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On the measurement of the orientational order parameters in biaxial liquid crystals using the polarised infrared technique

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The limits of the applicability of the Polarised Infrared (Fourier transform infrared) spectroscopy technique, which is used to measure the order parameters of biaxial liquid crystals, is investigated in detail for different experimental geometries and cell thicknesses. General expressions for the transmittance of the polarised infrared radiation by a biaxial liquid crystal material in planar and homeotropic cells are obtained in the general case of oblique incidence. These expressions are then simplified in the limiting cases of thin and thick cells, and in both cases the relationship is established between the cell transmittance and the components of the imaginary part of the infrared molecular permittivity. It is shown that simple expressions, used in the literature to extract the values of the biaxial order parameters, are valid only for thin cells and in specific geometries when light propagates along one of the optical axes of the material. For thicker cells typical for experimental conditions, approximate expressions are obtained which are to be used to reveal the order parameters of biaxial liquid crystals. Various types of experimental geometries are discussed including those suitable for measurements of the order parameters, and those to be avoided.

Keywords: infrared spectroscopy; biaxial nematics; theory; biaxial order parameters

1. Introduction

Polarised Fourier transform infrared (FT-IR) spectroscopy has been found to be a very powerful method for the investigation of liquid crystals on a microscopic level. IR spectroscopy has been used to study the orientational order in biaxial nematic and smectic phases including the smectic C and ferroelectric chiral smectic C (smectic C*) liquid crystal (LC) phases [1–4]. Orientational order parameters and the tilt angle of the primary director in the smectic C* phase have also been measured using FT-IR spectroscopy [5].

In particular, infrared spectroscopy is the only experimental technique which has been used to measure the complete set of orientational order parameters of biaxial nematic materials [2] composed of tetrapode molecules which have been discovered recently [2, 6, 7]. Biaxial nematic materials possess a lower symmetry and are characterised by four orientational order parameters, S, P, D and C, where P specifies the biaxial order of long molecular axes and C characterises the independent biaxial order of short molecular axes. Recently a number of biaxial order parameters, including the higher order ones, have also been measured using polarised Raman spectroscopy [8] in biaxial nematic materials composed of bent-core molecules [9, 10].

It should be noted, however, that extracting the information on the order parameters from the IR spectroscopy data requires a theoretical formalism, which should follow from the general theory of IR absorbtion. So far such a general theory has only been developed for the case of isotropic fluids, and no general expressions for IR absorption in LCs are available in the literature.

The development of the general theory of IR absorption in uniaxial and biaxial LCs is very important because it enables one not only to derive simple expressions, which can be used in practice to estimate the order parameters, but also to identify clearly the experimental geometries, for which these expressions are valid, and the limits of their applicability. In the existing literature the corresponding theoretical formulas are often used without a justification, and it is generally not known when they are actually valid.

The purpose of this paper is to develop a general theory of infrared absorption in biaxial LCs, to obtain simple approximate expressions for the transmittance of the polarised IR radiation in the limiting cases of thin and thick cells, and to find out in which experimental geometries these expressions can be applied.

The paper is arranged as follows. In Section 2 we derive approximate expressions for the components of the imaginary part of the susceptibility in terms of the

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orientational order parameters of a biaxial LC phase. Section 3 is devoted to the general analysis of the transmission properties of a LC cell with tilted director orientation. In this section the general expressions are obtained for the IR transmittance and reflectance of a LC cell at oblique incidence of the incoming beam. Special limiting cases are considered in Section 4, while Section 5 contains our conclusions.

2. Infrared permittivity

Consider an anisotropic LC molecule with long axis **a** and short axes **b** and **c**. Let the molecule contain a specific chemical bond absorbing the IR radiation. We describe the most general orientation of the corresponding transition dipole by its unit vector $\boldsymbol{\mu}$ specified by the angles α and β (see Figure 1). Assuming that the symmetry of the molecular distribution is not lower than C_{2h}, we have to account for a symmetric transition dipole $\boldsymbol{\mu}'$, which transforms into $\boldsymbol{\mu}$ upon rotation by the angle π around the C_{2h} symmetry axis. Accordingly,

$$\boldsymbol{\mu} = \mathbf{a}\cos\alpha + \mathbf{b}\sin\alpha\cos\beta + \mathbf{c}\sin\alpha\sin\beta, \qquad (1)$$

$$\boldsymbol{\mu}' = -\mathbf{a}\cos\alpha - \mathbf{b}\sin\alpha\cos\beta + \mathbf{c}\sin\alpha\sin\beta. \qquad (2)$$

For frequencies of IR radiation, ω, close to the absorption band, the whole molecular absorption $\hat{\sigma}(\omega)$ (the imaginary part of the molecular susceptibility) is determined by the orientation of the corresponding transition dipoles $\boldsymbol{\mu}$ *and* $\boldsymbol{\mu}'$, and it can be expressed as

$$\sigma_{ij}(\omega) = \frac{\sigma(\omega)}{2}(\mu_i\mu_j + \mu'_i\mu'_j), \qquad (3)$$

where we have averaged over 'up' and 'down' orientations and introduced the scalar strength of the transition σ.

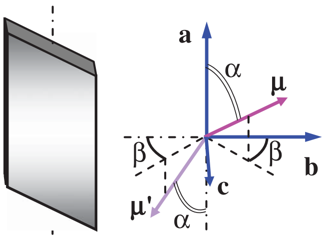

Figure 1. Skew brick possessing the C_{2k} symmetry of LC molecules and a schematic of the molecular axes and transition dipoles.

Formation of the overall LC permittivity from molecular susceptibilities is, in fact, a complex issue. In particular, various mutually interacting molecular fragments contribute collectively to the real part of the permittivity tensor. The formation of the imaginary part on the top of the resonant IR absorption peak is easier to understand since the dominating transition dipoles are well localised and are not likely to interact substantially. Neglecting the mutual influence of the absorbing dipoles in different molecules, we write the LC susceptibility as $\chi_{ij} = \chi'_{ij} + i\rho\sigma_{ij}$, where χ' is the real part of the susceptibility, and ρ is the number density of LC molecules. The LC infrared permittivity can be written in the form

$$\varepsilon_{ij}(\omega) = \varepsilon'_{ij}(\omega) + i\varepsilon''_{ij}(\omega), \qquad (4)$$

where the imaginary part is determined by the averages of the products of the transition dipoles:

$$\varepsilon''_{ij}(\omega) = \frac{\rho\sigma(\omega)}{2}\langle\mu_i\mu_j + \mu'_i\mu'_j\rangle. \qquad (5)$$

Substituting Equations (1) and (*2*) into Equation (5), taking into account the fact that $a_ia_j + b_ib_j + c_ic_j = \delta_{ij}$ and introducing the symmetric traceless tensor order parameters of a biaxial LC as described in [11],

$$Q_{ij} = \langle a_ia_j - \frac{\delta_{ij}}{3}\rangle, \qquad (6)$$

$$\Gamma_{ij} = \langle a_ib_j + b_ia_j\rangle, \qquad (7)$$

$$B_{ij} = \langle b_ib_j - c_ic_j\rangle, \qquad (8)$$

one obtains

$$\varepsilon''_{ij}(\omega) = \rho\sigma(\omega)$$
$$\times\left[\frac{1}{3}\delta_{ij} + P_2(\cos\alpha)\mathrm{Q_{ij}} + \frac{1}{2}\sin^2\alpha\cos^2\beta\mathrm{B_{ij}} + \frac{1}{2}\sin 2\alpha\cos\beta\Gamma_{\mathrm{ij}}\right]. \qquad (9)$$

One notes that in general the main axes of all three tensor order parameters on the right-hand side of Equation (9) do not necessarily coincide. However, if the deviations of the tensor eigenframes are small, one may assume that all three contributions to the overall permittivity tensor are diagonal in the same frame, which we denote as $(\mathbf{n}, \mathbf{m}, \mathbf{h})$. Then the tensor order parameters can be expressed in the common frame:

$$Q_{ij} = S(n_in_j - \frac{1}{3}\delta_{ij}) + \frac{1}{2}P(m_im_j - h_ih_j), \qquad (10)$$

$$B_{ij} = D\,(n_i n_j - \frac{1}{3}\delta_{ij}) + C\,(m_i m_j - h_i h_j), \qquad (11)$$

$$\Gamma_{ij} = G\,(n_i n_j - \frac{1}{3}\delta_{ij}) + H\,(m_i m_j - h_i h_j), \qquad (12)$$

and the definitions of the six scalar order parameters are given in our recent paper [11].

Accordingly, the permittivity of LC can be expressed as

$$\varepsilon_{ij} = \varepsilon_n n_i n_j + \varepsilon_m m_i m_j + \varepsilon_h h_i h_j, \qquad (13)$$

where the principal values of the imaginary part of the permittivity are explicitly expressed in terms of the order parameters:

$$\varepsilon''_n = \frac{\rho\sigma}{3}[1 + 2SP_2(\cos\alpha) + \mathrm{D}\,\sin^2\,\alpha\,\cos^2\,\beta + \mathrm{G}\sin 2\,\alpha\cos\beta], \qquad (14)$$

$$\varepsilon''_m = \frac{\rho\sigma}{6}[2 + (3P - 2S)\,P_2(\cos\alpha)$$

$$+(3C - D)\,\sin^2\,\alpha\,\cos^2\,\beta + (3H - G)\sin 2\,\alpha\cos\beta], \qquad (15)$$

$$\varepsilon''_h = \frac{\rho\sigma}{6}[2 - (3P + 2S)\,P_2(\cos\alpha)$$

$$-(3C + D)\,\sin^2\,\alpha\,\cos^2\,\beta - (3H + G)\sin 2\,\alpha\cos\beta]. \qquad (16)$$

Therefore, the actual experimental task is to determine the values of the permittivities $\varepsilon''_n, \varepsilon''_m, \varepsilon''_h$. To determine all six scalar order parameters one should use at least two different absorption resonances (transition bands with different α and β) and solve the corresponding two sets of Equations (14)–(16). In certain experimental geometries, however, not all three permittivity eigenvalues can be determined simultaneously and the use of more transition bands may be necessary. Another possibility is to neglect the additional order parameters G and H which are expected to be generally smaller than the others. For molecules of D_{2h} symmetry and higher (i.e. for molecules with three mutually orthogonal mirror planes) the order parameters G and H vanish identically.

3. Infrared absorption

In this section we develop the theory of the IR absorption for the most important geometries of the LC cell. Depending on the substrates, a LC material can have either planar or homeotropic alignment, i.e. the primary director **n** can either be perpendicular or parallel to the substrate. Next, in both orientations two possible orthogonal directions of the polarisation of the incident IR radiation can be employed.

In some cases the primary director **n** may tilt with respect to the substrate. It is shown below that this affects the IR absorption substantially if the incident wave is polarised in the symmetry plane of the phase (transverse magnetic, TM, polarisation).

3.1 Tilted homeotropic cell

In the tilted homeotropic cell, the primary director **n** is tilted with respect to the substrate normal. The geometry of the tilted homeotropic cell is presented in Figure 2. In such a cell the director **n** is tilted while the secondary director **h** is parallel to the substrate. This geometry corresponds to a smectic LC in the C-phase with smectic layers parallel to the substrate or to a biaxial nematic LC with the tilted primary director **n**.

In such a case the apparent permittivity tensor in the cell frame is non-diagonal and has four non-zero components

$$\varepsilon_{xx} = \varepsilon_m\,\cos^2\,\theta + \varepsilon_n\,\sin^2\,\theta, \qquad (17)$$

$$\varepsilon_{yy} = \varepsilon_h, \qquad (18)$$

$$\varepsilon_{zz} = \varepsilon_n\,\cos^2\,\theta + \varepsilon_m\,\sin^2\,\theta, \qquad (19)$$

$$\varepsilon_{xz} = \varepsilon_{zx} = (\varepsilon_m - \varepsilon_n)\sin\theta\cos\theta. \qquad (20)$$

The eigenvalues of the permittivity tensor related with the LC ordering via Equations (14)–(16) and the tilt angle of the primary LC axis can be expressed as

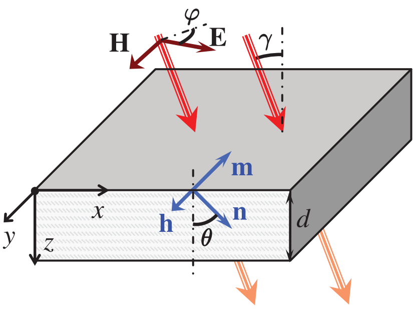

Figure 2. Schematic of the setup of IR absorbance in a homeotropically aligned cell.

$$\tan 2\theta = \frac{2\varepsilon_{\mathrm{xz}}}{\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{zz}}}, \tag{21}$$

$$\varepsilon_n = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{zz}) - \frac{\varepsilon_{xz}}{\sin 2\theta}, \tag{22}$$

$$\varepsilon_m = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{zz}) + \frac{\varepsilon_{xz}}{\sin 2\theta}, \tag{23}$$

$$\varepsilon_h = \varepsilon_{yy}. \tag{24}$$

Consider the transmission properties of an anisotropic slab with non-zero permittivity tensor components ε_{xx}, ε_{yy}, ε_{zz} and $\varepsilon_{xz} = \varepsilon_{zx}$. The slab is sandwiched between transparent thick isotropic plates with real permittivity ε_s. Choosing the plane of incidence as that of the tilting plane, we decouple the transverse electric (TE) and TM polarisations. This means that those waves are reflected, absorbed and transmitted independently and the transmittance of an arbitrarily polarised wave can be written as

$$T = T_{TM} \cos^2\varphi + T_{TE} \sin^2\varphi, \tag{25}$$

where ϕ characterises the incident polarisation (see Figure 2).

Consider first the TM-polarised incident wave. Spatially-dependent electric fields of the light waves can be expressed as complex plane waves. Above the cell, at $z < 0$, there is an incident wave (of unit amplitude for simplicity) and a reflected wave with amplitude r:

$$E_x = \cos\gamma\ \mathrm{e}^{-\mathrm{i}\omega\mathrm{t}+\mathrm{ik_0}\sin\gamma\ \mathrm{x}}[\mathrm{e}^{\mathrm{ik_0}\cos\gamma\ \mathrm{z}} - \mathrm{re}^{-\mathrm{ik_0}\cos\gamma\ \mathrm{z}}], \tag{26}$$

$$E_z = \sin\gamma\ \mathrm{e}^{-\mathrm{i}\omega\mathrm{t}+\mathrm{ik_0}\sin\gamma\ \mathrm{x}}[-\mathrm{e}^{\mathrm{ik_0}\cos\gamma\ \mathrm{z}} - \mathrm{re}^{-\mathrm{ik_0}\cos\gamma\ \mathrm{z}}], \tag{27}$$

where $k_0 = \sqrt{\varepsilon_s}\omega/c$.

Below the slab, at $z > d$, only the transmitted wave with the amplitude τ exists and

$$E_x = \tau\cos\gamma\ \mathrm{e}^{-\mathrm{i}\omega\mathrm{t}+\mathrm{ik_0}\sin\gamma\ \mathrm{x}+\mathrm{ik_0}\cos\gamma\ (\mathrm{z-d})}, \tag{28}$$

$$E_z = -\tau\sin\gamma\ \mathrm{e}^{-\mathrm{i}\omega\mathrm{t}+\mathrm{ik_0}\sin\gamma\ \mathrm{x}+\mathrm{ik_0}\cos\gamma\ (\mathrm{z-d})}. \tag{29}$$

Inside the slab, the fields can generally be expressed as sums of the contributions from the waves travelling in opposite directions:

$$E_x = e^{-i\omega t+ik_0\sin\gamma\ \mathrm{x}}[E_x^+ e^{i\kappa^+ z} + E_x^- e^{-i\kappa^- z}], \tag{30}$$

$$E_z = e^{-i\omega t+ik_0\sin\gamma\ \mathrm{x}}[E_z^+ e^{i\kappa^+ z} + E_z^- e^{-i\kappa^- z}]. \tag{31}$$

Substituting the components of the electric displacement $D_x = \varepsilon_{xx}E_x + \varepsilon_{xz}E_z$ and $D_z = \varepsilon_{xz}E_x + \varepsilon_{zz}E_z$ into Gauss's law $\nabla.\mathbf{D} = 0$ one obtains

$$E_z^{\pm}(k_0\sin\gamma\,\varepsilon_{\mathrm{xz}} \pm \kappa^{\pm}\varepsilon_{\mathrm{zz}}) = -\mathrm{E}_{\mathrm{x}}^{\pm}(\mathrm{k_0}\sin\gamma\,\varepsilon_{\mathrm{xx}} \pm \kappa^{\pm}\varepsilon_{\mathrm{xz}}). \tag{32}$$

Next, using Maxwell's equations $\nabla \times \mathbf{E} = -1/\mathrm{c}\ \partial\mathbf{B}/\partial\mathrm{t}$ and $\nabla \times B = 1/c\ \partial\mathbf{D}/\partial\mathrm{t}$ one obtains for the only component of the magnetic induction $\omega/c\ B_y^{\pm} = \pm\kappa^{\pm}E_x^{\pm} - k_0\sin\gamma\,\mathrm{E}_{\mathrm{z}}^{\pm}$ and, on the other hand, $k_0\sin\gamma\ \mathrm{B}_{\mathrm{y}}^{\pm} = -\omega/\mathrm{c}(\varepsilon_{\mathrm{xz}}\mathrm{E_x} + \varepsilon_{\mathrm{zz}}\mathrm{E_z})$. Excluding the magnetic induction and using Equation (32) it is possible to write the dispersion equation for the propagating constants $K^{\pm}$ in the form

$$\begin{aligned}(\kappa^{\pm})^2\varepsilon_{zz} \pm 2\kappa^{\pm}k_0\varepsilon_{xz}\sin\gamma + \mathrm{k}_0^2\varepsilon_{\mathrm{xx}}\ \sin^2\gamma \\ = (\varepsilon_{xx}\varepsilon_{zz} - \varepsilon_{xz}^2)\omega^2/c^2\end{aligned}\ . \tag{33}$$

This equation apparently has different solutions for the waves travelling upwards and downwards in the tilted anisotropic slab, and one can readily obtain that

$$\kappa^{\pm} = \kappa \pm \Delta, \tag{34}$$

where

$$\kappa = \sqrt{(\varepsilon_{xx}\varepsilon_{zz} - \varepsilon_{xz}^2)(\varepsilon_{zz}\omega^2/c^2 - k_0^2\sin^2\gamma)}/\varepsilon_{zz}, \tag{35}$$

and where the square root with a positive imaginary part is to be used in the complex case, while

$$\Delta = -k_0\sin\gamma\frac{\varepsilon_{\mathrm{xz}}}{\varepsilon_{\mathrm{zz}}}. \tag{36}$$

The continuous boundary conditions for E_x and D_z at $z = 0$ are

$$(1 - r)\cos\gamma = \mathrm{E}_{\mathrm{x}}^+ + \mathrm{E}_{\mathrm{x}}^-, \tag{37}$$

$$-\varepsilon_s(1 + r)\sin\gamma = \varepsilon_{\mathrm{xz}}(\mathrm{E}_{\mathrm{x}}^+ + \mathrm{E}_{\mathrm{x}}^-) + \varepsilon_{\mathrm{zz}}(\mathrm{E}_{\mathrm{z}}^+ + \mathrm{E}_{\mathrm{z}}^-), \tag{38}$$

while those at $z = d$ yield

$$\tau\cos\gamma = \mathrm{E}_{\mathrm{x}}^+\mathrm{e}^{\mathrm{i}\kappa^+\mathrm{d}} + \mathrm{E}_{\mathrm{x}}^-\mathrm{e}^{-\mathrm{i}\kappa^-\mathrm{d}}, \tag{39}$$

$$
\begin{aligned}
-\varepsilon_s \tau \sin\gamma =& \varepsilon_{xz}(E_x^+ e^{i\kappa^+ d} + E_x^- e^{-i\kappa^- d}) \\
&+ \varepsilon_{zz}(E_z^+ e^{i\kappa^+ d} + E_z^- e^{-i\kappa^- d}).
\end{aligned} \tag{40}
$$

Together with Equation (32), Equations (37)–(40) form a system of simultaneous linear equations for the remaining six unknown field amplitudes. The straightforward solution yields for the transmitted amplitude

$$
\begin{aligned}
\tau =& -4e^{id\Delta} k_0 \kappa \cos\gamma \; \left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{xz}}^2\right) \varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{s}} \\
&\times\{\left[k_0 \cos\gamma \; \left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{xz}}^2\right) - \kappa\,\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{zz}}\right]^2 e^{id\kappa} \\
&- \left[k_0 \cos\gamma \; \left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{xz}}^2\right) + \kappa\,\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{zz}}\right]^2 e^{-id\kappa}\}^{-1},
\end{aligned} \tag{41}
$$

while the reflected wave amplitude is expressed as

$$
\begin{aligned}
r =& 2i\left(k_0^2 \cos^2\gamma \; \left(\varepsilon_{zz}\varepsilon_{xx} - \varepsilon_{xz}^2\right)^2 - \kappa^2 \varepsilon_s^2 \varepsilon_{zz}^2\right) \sin(\mathrm{d}\kappa) \\
&\times\{\left[k_0 \cos\gamma \; \left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{xz}}^2\right) - \kappa\,\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{zz}}\right]^2 e^{id\kappa} \\
&- \left[k_0 \cos\gamma \; \left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}} - \varepsilon_{\mathrm{xz}}^2\right) + \kappa\,\varepsilon_{\mathrm{s}}\varepsilon_{\mathrm{zz}}\right]^2 e^{-id\kappa}\}^{-1}.
\end{aligned} \tag{42}
$$

The transmittance $T_{TM}(\gamma)$ and reflectance $R_{TM}(\gamma)$ of the sample are expressed as

$$
T_{TM}(\gamma) = |t|^2, \quad \textit{and} \quad R_{TM}(\gamma) = |r|^2, \tag{43}
$$

and those relations provide the formal exact solution to the general problem of TM transmittance.

We see that the TM-polarised wave tests all three components ε_{xx}, ε_{zz} and ε_{xz} simultaneously. The complexity of this exact solution does not allow a straightforward extraction of the permittivity components. However, in certain difficult situations, when, for example, the orientation of the LC main axes is unknown, one may fit the data for different angles of incidence by Equations (41) and (42) and determine the permittivity main values and main axes.

At the same time, if the orientation of the LC is reasonably restricted, one may consider several limiting cases of practical interest, which provide a more transparent connection between the IR transmittance and the LC permittivity. This will be demonstrated in the next section.

For the TE-polarised IR radiation, the electric field is orthogonal to the director **n** and always tests the permittivity component $\varepsilon_{yy} = \varepsilon_h$. Already the simple case of normal incidence is sufficient for determining this permittivity component. The corresponding expression can be obtained from the TM transmittance by putting $\gamma = 0$, $\varepsilon_{xz} = 0$ and replacing ε_{xx} by $\varepsilon_{yy} = \varepsilon_h$. This yields

$$
T_{TE}(0) = \frac{16\varepsilon_s|\varepsilon_h|}{|(\sqrt{\varepsilon_h} - \sqrt{\varepsilon_s})^2 e^{id\sqrt{\varepsilon_h}\omega/c} + (\sqrt{\varepsilon_h} + \sqrt{\varepsilon_s})^2 e^{-id\sqrt{\varepsilon_h}\omega/c}|^2}. \tag{44}
$$

3.2 Planar cell with normal incidence

Consider now the absorbance of normally incident IR radiation in a LC with planar alignment. In this case the directors n and m of the biaxial LC material are parallel to the substrate and one can choose the coordinate system along the main axes of the molecular order:

$$
\varepsilon_{xx} = \varepsilon_n, \quad \varepsilon_{yy} = \varepsilon_m, \quad \varepsilon_{zz} = \varepsilon_h, \tag{45}
$$

while the polarisation of the incident beam can be specified by the angle ϕ (see Figure 3).

The incident radiation can be presented as a superposition of two beams, polarised along the main axes of the LC with input electric field amplitudes $E\cos\varphi$ and $E\sin\varphi$. These two parts are reflected, transmitted and absorbed independently, which again results in the well-known dependence of the transmittance on the polarisation angle:

$$
T(\varphi) = T_n \cos^2\varphi + T_m \sin^2\varphi. \tag{46}
$$

The expressions for the two fundamental transmittances here can be obtained from the results of the previous subsection. Indeed, one can set both γ and θ to zero, notice that the result is independent of ε_{zz}, and set ε_{xx} to be equal either to ε_n or ε_m to obtain T_n or T_m, respectively. This yields the following expression:

$$
T_n = \frac{16\varepsilon_s|\varepsilon_n|}{|(\sqrt{\varepsilon_n} - \sqrt{\varepsilon_s})^2 e^{id\sqrt{\varepsilon_n}\omega/c} + (\sqrt{\varepsilon_n} + \sqrt{\varepsilon_s})^2 e^{-id\sqrt{\varepsilon_n}\omega/c}|^2}; \tag{47}
$$

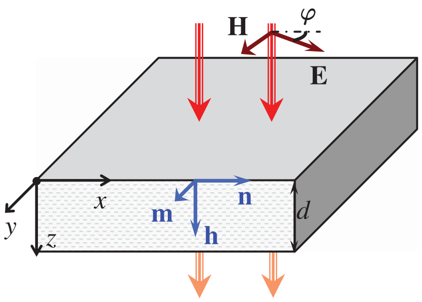

Figure 3. Schematic of the setup of IR absorbance in a planar aligned cell.

the expression for T_m can be obtained by replacement of ε_n by ε_m.

4. Simple limiting cases

4.1 Thin cell

If the cell thickness is comparable with the wavelength of IR radiation in the LC, $\kappa d \geq 1$, the transmission is affected by multiple reflections (oscillating exponents in the denominators of T and R). Transmission of thinner cells (or at larger IR wavelengths) is free of such complications. In the limit of thin cells we assume that $\kappa d \ll 1$ and expand (41) in κd to obtain

$$\tau \approx 1 + i\, d\, \frac{\omega}{c} \frac{\varepsilon_{zz}\left(\varepsilon_{xx}\cos^2\gamma + \varepsilon_s\right) - \left(\varepsilon_{xz}\cos\gamma + \varepsilon_{\mathrm{s}}\sin\gamma\right)^2}{2\sqrt{\varepsilon_s}\varepsilon_{zz}\cos\gamma}, \tag{48}$$

and

$$T_{TM}(\gamma) \approx 1 - d\frac{\omega}{c}\frac{1}{\sqrt{\varepsilon_s}}\, M(\gamma), \tag{49}$$

where

$$M(\gamma) = \cos\gamma\, \left[\varepsilon''_{\mathrm{xx}} - \mathrm{Im}\left(\frac{\varepsilon^2_{\mathrm{xz}}}{\varepsilon_{\mathrm{zz}}}\right)\right] - \sin\gamma\, 2\varepsilon_{\mathrm{s}}\, \mathrm{Im}\left(\frac{\varepsilon_{\mathrm{xz}}}{\varepsilon_{\mathrm{zz}}}\right) + \frac{\sin^2\gamma}{\cos\gamma}\varepsilon''_{zz}\frac{\varepsilon_s^2}{|\varepsilon^2_{zz}|}. \tag{50}$$

It is important to note that in the case of thin cells the transmittance should be close to 100% as $\tau \approx 1$ in the zeroth approximation according to (48).

4.1.1 Normal incidence

Consider now the case of normal incidence for both homeotropic and planar cells. Putting $\gamma = 0$ one obtains the following simplified expression for the TM transmittance of a thin homeotropic cell:

$$T_{TM} \approx 1 - d\, \frac{\omega}{c}\frac{\varepsilon''_{xx}}{\sqrt{\varepsilon_s}} + d\frac{\omega}{c}\, \frac{1}{\sqrt{\varepsilon_s}}\, \mathrm{Im}\left[\frac{\varepsilon^2_{xz}}{\varepsilon_{zz}}\right]. \tag{51}$$

The second term corresponds to the simple result which has been used in the literature (see, e.g., (*1*)). The absorbed energy is proportional to the imaginary part of the permittivity along the polarisation of the incident wave. However, if the phase is tilted with respect to the substrates, and the LC is substantially anisotropic, the last term provides a substantial correction. The physical origin of this counterintuitive correction is the change of IR polarisation when the radiation enters the LC. It propagates in the form of an extraordinary wave, which is not transversal, and the electric field tests the permittivity not along the x-axis but along a certain direction in the xz-plane which depends on the parameters of the system.

Accordingly, the result reduces to the form used in [1] only if one assumes that one of the axes (i.e. one of the directors) of the biaxial LC phase is perpendicular to the substrate. This case corresponds to the non-tilted alignment of the biaxial LC in a homeotropic or planar cell. Then $\varepsilon_{zx} = 0$, the last term vanishes and the transmittance of a thin cell is given by the following simple equation:

$$T_{TM} \approx 1 - d\, \frac{\omega}{c}\frac{\varepsilon''_{xx}}{\sqrt{\varepsilon_s}}. \tag{52}$$

For the TE polarisation in homeotropic geometry as well as for both polarisations in the planar cell, the transmittance of a thin cell is given by the similar simple equation

$$T_{TE,n,m} \approx 1 - d\, \frac{\omega}{c}\frac{\varepsilon''_{h,n,m}}{\sqrt{\varepsilon_s}}. \tag{53}$$

According to this equation and depending on the geometry, the transmittance of a thin cell is directly related to the corresponding component of the imaginary part of the dielectric susceptibility of the LC material at a given frequency, which can be expressed in terms of the orientational order parameters of the LC. Thus this enables one, in principle, to determine the order parameters of the biaxial LC using different polarisations of the incoming light wave and different orientations of the primary director (normal or parallel to the substrate). These equations have been used in [1, 2, 4] to determine the order parameters of biaxial nematic and smectic C LCs. It should be noted, however, that this simple result is justified only in the case of thin films when the transmission is of the order of one. This result is also valid only if the director of the LC phase is not tilted with respect to the substrate, or if the light is polarised in the direction perpendicular to the tilt plane.

4.2 Thick cells

In most of the experiments, however, the transmittance is very low which indicates that the real systems are closer to the opposite limiting case of thick cells. On the top of a resonance the LC absorbs the most part of the IR radiation and only a few percent of the energy is transmitted. One can neglect multiple reflections in the cell by neglecting the first exponentially small term in the denominator of Equation (41). Then one obtains

$$\tau = 4\,\frac{e^{i(\kappa+\Delta)d}\varepsilon_{zz}\varepsilon_s k_0\kappa\left(\varepsilon_{zz}\varepsilon_{xx}-\varepsilon_{xz}^2\right)\cos\gamma}{\left(k_0\cos\gamma\left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}}-\varepsilon_{\mathrm{xz}}^2\right)+\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{s}}\kappa\right)^2} \tag{54}$$

and the transmittance is expressed as

$$T_{TM} = 16\,\frac{\varepsilon_s^2 k_0^2\cos^2\gamma\,|\varepsilon_{zz}|^2|\varepsilon_{zz}\varepsilon_{xx}-\varepsilon_{xz}^2|^2|\kappa|^2}{|k_0\cos\gamma\left(\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{xx}}-\varepsilon_{\mathrm{xz}}^2\right)+\varepsilon_{\mathrm{zz}}\varepsilon_{\mathrm{s}}\kappa|^4}\;e^{-2d\,\mathrm{Im}(\kappa+\Delta)}. \tag{55}$$

4.2.1 *Normal incidence*

Similar to the transmittance of thin cells, the general equation can be simplified in the case of normal incidence. Remarkably, for normal incidence the transmittance can be explicitly written as a function of the propagation constant

$$T = \frac{16\,k_0^2|\kappa|^2\,e^{-2\,\mathrm{Im}(\kappa)d}}{|k_0+\kappa|^4}, \tag{56}$$

where the propagation constant κ is given by one of the following equations which correspond to the four cases of interest:

$$\kappa_{TM} = \omega/c\sqrt{\varepsilon_{xx}-\varepsilon_{xz}^2/\varepsilon_{zz}}, \tag{57}$$

for the TM beam and the homeotropic cell,

$$\kappa_{TE} = \omega/c\,\sqrt{\varepsilon_h}, \tag{58}$$

for the TE beam and the homeotropic cell, and

$$\kappa_{n,m} = \omega/c\,\sqrt{\varepsilon_{n,m}}, \tag{59}$$

for the planar cell and different polarisations of the incoming beam.

It appears to be useful to consider the natural logarithm of the transmittances of thick cells. Indeed, for (56) the logarithm of the transmittance can be written in the form

$$\ln(\mathrm{T}) = \mathrm{C} - 2\mathrm{d}\frac{\omega}{\mathrm{c}}\mathrm{Im}(\sqrt{\varepsilon}), \tag{60}$$

where C stems from the logarithm of the pre-exponential factor and ε equals $\sqrt{\varepsilon_{xx}-\varepsilon_{xz}^2/\varepsilon_{zz}}$, ε_h, ε_n or ε_m depending on the geometry. If the cell thickness d is large enough, the last term in (60) is predominant and determines the overall variation of the transmittance.

Equation (60) is still too complicated to be used directly in the measurements of the order parameters. However, a useful approximation can be made if one assumes that on the top of the resonance the permittivity is dominated by the imaginary part, i.e. for each component

$$\varepsilon \simeq i\varepsilon''. \tag{61}$$

The square roots in Equation (60) can then be approximated as $\sqrt{\varepsilon} \simeq (1+i)\sqrt{\varepsilon''/2}$ and the main term in the logarithm of the transmittances takes the simple form

$$\ln(\mathrm{T}) = \mathrm{C} - \mathrm{d}\frac{\omega}{\mathrm{c}}\sqrt{2\varepsilon''}, \tag{62}$$

allowing for the explicit determination of the components of the imaginary parts of the permittivity.

5. Conclusions

In this paper we have derived general expressions for the transmittance and reflectance of the obliquely incident polarised IR light by a biaxial LC cell. We have considered both the homeotropic cell with the primary director normal or tilted with respect to the substrates, and the planar cell with the LC directors parallel to the substrates. Those general expressions can be used for determining the LC order parameters in the most difficult case: for the unknown orientation of the LC main axes and arbitrary cell thickness.

It has been shown that the general expressions significantly simplify in the limiting cases of thin and thick cells for the normally incident IR radiation and LC oriented orthogonally to the substrates.

The simple approximate expressions, which have been used in the literature to measure the biaxial order parameters, have only been obtained in the case of thin cells and normal incidence, when the light wave is polarised along one of the optical axes of a biaxial LC phase. In this case the transmittance is directly related to the corresponding component of the imaginary part of the IR dielectric permittivity, which is explicitly expressed in terms of the order parameters of the LC phase. In contrast, if the light is not polarised along any of the directors of a biaxial LC phase (for example, when the polarisation is parallel to the tilt plane in the smectic C phase), even the simplified expressions for the transmittance appear to be too complicated and cannot be used to determine the order parameters. Thus the tilted geometries should be avoided.

This is related to the fact that in a tilted geometry the electric field of the light wave in the biaxial medium (when the polarisation of the incoming beam is not parallel to an optical axis) is no longer transverse, and thus it is not parallel to the polarisation direction of the incoming beam. As a result, the electric field tests several components of the polarisability tensor simultaneously, and the expressions for the transmittance contain a number of unknown parameters.

Thus one concludes that simple expressions for the IR transmittance, which have been used in the literature, correspond to the case of thin films and are valid only when the transmittance is of the order of one and one of the LC main axes is exactly orthogonal to the substrates.

In a typical experiment, the transmittance is of the order of a few percent, and thus the system is closer to the limiting case of thick cells with exponentially low transmittance. Simple approximate expressions have also been obtained in the case of thick cells for the normal incidence. If the resonant peak in the IR spectrum of the LC material is sufficiently high, the components of the imaginary part of the IR permittivity are approximately proportional to the square of the logarithm of the transmittance. This is very different from the case of thin cells, where the same components are proportional to the transmittance itself.

The approximate relations (60) and (62) obtained in the case of thick cells can be used to determine the orientational order parameters of biaxial nematic and smectic C LCs provided that several different geometries and/or different resonance peaks are employed to obtain the sufficient number of independent equations for the order parameters. If the orientation of the mirror plane of the biaxial LC material can be determined experimentally (for example, by ellipsometry), it is possible to use the geometry in which the incoming beam propagates perpendicularly to the mirror plane. In this case the light beam propagates along an optical axis of the material while the other two optical axes are parallel to the plane. Even if their particular orientation is unknown, the principal values of the transmittance (which correspond to the polarisation of the light wave along one of the two optical axes in the mirror plane) can be determined experimentally by rotating the polariser and fitting the transmittance by Equations (25) and (46). Using two different resonance peaks one may obtain four independent equations which can be used to determine the values of the traditional set of four orientational order parameters of the biaxial LC phase.

As discussed in Section 2, in the general case biaxial LCs composed of molecules of low symmetry are characterised by six independent orientational order parameters. The full set of six order parameters can also be determined experimentally if the additional experimental geometry is used in which light propagates along the mirror plane and is polarised in the direction perpendicular to the plane.

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