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Application of Infrared ATR Spectroscopy to Liquid Crystals. I. Surface-Induced Orientation in Thin Films of Nematic MBBA1)

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Infrared dichroism of nematic liquid *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) was measured using a conventional transmission method and an ATR method. In the former, KBr windows were used as substrates. The degree of orientation order of the homogeneous structure, which was achieved by a rubbing procedure, was obtained to be $S=0.40$. Using the measured dichroic ratios, the angles between the transition moments and the long axis of the molecule were calculated. The calculated values are in satisfactory agreement with the molecular conformation already suggested. In the ATR method, In_2O_3-coated glass plates were used as substrates. Rubbing of the In_2O_3 surface gave a uniform homogeneous orientation with an S value of 0.57. An In_2O_3 surface treated with dimethyldichlorosilane gave a homeotropic texture with an S value of 0.53. The directions of the transition moments relative to the long axis of the molecule closely agreed with those obtained from transmission spectra.

The orientation of the thin liquid-crystal film in contact with the solid surface is very often determined by the orientation of the liquid-crystal molecules interacting with the solid surface. Therefore, if the interaction between the molecules and the solid surface is very strong, the surface orientation can greatly contribute to the long-range ordering of the liquid crystal. Such an orientation behavior is not only a phenomenon of fundamental interest, but is also a practical problem for application to display elements.2) In this connection, it is interesting to observe the infrared dichroism arising from molecular orientation in thin films of the liquid crystals in contact with various substrate surfaces.

The effects of temperature3) and electric field4) on molecular orientation have been investigated by the infrared dichroism method. All of these studies, however, have resorted to the use of the transmission method. Absorption measurements on liquid crystals using transmission techniques are often difficult because of the strong absorption and, therefore, extremely thin films are required. This difficulty does not arise when the ATR method5) is used, because the observed intensities are determined by an electric-field penetration into the sample of a few microns and are independent of the sample thickness.

The most significant advantage of using the ATR method is that the electric fields exist in all spatial directions at the reflecting interface. Therefore, the ATR technique is capable of giving information about any orientational state of the liquid crystal.

Vergoten and Fleury6) have recently reported infrared and Raman spectra of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) in the solid state and in nematic and isotropic liquids. However, no infrared dichroism measurements have yet been reported.

The objective of this report is to show the versatility of the infrared ATR method in studying the structure of oriented liquid films of MBBA induced by the surface effect of the substrate.

Experimental

ATR spectra were recorded using a JASCO model IR-G grating spectrophotometer equipped with a double-beam ATR attachment and a conventional AgCl polarizer. Two trapezoidal prisms made from high-purity monocrystalline silicon were used as internal reflection elements in an optically-balanced double-beam system; one prism was put in the sample beam and the other in the reference beam.

The prisms were cut and polished so as to provide an internal reflection angle of incidence of 40° and give one reflection. The Si prism used has a constant transmittance (55%) from 2.5 to 6.6 μ. Beyond 6.6 μ, however, the transmittance of silicon falls off due to impurities and lattice bands, for example, three weak bands appear between 6.6 and 8 μ and a strong band appears at 9 μ. Careful balancing of the sample and reference beams provided a flat background level over the 2.5—10 μ wavelength range with sufficient sensitivity. In the present study, mainly the 6—10 μ range was investigated.

The sandwich cell shown in Fig. 1 was used for the ATR measurements. The sample of the liquid crystal is sandwiched between the Si prism and a substrate plate which is separated from the prism by a polyester spacer. The substrate chosen for the present study was an In_2O_3-coated conducting glass plate. The substrate was in contact with the wall of a brass box containing a nichrome wire heater. The tempera-

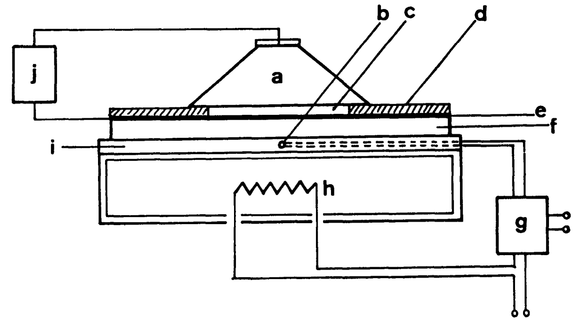

Fig. 1. Liquid crystal cell for ATR measurements. a: Si prism, b: thermocouple, c: liquid crystal, d: spacer, e: In_2O_3 electrode, f: glass plate, g: temperature regulator, h: heater, i: single-bored glass plate, j: voltage generator.

ture of the liquid crystal was controlled by a conventional on-off power supply. The accuracy of the temperature was ±2 °C. Guaranteed-grade MBBA reagent was obtained from Tokyo Chemical Industry Co. and was used without further purification.

To obtain homeotropic alignment, the substrate of the In_2O_3-coated glass plate was immersed in a 5% toluene solution of $(CH_3)_2SiCl_2$, following the experimental procedure given by Uchida *et al.*[14] After standing for 30 min at room temperature, the substrate was taken out of the solution and then rinsed with toluene to remove the remaining $(CH_3)_2SiCl_2$. The substrate thus treated was dried at 100°C for 1 h.

Results and Discussion

First, the transmission spectra of oriented MBBA at 30 °C will be discussed. The MBBA sample was held between two KBr windows whose surfaces were rubbed in one direction with a buff.

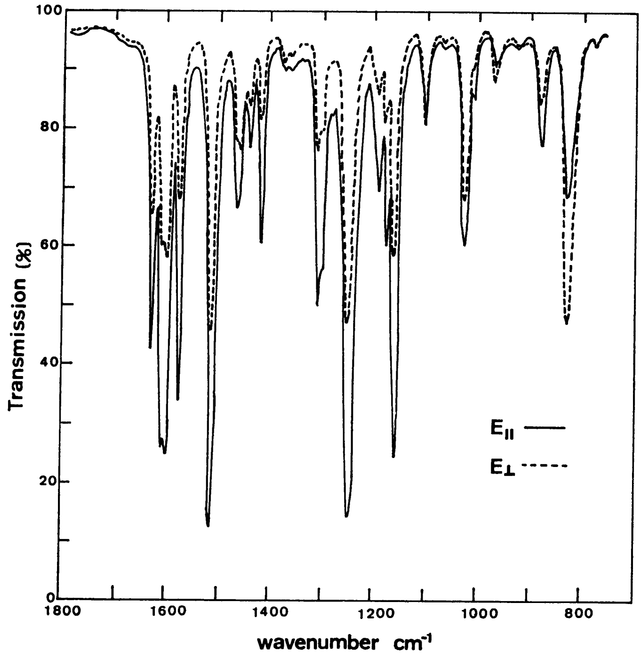

Fig. 2. The polarized transmission spectra of oriented thin MBBA film at 30 °C. $E_{/\!/}$ and $E_\perp$ refer to the electric vector of radiation polarized parallel and perpendicular to the optic axis (rubbing direction), respectively.

Spectra were taken for radiation with the electric vector polarized parallel and perpendicular to the rubbing direction. Because of the high degree of absorption, no spacer was used between the windows. The polarized transmission spectra for MBBA are shown in Fig. 2. The observed dichroic ratios and vibrational assignments for several important bands are given in Table 1.

The degree of orientational order in liquid crystals is generally defined by the degree of order, S[7]

$$S=\frac{1}{2}(3\cos^2\alpha-1),\qquad(1)$$

where α is the angle between the long axis of the molecule and the optical axis of the uniformly oriented liquid crystal.

Table 1. Observed frequencies, vibrational assignments, and dichroic ratios for homogeneously-oriented MBBA ($S=0.40$; $\alpha=39.2°$)

Observed (cm^{-1})	Assignment	R	β[a]
1630	C=N stretching	2.03	29.4°
1600	phenyl ring stretching	2.51	19.3°
1578	phenyl ring stertching	2.85	10.2°
1520	phenyl ring stretching	2.52	19.0°
1250	C–O–C asym. stretching	2.51	19.2°
1160	phenyl C–H in-plane deformation	2.63	16.4°
1030	CH_3–O stretching (C–O–C sym. str.)	1.34	44.8°
830	phenyl C–H out-of-plane deformation	0.50	90.0°[b]

a) The angle between the direction of the transition moment and the long axis of the molecule. b) Assumed.

On the other hand, the dichroic ratio is given by[8]

$$R=\frac{k_{/\!/}}{k_\perp}=\frac{4\cos^2\beta\cos^2\alpha+2\sin^2\beta\sin^2\alpha}{2\cos^2\beta\sin^2\alpha+\sin^2\beta(1+\cos^2\alpha)}.\qquad(2)$$

In Eq. 2, $k_{/\!/}$ and $k_\perp$ are the absorption coefficients measured with the infrared radiation polarized parallel and perpendicular to the optical axis, respectively. The angle β designates the angle between the long axis and the vibrational transition moment of the molecule. The coordinate system defined above is shown in Fig. 3. In this figure, all the long axes of the molecules are assumed to be inclined at a common angle α with respect to the optical axis. Furthermore, the molecules are assumed to rotate freely about their own long axes.

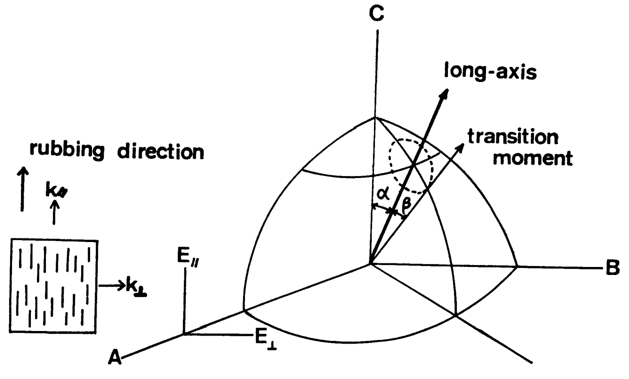

Fig. 3. Uniaxial orientation of the long-axis of the molecule around the optical axis and of the transition moment around the long-axis of the molecule.

From Eqs. 1 and 2, the degree of order is expressed in the simple form,

$$S=\frac{R-1}{S_\beta(R+2)},\qquad(3)$$

where

$$S_\beta=\frac{1}{2}(3\cos^2\beta-1).$$

Thus, the degree of order is expressed in terms of R and

S_β. Accordingly, if the angle β is known for a given vibrational band, the value of S can be obtained from its R value. Furthermore, by using the S value obtained above, the β value can be calculated for any other vibrational band.

According to Eq. 1, the S value in Eq. 3 should vary from -0.5 to 1, the former corresponding to liquids oriented with the long axes of molecules perpendicular to the rubbing direction and the latter to liquids oriented with the long axes parallel to that direction. If the liquid crystal is isotropic, that is $R=1$, the S value becomes zero.

On the other hand, there is a high tendency for nematic molecules to line up with their long axes parallel to the direction of rubbing[3,9] and, therefore, the optical axis of the uniaxial liquid crystal can be assumed to coincide with the rubbing direction, as shown in Fig. 3. Accordingly, we may consider only the case in which the long axis of the molecule is oriented preferably parallel to the optical axis of the liquid so that the long axis has a positive S value. If the vibrational transition moment is oriented along the long axis of the molecule, Eq. 3 reduces to $S=(R-1)/(R+2)$. Because R varies between 1 and infinity in this case, the degree of order varies from 0 and 1, the former corresponding to an isotropic liquid and the latter to a liquid oriented parallel to the optical axis. On the other hand, when the transition moment is directed perpendicular to the long axis, the degree of order is given by $S=2(1-R)/(R+2)$. In this case, R would vary from 0 and 1, and then S is positive with a maximum value of 1 which also corresponds to a completely parallel liquid. Consequently, the degree of order S varies from 0 and 1 provided the $k_{/\!/}$ component of the absorption coefficients is taken to be parallel to the optical axis of MBBA molecule.

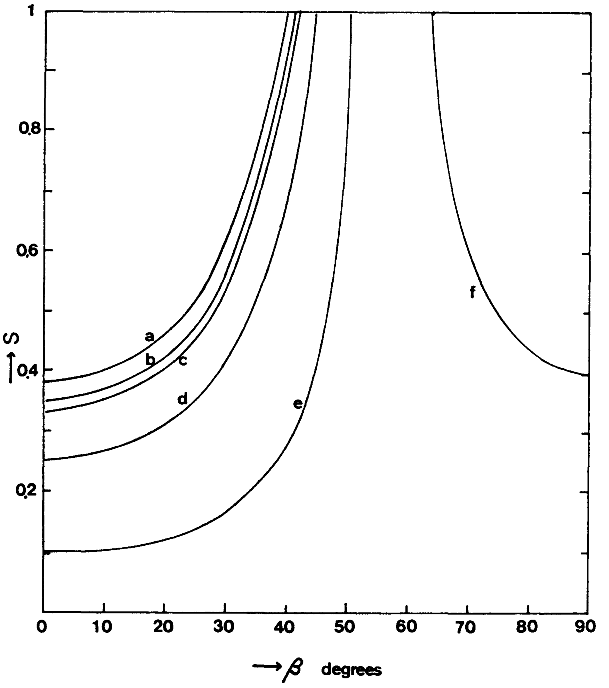

Fig. 4. The degree of orientation order S as a function of angle calculated from experimental dichroic ratio. a: 1578 cm^{-1}, b: 1160 cm^{-1}, c: 1600 cm^{-1}, d: 1630 cm^{-1}, e: 1030 cm^{-1}, f: 830 cm^{-1}.

The S values estimated from Eq. 3 are plotted against β in Fig. 4, using the R values listed in Table 1. The plots vary in a characteristic way and provide useful information about molecular structure: they afford the relative direction of the transition moment of the molecule and can, therefore, give confirmation of assignments already given. It is evident from Fig. 4 that the angle for the 1578 cm^{-1} band must have the lowest value; its transition moment is oriented nearly parallel to the direction of the long axis of the molecule. In contrast to this band, the 830 cm^{-1} band very probably has a much different direction of transition moment from that of the above band.

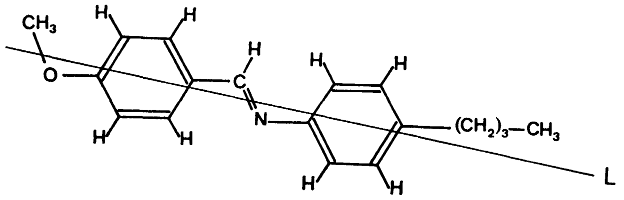

Fig. 5. Structural model for MBBA. L is the approximate direction of the long-axis of the molecule (from Ref. 10).

Based on the NMR study, Pines and Chang[10] suggested the structure of the MBBA molecule as shown in Fig. 5, where the long axis **L** is shown as the line passing through the centers of the co-planar benzene rings. If the transition moment of the 830 cm^{-1} band is assumed to be perpendicular to the long axis, *i.e.*, $\beta=\pi/2$, the S value is found, from Fig. 4, to be 0.40. From Eq. 1, the value of α is calculated to be 39.2°. If an S value of 0.40 is used, one can estimate β values for the remainder of the vibrational bands. The results are presented in Table 1.

The angle β between the transition moment of the phenyl ring stretching mode at 1578 cm^{-1} and the long axis of the molecule is calculated to be 10.2°, which is in excellent agreement with the experimental value of 9° given by Pines and Chang.[10] The above-mentioned value $S=0.40$ is rather low compared with the 0.62 value obtained from optical anisotropy measurements.[11] Nevertheless, in view of the fact that a sample in the form of very thin film was used, the uniformity of orientation may be affected by the container surfaces.

Saupe and Maier[7] have pointed out that the observed dichroic ratios contain a contribution from the anisotropy in the refractive indices, *viz.*, birefringence, $\Delta n=n_e-n_o$, where the extraordinary index n_e and ordinary index n_o correspond to the directions parallel and perpendicular to the optical axis of the medium, respectively: the correction factor to the dichroic ratio should increase with increasing S. If we conveniently assume that the birefringence of MBBA[12] obtained at 6328 Å is applicable to the present case, the corrected S value is found to be 0.44. In this case, however, the resulting β value for the 1578 cm^{-1} band is as large as 22°, which cannot be considered reasonable in view of the structural model mentioned above. Therefore, the birefringence in the infrared region is probably small compared with that in the visible region. Support for this deduction is given by the ATR measurements of highly-oriented MBBA.

In the ATR method,[13] electromagnetic fields interacting with the absorbing medium are present in three directions at the reflecting interface and then the measurement of the reflectivity losses provides information about the anisotropy of the medium. In this respect, the ATR method is valuable for all types of oriented liquid crystals. However, no ATR spectra of liquid crystals have yet been reported. Brief mention is made of a procedure for the determination of the orientation of MBBA induced by substrate surfaces.

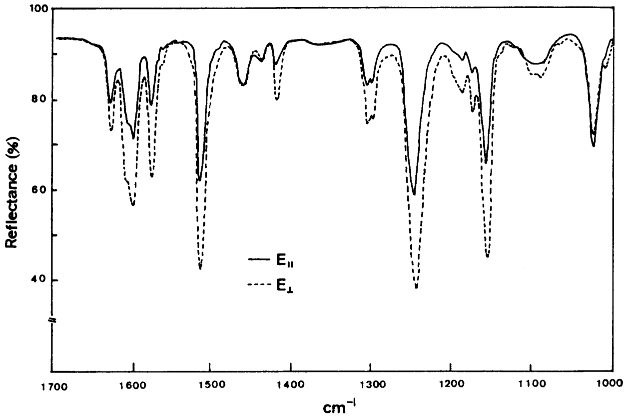

Fig. 6. The ATR spectra of uniformly homogeneous MBBA kept at 25 °C, measured with the electric vector of the radiation polarized parallel (solid line) and perpendicular (broken line) to the plane of incidence.

Figure 6 shows the polarized ATR spectra of a 25-μ sandwich of nematic MBBA between indium-oxide coated glass and a single reflection silicon prism. The temperature of the liquid cell was maintained at 25 °C and the incident angle was 40°. In order to obtain homogeneous orientation, the In_2O_3 surface was rubbed with alumina in one direction. The rubbed substrate was positioned to form the liquid cell so that the direction of rubbing coincided with the x-axis of the prism (see Fig. 8).

Figure 7 shows the polarized ATR spectra of homeotropically-oriented MBBA film at a constant temperature of 25 °C with the long axis of the molecule perpendicular to the substrate. This homeotropic structure was attained when the surface of the In_2O_3 coated glass was treated with dimethyldichlorosilane[14] or lecithin. The dichroic behavior exhibited in Fig. 7 shows clearly that the sample is quite well oriented, in agreement with the literature.[14] The observed dichroic ratios, D, taken from Figs. 6 and 7 are listed in Table 2.

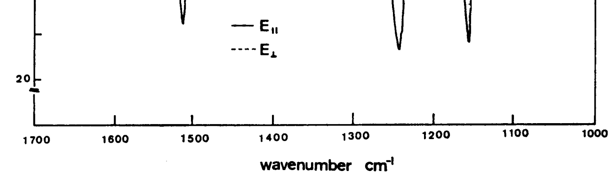

Fig. 7. The ATR spectra of homeotropic MBBA kept at 25 °C, measured with the electric vector of the radiation polarized parallel (solid line) and perpendicular (broken line) to the plane of incidence.

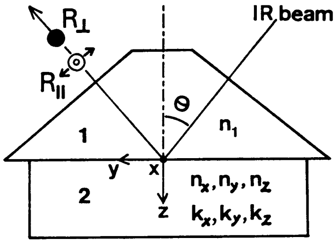

Fig. 8. Coordinate system for the attenuated total reflection from anisotropic absorbing medium. 1: Silicon prism, 2: anisotropic liquid crystal.

Table 2. Observed dichroic ratios, calculated β values, and S values for homogeneous and homeotropic liquids of MBBA

Wavenumber (cm^{-1})	Homogeneous			Homeotropic		
	D_{obsd}	k_x/k_z	β	D_{obsd}	k_z/k_x	β
1630	0.74	2.556	31.6°	4.35	2.277	32.6°
1600	0.53	3.568	20.9°	5.72	3.144	22.1°
1578	0.42	4.502	11.0°	7.18	4.068	10.0°
1520	0.51	3.708	19.6°	5.90	3.258	20.9°
1250	0.51	3.708	19.6°	5.74	3.156	22.0°
1160	0.46	4.110	15.5°	6.48	3.625	16.3°
1030	1.19	1.589	43.6°	3.29	1.606	42.4°
	$S=0.57$; $\alpha=32.4°$			$S=0.53$; $\alpha=34.0°$		

We now consider the two-phase system having a flat boundary shown in Fig. 8. In the figure, medium **1** is the Si ATR prism (refractive index of 3.42)[15] from which the infrared radiation is incident on medium **2**, which is a semi-infinite absorbing liquid crystal. The plane of incidence is the yz plane, the x-axis being perpendicular to this plane.

When total reflection occurs, the electromagnetic wave penetrates into medium **2** beyond the reflecting interface. For bulk material in which the thickness is much greater than the penetration depth of the evanescent wave, the change in reflection absorbance is respectively expressed for radiation polarized perpendicular and parallel with respect to the plane of incidence,[16] as

$$\ln\left(\frac{R_0}{R_\perp}\right) = pk_x$$

and

$$\ln\left(\frac{R_0}{R_{/\!/}}\right) = qk_y + rk_z, \tag{4}$$

with

$$p = \frac{4n_{x1}^2}{\tan\theta(1-n_{x1}^2/\sin^2\theta)^{1/2}(1-n_{x1}^2)},$$

$$q = r(1-n_{z1}^2/\sin^2\theta), \tag{5}$$

and

$$r = \frac{4n_{y1}n_{z1}}{\tan\theta(1-n_{z1}^2/\sin^2\theta)^{1/2}(1-n_{z1}^2/\sin^2\theta+n_{y1}^2n_{z1}^2\cot^2\theta)}.$$

In Eq. 4, R_0 is the reflectivity when the absorption of medium **2** is zero and k_x, k_y, and k_z are the components of the absorption coefficient along the x, y, and z axes, respectively. In Eq. 5, θ is the incident angle and n_{x1}, n_{y1}, and n_{z1} are the components of the ratio of the refractive index of medium **2** to that of medium **1**.

From Eq. 4, the experimental dichroic ratio D, obtained from ATR spectra can be written as

$$D = \frac{q}{p}\left(\frac{k_y}{k_x}\right) + \frac{r}{p}\left(\frac{k_z}{k_x}\right). \tag{6}$$

In a particular case where the liquid is isotropic, *i.e.*, where $k_x=k_y=k_z$, D becomes $(q+r)/p$. Since the nematic liquid crystal has a uniaxial symmetry about the optical axis, the Eq. 6 can be reduced to a simpler expression.

If the molecules are oriented normal to the Si prism surface (homeotropic orientation), one finds $k_x=k_y$ from Fig. 8, and Eq. 6 reduces to

$$D = \frac{q}{p} + \frac{r}{p}\left(\frac{k_z}{k_x}\right). \tag{7}$$

If the molecules are oriented parallel to the x axis (homogeneous orientation), one has $k_y=k_z$ and then obtains

$$D = \frac{q+r}{p}\left(\frac{k_z}{k_x}\right). \tag{8}$$

Thus, if the values of p, q, and r can be calculated from Eq. 5, the value of the degree of order, S, can be obtained as a function of β in the manner described above for the case of transmission spectra. One should note that the k_z/k_x in Eq. 7 corresponds to the R in Eq. 3 in the case of homeotropic orientation, while in the case of homogeneous orientation the k_x/k_z in Eq. 8 corresponds to the R in Eq. 3. In order to calculate coefficients p, q, and r, however, it is necessary to know the anisotropic refractive indices in the infrared region for truly-oriented MBBA, however, no data are available at present.

On the other hand, in the visible region, detailed determinations of the birefringence and indices of refraction of MBBA at two wavelengths have been made by Haller, Huggins, and Freiser.[12)] Their results are $n_0=1.54$ and $\Delta n=0.22$ at 6328 Å. These values are in good agreement with those obtained by Labrunie and Valette[17)] at the same wavelength. Therefore, the values of p, q, and r were calculated assuming the above values.

Using an appropriate β value and the D value observed for any one vibration band, we can determine the degree of order S by the combined use of Eq. 3 and Eq. 7 or 8 corresponding to the case of homeotropic or homogeneous orientation. The β values for any other vibration can be derived using the S value thus determined. In the present study, the S value was changed independently for the homeotropic and the homogeneous cases so as to obtain agreement of the resulting β values for all vibration bands listed in Table 2 for both cases, because the β values cannot be altered by changes of orientation and the degree of orientation order. However, no set of reasonable S values could be obtained that fit the corresponding β values for both cases. Therefore, the most reasonable set of β values was obtained by changing only Δn, because the contribution of Δn to the calculated β and S values is much more sensitive than that of n_o. For these calculations, a least-squares refinement gave S values of 0.57 for the uniform homogeneous orientation and 0.53 for the homeotropic orientation. In these cases, the values of α are calculated to be 32.4 and 34.0° for the homogeneous and homeotropic cases, respectively. As a result of the above calculations, the most probable birefringence was obtained to be 0.05. In view of the experimental accuracy, however, a birefringence of 0.10 should also be considered to give good fit to the observations. The values of β obtained for the two liquid crystals are presented in Table 2, together with the values of k_z/k_x and k_x/k_z. The values of the degree of order S thus derived are compatible with the value of 0.62 for MBBA given by Chang.[11)] In addition, values of β for the vibrational bands investigated here are in satisfactory agreement with those obtained by the transmission method mentioned previously.

It should be noted that the dichroisms observed for the two types of oriented film both arise from orientations of the liquid crystal very near the Si surface. In spite of this fact, dichroic analysis revealed a high degree of orientation, as mentioned above, which strongly suggests that the influence of the silicon surface on the orientational structure is much weaker than the aligning forces of the wall of the substrate side.

For practical reasons, several techniques for obtaining uniform orientation of liquid crystals have been investigated.[18)] In order to understand the alignment mechanism, it is important to elucidate the structure of the liquid crystal as well as the surface structure of the substrate.[14,19)] The infrared ATR technique permits experiments directed towards these problems.

Another important objective of the present ATR study on liquid crystals was to observe the molecular orientation under electric fields. This has been partly completed and the results of the experiment will be reported in the near future.

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