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A. Kocot[ab]; R. Wrzalik[ab]; J. K. Vij[a]
[a] Department of Microelectronics and Electrical Engineering, University of Dublin, Trinity College, Dublin, Ireland [b] Institute of Physics, Silesian University, Katowice, Poland

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Angular dependence of absorbance on the polarization angle of an IR beam in liquid crystals

by A. KOCOT†, R. WRZALIK† and J. K. VIJ*
Department of Microelectronics and Electrical Engineering, University of Dublin,
Trinity College, Dublin 2, Ireland

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The angular dependence of the IR absorption on the polarization angle is studied using a model based on IR dichroism and it is found to be modified by the anisotropy in the IR absorbances. This is obtained from the rotation of the electric field acting at a particular point in a liquid crystal with respect to that of the incident beam. The angular rotation is found to depend mainly on the distance of this point from the plane of incidence and the IR dichroism of the liquid crystal and less on the anisotropy in refractive indices.

The long-range orientational order in liquid crystals (LCs) has been extensively studied using several spectroscopic techniques. A study of the IR absorption of a LC sample is one of the important methods used to determine the order parameter of the distribution function of the molecules. The technique is particularly sensitive for determination of the order of the different groups of atoms in the system. Nevertheless certain features concerning the interaction of the electro-magnetic field with the LC sample are not yet completely understood. One of the outstanding problems has consisted of determining a relationship between the macroscopic and the microscopic tensor properties of the electric field. The latter is different from the former by a factor known as the local field corrector factor [1, 2]. In the past however, no account was taken of dichroism, perhaps for the reason that it is negligible for visible wavelengths.

The infrared absorption due to a single molecule is proportional to $(\mathbf{E}\cdot\mathbf{p})^2$ where $\mathbf{E}$ is the local electric field and $\mathbf{p}=\partial\mu/\partial q$ is the transition dipole moment of a vibrational mode characterized by the normal coordinate q. The IR absorption can be used to investigate the orientational distribution of transition dipoles instead of determining the orientation of the entire molecule characterized by its permanent dipole moment. The field acting on a particular vibrating mode $\mathrm{E}^{\mathrm{LOC}}$ is different from $\mathbf{E}$ by a factor called the local-field correction factor. Several researchers including Vuks [1], Dunmur [2] and Blinov [3] have attempted to determine a correction factor based on different models to include the anisotropy in refractive indices, but these models have not included the anisotropy in the optical absorbance (optical dichroism). This is perhaps because optical dichroism at visible wavelengths for liquid crystals is negligible.

Our experiments on the absorption spectrum are made at IR wavelengths where, especially for certain bands, dichroism in absorbance is significant. For simplicity, the local-field anisotropy is assumed to be negligibly small [3, 4]. The electric field of the incident beam is assumed to lie in the x–z plane as shown in figure 1, making an angle θ with the z direction. The z axis is chosen to coincide with the director of the homogenously aligned sample. At a distance y from the incident plane, the polarization angle α, is determined by the x and z components of the electric field E_x, E_z:

$$\tan\alpha(\theta,u)=\frac{|E_x(u)|}{|E_z(u)|} \tag{1}$$

where u is a dimensionless variable ($u=y/d$), normalized by the total thickness of the sample d; u varies between 0 and 1. Due to the IR dichroism, the amplitudes of the two field components are continuously reduced in magnitude while passing through the sample. Following the definition of the absorbance, we have

$$E_x^2(u)=10^{-uA_\perp}\cdot E_x^2(0) \tag{2}$$

$$E_z^2(u)=10^{-uA_\parallel}\cdot E_z^2(0) \tag{3}$$

where $A_\perp$ and $A_\parallel$ are components of the infrared absorbance for the perpendicular and parallel polarization of the incident beam, respectively. For this study, relative variations in the phase part of the electric field for the two directions are neglected. It is known that molecular modes of vibrations in liquids and those likely in liquid crystals are uncorrelated with each other. Hence

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*Author for correspondence.

†Permanent address: Institute of Physics, Silesian University, Katowice, Poland.

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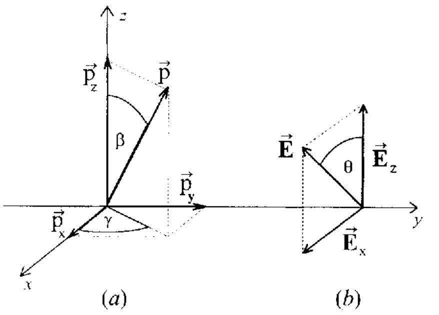


Figure 1. (*a*) Orientation of the vibrational transition dipole moment **p** in the laboratory frame with the z axis parallel to the optical axis of the sample. (*b*) Electric field orientation in the laboratory frame; θ is the angle of polarization.

variation brought about by the phase may not affect the intensity of the beam. Using equations (1), (2) and (3), we get

$$\tan^2\alpha(\theta,u)=\left[\frac{E_x^2(u)}{E_z^2(u)}\right]=10^{-u(A_\perp-A_\parallel)}\frac{E_x^2(0)}{E_z^2(0)}$$
$$=\tan^2\theta\times 10^{-u(A_\perp-A_\parallel)} \qquad (4)$$

If $A_\perp \neq A_\parallel$, then the polarization angle, α, is dependent on u, and differs from the incident angle θ.

Next we calculate [5] the absorption due to an arbitrarily oriented transition dipole **p** ($p\sin\beta\cos\gamma$, $p\sin\beta\sin\gamma$, $p\cos\beta$) and normalize it to the total absorption; angles β and γ are defined in figure 1 (*a*).

$$\frac{(\mathbf{E}(\theta,u)\cdot\mathbf{p})^2}{(|\mathbf{E}(\theta,u)|\cdot|\mathbf{p}|)^2}=\frac{1}{3}+\frac{2}{3}P_2(\cos\beta)$$
$$+\left[\frac{1}{2}\sin^2\beta\cos 2\gamma-P_2(\cos\beta)\right]\sin^2\alpha(\theta,u)$$
$$+\frac{1}{2}\sin 2\beta\cos\gamma\sin 2\alpha(\theta,u) \qquad (5)$$

where the angle $\alpha(\theta,u)$ is given by equation (4) and $P_2(\cos\beta)=3/2\cos^2\beta-1/2$ is the second-order Legendre polynomial.

In order to obtain the absorption coefficient of a thin layer situated at a distance u from the incident plane, we multiply the absorption of a single dipole by its distribution function $F(\beta,\gamma)$, given here for the case of the symmetry of the S_C^* phase [6],

$$F(\beta,\gamma)=\frac{1}{4\pi}\Bigg[1+3A\sin\beta\sin\gamma+5BP_2(\cos\beta)$$
$$+\frac{15}{4}C\sin 2\beta\cos\gamma+\frac{15}{4}D\sin^2\beta\cos 2\gamma\Bigg]+\ldots \qquad (6)$$

and integrate over all values of the angles β and γ. The coefficient A measures the polar order. B is the second order parameter, $\langle P_2\rangle$, often simply called P_2 and this pertains to the order relative to the z axis. C and D are the parameters connected with the quadrupolar order. The absorption of the layer $\Delta A(\theta,u)$ relative to the absorption of the disordered or isotropic sample is then given by

$$\frac{\Delta A(\theta,u)}{A_{\mathrm{iso}}}=\Bigg[1+2B+\left(\frac{3}{2}D-3B\right)\sin^2\alpha(\theta,u)$$
$$+\frac{3}{2}C\sin 2\alpha(\theta,u)\Bigg]\Delta u. \qquad (7)$$

On using the trigonometric identities,

$$\sin^2\alpha=\frac{\tan^2\alpha}{1+\tan^2\alpha},\quad \sin 2\alpha=\frac{2\tan\alpha}{1+\tan^2\alpha}$$

and equation (4), the angle α in equation (7) can be expressed in terms of θ. On integrating over the limits 0 to 1 for u, the total absorption of the sample is calculated to be as follows:

$$\frac{A(\theta)}{A_{\mathrm{iso}}}=1+2B+\frac{(\frac{3}{2}D-3B)}{(A_\parallel-A_\perp)\ln 10}$$
$$\times\ln\left[\frac{1+\tan^2\theta\times 10^{(A_\parallel-A_\perp)}}{1+\tan^2\theta}\right]$$
$$+\frac{6C}{(A_\parallel-A_\perp)\ln 10}$$
$$\times[\tan^{-1}\tan\theta\times 10^{0\cdot 5(A_\parallel-A_\perp)}-\tan^{-1}(\tan\theta)] \qquad (8)$$

Equation (8) is a general formula depicting the absorption suffered by an incident IR beam polarized at an angle θ, in passing through an anisotropic medium. For $\theta=0$, equation (8) reduces to

$$\frac{A_\parallel}{A_{\mathrm{iso}}}=1+2B \qquad (9)$$

and for $\theta=90°$, equation (8) becomes

$$\frac{A_\perp}{A_{\mathrm{iso}}}=1-B+\frac{3}{2}D \qquad (10)$$

Equations (9) and (10) are the same as those derived previously by Zgonik *et al.* [6]. Equation (8) however is derived now possibly for the first time in the literature for the liquid crystal phase and predicts an altered dependence of the absorbance caused by the anisotropy in the absorbance (dichroism).

The order parameter B (or $\langle P_2\rangle$) can be calculated from the measured values of $A_\parallel$ and A_{iso}. On knowing B, D can be calculated from $A_\perp$ and A_{iso}. For $D=0$, $\langle P_2\rangle$ can be calculated from $A_\parallel$ and $A_\perp$.

Liquid crystals in their smectic and nematic phases can be regarded as approximately uniaxial; for these cases the coefficients $C = D = 0$. For a uniaxial LC, equation (8) reduces to

$$\frac{A(\theta)}{A_{\mathrm{iso}}} = 1 + B\left(2 - \frac{3}{(A_{\parallel} - A_{\perp})\ln 10} \times \ln\left[\frac{1 + \tan^2\theta \times 10^{(A_{\parallel} - A_{\perp})}}{1 + \tan^2\theta}\right]\right). \qquad (11)$$

For a uniaxial LC and for the case $A_{\perp} - A_{\parallel} \rightarrow 0$, equation (11) reduces to

$$\frac{A(\theta)}{A_{\mathrm{iso}}} = 1 + B(2 - 3\sin^2\theta). \qquad (12)$$

Equation (12) is valid for the above case and also included is the condition that the correction factor for the local field anisotropy in the refractive indices is negligibly small.

In order to obtain a more general formula for $A(\theta)$, we can now introduce the local field correction factor g, i.e. by replacing $(\mathbf{E} \cdot \mathbf{p})^2$ in equation (5) by $g \cdot (\mathbf{E} \cdot \mathbf{p})^2$. As a consequence of this alteration, the order parameters B, C and D can be obtained from a revised formula that will also include the local field anisotropy factor g. In this case, the right hand side of equation (8) and hence that of equation (11) will be multiplied by g. The local field anisotropy factor, g, as defined by Blinov [3] is

$$g = \frac{n_{\parallel}}{n_{\perp}} \left|\frac{E_{\parallel}}{E_{\parallel}^{\mathrm{LOC}}}\right|^2 \left|\frac{E_{\perp}^{\mathrm{LOC}}}{E_{\perp}}\right|^2 \qquad (13)$$

$$E_{\parallel} = E_z \quad \text{and} \quad E_{\perp} = E_x.$$

The low molar mass liquid crystal investigated was: E Merck LC, 4-*n*-octyl-4′-cyanobiphenyl (8CB) with transition temperatures Cr/294·7 K/S_A/306·7 K/N/313·7 K/I. The samples were aligned homogenously between two optically polished Si windows. A Mylar foil of 6 μm thickness was used as spacer between these two windows of the cells. The cells were filled with the LC sample in the isotropic phase utilising the capillary effect. The infrared absorption spectra were recorded using a Digilab FTS60A, FFT Spectrometer. The accuracy of the instrument has been improved by reducing stray light and zero fluctuation and improving the temperature stability of the interferometer. Absorbance of 3 units is measured with an accuracy of 3%, whereas that of one unit is made with an accuracy of 1%. The resolution of the spectra was fixed to 0·5 cm^{-1}. An infrared polarizer (SPECAC IR-KRS5) was used to vary the polarization angle of the incident beam. The polarisation angle was measured with reference to the rubbing direction on the windows. The optic axis is assumed to lie along the rubbing direction.

The IR spectra were recorded for temperatures of 308 K (nematic phase) and 300 K (S_A phase) as a function of the polarization angle. The spectra for polarization angles of 0° and 90° are shown in figure 2. As is obvious from this figure, the spectra are free from the interference fringe pattern formed in the sample. This is due to the relatively thick samples. The absorption bands for which the measurements are illustrated are the C–N stretching band lying at 2227 cm^{-1} and two C–C in-plane benzene ring vibrations lying at approximately 1607 and 1006 cm^{-1}. Dependences of the absorbance on the polarization angle for the incident beam, for a temperature of 308 K (nematic phase of 8CB) for the three different absorption bands at 2227, 1607 and 1006 cm^{-1} are shown in figures 3 (*a*), 3 (*b*) and 3 (*c*), respectively. Similar plots for the smectic phase of 8CB (i.e. at 300 K) for 2227 and 1607 cm^{-1} are shown in figures 4 (*a*) and 4 (*b*).

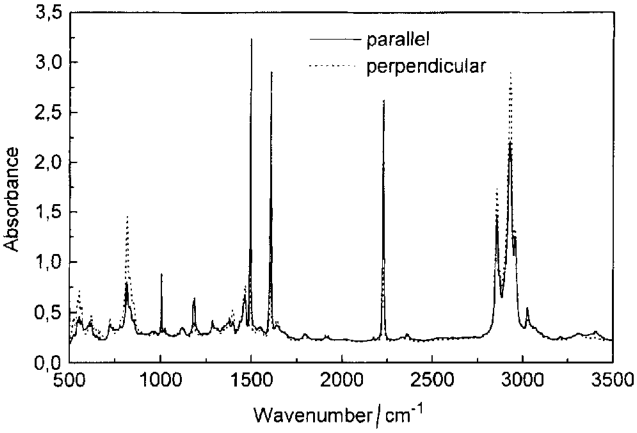
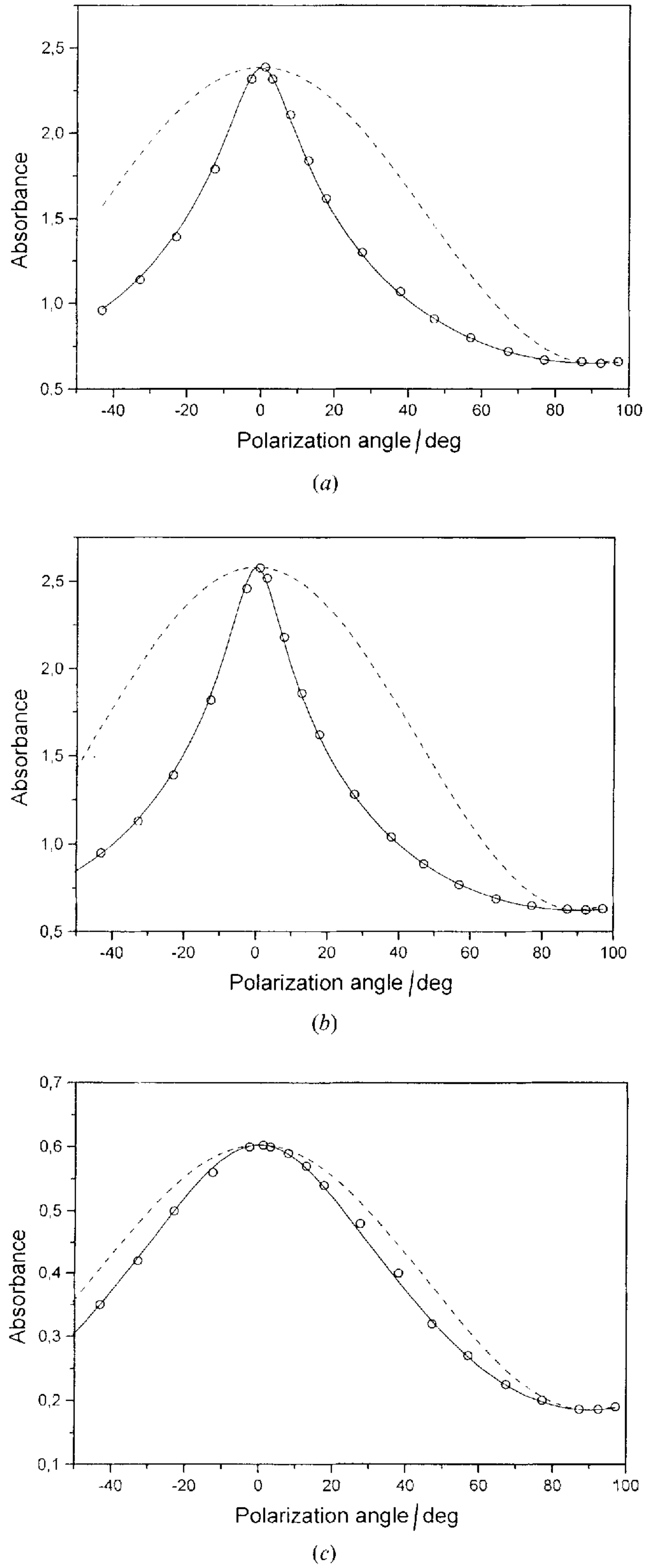


Figure 2. Infrared absorption spectrum of 8CB at 308 K for polarization angles of 0° (solid line) and 90° (dotted line); parallel and perpendicular vibrations, respectively.

The normalized absorbance is calculated as a function of the angle θ using equation (12), derived in the limit $A_{\parallel} - A_{\perp} = 0$ and is shown in the figures as dotted line. We find an apparent large discrepancy between the dotted plots and the plots generated by the measured values. The magnitude of this apparent discrepancy is found to be dependent on the absolute magnitude of the anisotropy in the absorbance ($A_{\parallel} - A_{\perp}$), i.e. dichroism. The absorbance is recalculated using equation (11) with the measured values of $A_{\parallel}$ and $A_{\perp}$ and is shown by

Order parameter for different vibrational bands

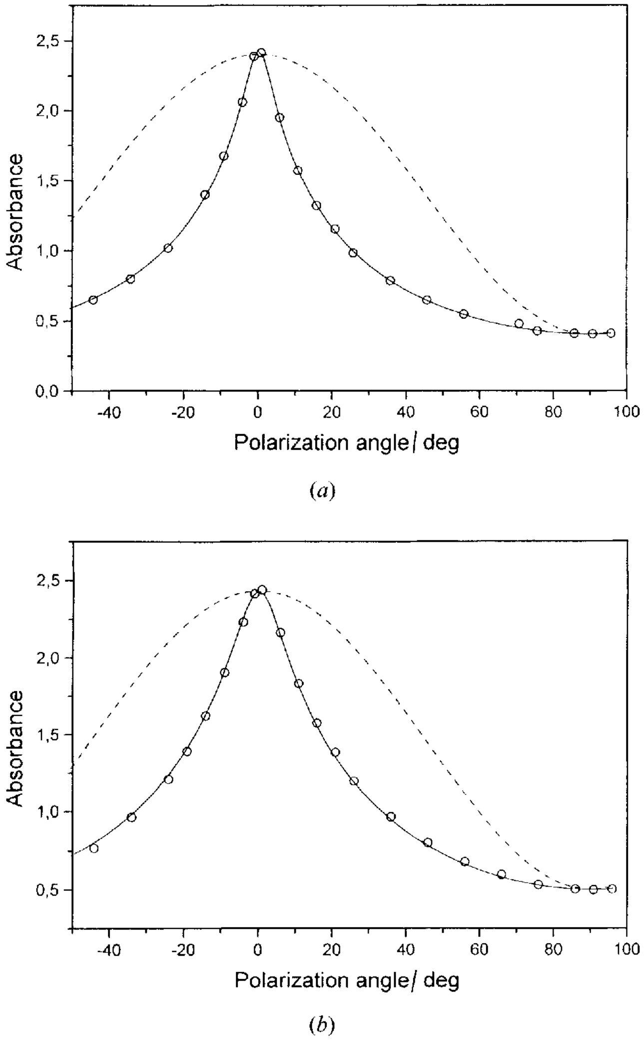
T/K	ν/cm^{-1}	S_2
300	2227	0·56
	1607	0·62
	1006	0·55
308	2227	0·47
	1607	0·51
	1006	0·43



(*a*)

(*b*)

(*c*)



(*a*)

(*b*)

Figure 4. Same as in figure 3 except $T = 300$ K; (*a*) 2227 cm^{-1} band, (*b*) 1607 cm^{-1} band. Open circles denote experimental data; solid continuous line (theory, equation (11)); dotted line (plot without correction).

the continuous lines in these figures. We find that the continuous curves for each of the five cases perfectly reproduce the experimental data. Values of the orientational order parameter $\langle P_2 \rangle$ (or B) are listed in the table. B is found using

$$B = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{14}$$

Figure 3. Angular dependence of the IR absorbance for 8CB in the nematic phase, $T = 308$ K, for bands (*a*) 2227 cm^{-1}, (*b*) 1607 cm^{-1} and (*c*) 1006 cm^{-1}. Open circles denote experimental data, solid lines calculated from equation (11), dashed lines calculated without the local field correction and the IR dichroism.

which is obtained by combining equations (9) and (10) for $D = 0$.

There may exist two possible ways of finding the effect of the local field anisotropy. First we fit the data to the modified equations (8) and (11), where their right hand sides are multiplied by g. From a comparison of the theory and the experiment we find that $g \cong 1$ within experimental error. Secondly we can theoretically estimate the value of g as follows: using the simplest model for the local field due to Lorentz, we can write

$$g = \frac{n_\parallel}{n_\perp}\left(\frac{n_\perp^2 + 2}{n_\parallel^2 + 2}\right)^2. \qquad (15)$$

For $T = 308\,\mathrm{K}$, our measured refractive indices at the sodium-D line are for 8CB $n_\parallel = 1{\cdot}666$ and $n_\perp = 1{\cdot}520$. Using equation (15) we obtain $g = 0{\cdot}893$ which is less than 1 by ~10%. It may be remarked however that the Lorentz model for the local field is the crudest of the available models and assumes the molecules to be spherical in shape. The reason for this apparent discrepancy between the two methods for determining g may lie in the invalidity of this assumption. Recent work [6] on local field anisotropy has also found $g \cong 1{\cdot}05$ for cyanobiphenyl-type liquid crystals. This is again close to unity as shown by a comparison of our experimental data for the angular dependence of the IR absorption with the theory.

The results thus show that the plane of polarization of the electric vector is rotated mainly by the IR dichroism of a liquid crystalline material and is not significantly affected by the anisotropy in optical refractive indices. The angle of rotation can be calculated from equation (4), by measuring beforehand the absorbance parallel and perpendicular to the optic axis for a vibrational band under investigation. A close fit between theory and experiment shows that the assumptions under which equation (11) is derived are correctly satisfied by liquid crystals.

The effect of the rotation of the polarization angle (rotation of the field vector **E**) is of great importance in studying the shape of the IR spectra. The effect manifests itself closer to the centre of the band than at its wings, and consequently a significant change in the shape of the band can be produced. The shape of spectra can be calculated as a function of polarization angle, using equation (8) or simply for a uniaxial LC using equation (11).

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