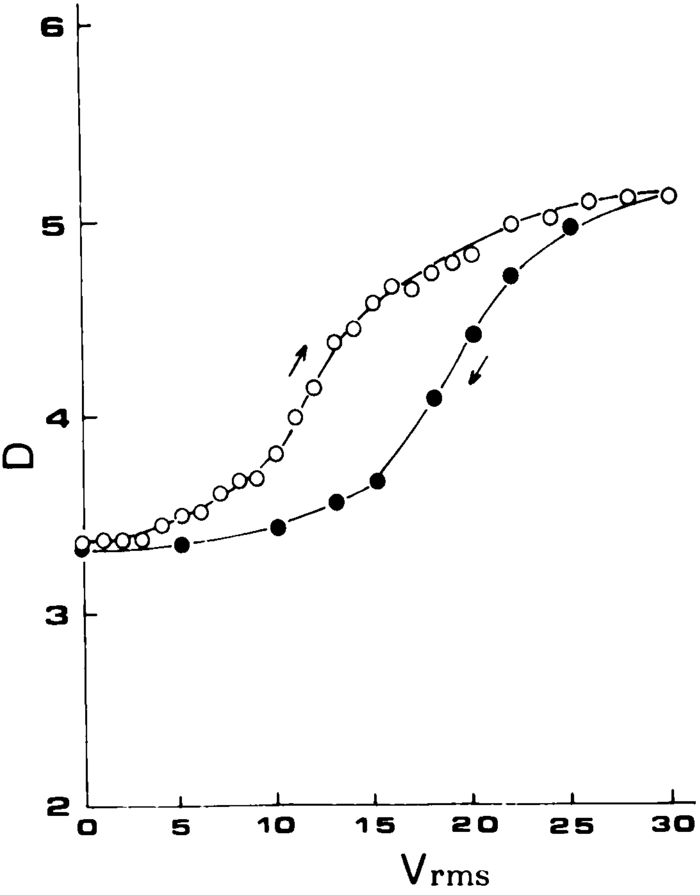

FIGURE 5 The "dichroic ratio" D of the C≡N stretching band versus applied DC voltage.

$+ \mu_z^2$. Furthermore, since the j-th component of absorption coefficient, k_j, is also proportional to μ_j^2, it can be easily shown that $k = k_x + k_y + k_z$. Accordingly, if a k value can be evaluated from measured reflection absorbances for the isotropic phase, it is possible to determine the absorption coefficients for the nematic phase from the measured amounts of $R_{\parallel}$ and $R_{\perp}$.

To begin with, it may be of importance to obtain k_x, k_y, and k_z for the nematic phase at 20° C in the absence of an electric field by the use of reflection absorbance data for the C≡N stretching band which has already been mentioned. Using Eq. (2), the quantity k can be evaluated directly from the reflection absorbance ln $(R_{\perp}^0/R_{\perp})$ for the isotropic phase. The result is $k = 3\ k_x = 7.72 \times 10^{-2}$. On the other hand, if k_z is allowed to be equivalent to k_y in Eq. (3), then k is calculated to be $k = 3k_y = 7.91 \times 10^{-2}$ using the value of ln

($R^0_{\parallel}/R_{\parallel}$). To reflect these data best on k, however, it is convenient to express k in the form $k = k_x + 2k_y$ where $k_y = k_z$. Thus, one finds $k = 7.85 \times 10^{-2}$. If one notices again that the k value derived here is taken as the sum of k_x, k_y, and k_z, then the combined use of the k value and the reflection absorbances obtained for the nematic phase provides $k_x = 1.68 \times 10^{-2}$; $k_y = 4.35 \times 10^{-2}$; $k_z = 1.82 \times 10^{-2}$. Since the values thus derived are accurate to a few per cent, the approximate equality of the values of k_x and k_z is a strong confirmation of the uniaxial alignment of the molecules around the y-axis.

In a similar fashion as above, the complete sets of anisotropic absorption coefficients changing with the strength of applied DC electric field were computed based on the measured reflection absorbances. The results are shown in Figure 6. From the figure the threshold voltage for causing an orientational change in the boundary layer may be taken to be about 5 V. Moreover, the simultaneous observation of increasing k_z and decreasing k_y with increasing electric field gives a powerful evidence in support of the positive dielectric anisotropy of the molecules. This trend reaches saturation at 28 V, suggesting the completion of the molecular orientation along the field direction. Nevertheless, it is very significant to note that the resulting texture is not uniaxial. On the other hand, a recent Raman study on a 5CB liquid crystal has shown that

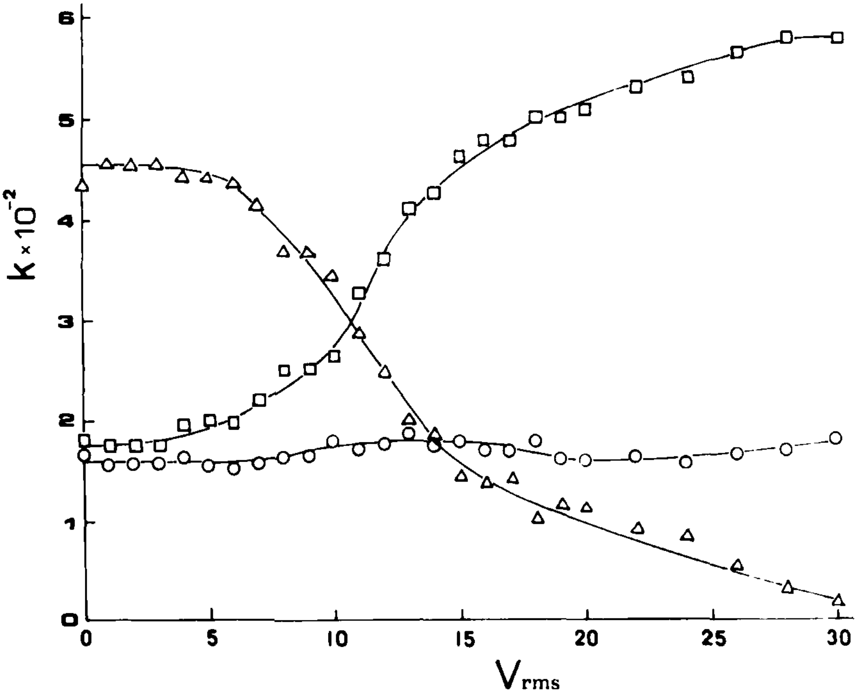

FIGURE 6 Variations of anisotropic absorption coefficients with increasing DC electric field; ○: k_x, △: k_y, □: k_z.

reorientation of the bulk liquid 14 μm thick between 90° twisted electrodes has a threshold of about 1 V and reaches saturation at 6 V.[16] Therefore it is evident that field-induced orientation occurs in the central area of the cell first, followed by propagating towards the boundary regions.

The relative magnitudes of absorption coefficients in Figure 6 can then be used in the determination of the average direction of the cyano dipolar axis. If θ_{ij} is the angle between the ij-plane and the cyano dipolar axis, it is given by $\sin^{-1} (k_k/k)^{1/2}$ (see Figure 4). Furthermore, the angle θ_z which is measured between the cyano dipolar axis and the z-axis is written by $\cos^{-1}(k_z/k)^{1/2}$. In Figure 7 the values of θ_{ij} and θ_z are plotted versus applied DC voltage. The constancy of θ_{yz} as the field is increased comes from the constancy of the k_x previously mentioned. On the other hand, θ_z falls off gradually with the increase in field strength and comes close to the value of θ_{yz} which is about 28°. Of course, since the value of θ_z does not fall lower than the value of θ_{yz}, the lower limit of θ_z is determined by θ_{yz} and hence k_x.

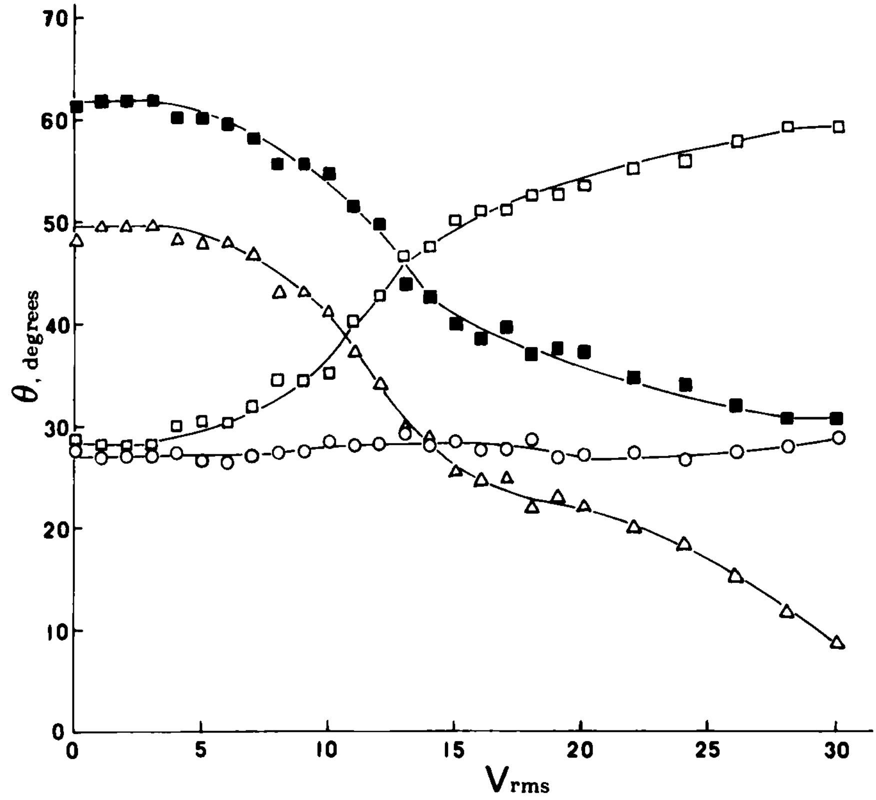

FIGURE 7 Plots of θ_{ij} ($i, j = x, y, z$) and θ_z against increasing DC voltage; ○: θ_{yz}, △: θ_{zx}, □: θ_{xy}, ■: θ_z. For details see text.

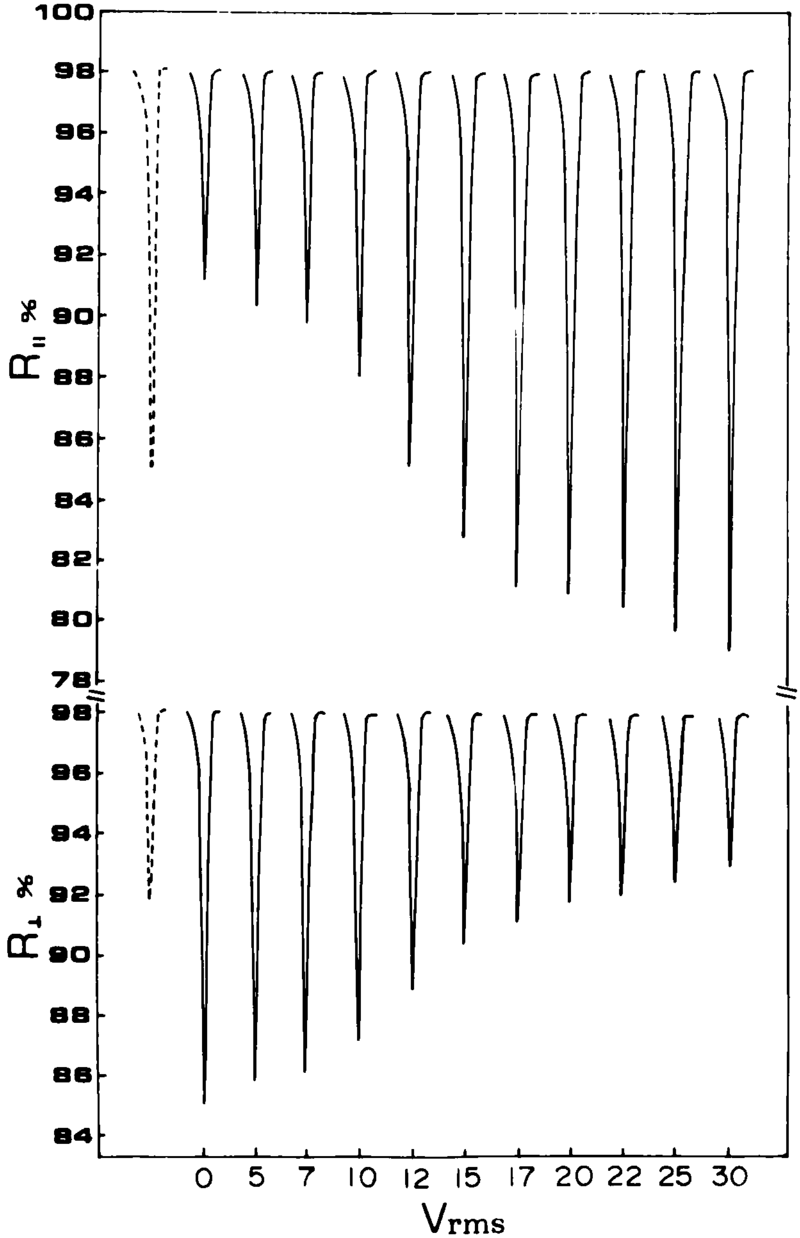

FIGURE 8 Polarized ATR spectra of the C≡N stretching of 5CB. The solid and broken lines have the same meaning as given in Figure 3, but note the unique axis at the prism side is parallel to the x-axis and the effective thickness is 3400 Å.

ATR measurements were also performed on the case where the unique molecular orientation axis at the Si prism side was specified to be parallel to the x-axis. Experimental conditions were the same as described before, except the thickness of the SiO films deposited on the Si prism and Si plate was 1100 Å. A few of the spectra for the C≡N stretching recorded with increasing DC voltage are shown in Figure 8. Information derived from the present analysis may be summarized as follows: the degree of orientational order for the boundary homogeneous texture in the field-off state at 20° C is 0.62, which is much larger than that found in the previous case; in spite of this, the threshold voltage for deformation of the texture is nearly the same; the results of the anisotropic absorption coefficient analysis are in further support of the validity of the molecular reorientation model as was illustrated in Figure 4.

Thus far particular attention has been paid to the question to what extent 5CB molecules in contact with an obliquely evaporated SiO film respond to external DC electric field. However, one of the most important aspects of the present method of analysis is that polarized ATR spectra enable us to determine the anisotropy of a liquid crystalline film in three dimensions. To enhance its usefulness, the author has recently started ATR experiments on nematic liquid crystals using an experimental setup for continuous observation of reflectivity changes with the incident angle of radiation and thereby obtaining more information about the depth profile of liquid crystal structures.

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