I. INTRODUCTION

In our previous paper [1], we developed the theory of the propagation of an electromagnetic homogeneous plane wave in a semi-infinite, optically anisotropic, and absorbing medium. A homogeneous wave is defined as one in which the planes of constant amplitude and of phase are parallel to each other. From first principles, we derived an equation for the infrared (IR) absorbance at a given frequency as a function of the angle of polarization of the absorbance $A(\omega, \theta) = - \log_{10} \left[ 10^{\Delta A(\omega)} \cos^2 \theta + 10^{-(\Delta A(\omega) - 2)} \sin^2 \theta \right]$, which was later proposed empirically by Jang et al. [4]. The absorbance $A(\omega, \theta)$ is independent of the birefringence of the material subjected to the IR beam and, in general, to the biaxiality of the material. An earlier attempt was made in deriving this formula based on the rotation of the plane of polarization of light by the anisotropies in the infrared absorbances by Kocot et al. [5].

II. MICROSCOPIC CONSIDERATIONS

In the analysis that we carried out, we assumed that the medium consisted of long rodlike molecules having an axial polarizability only. However, if the polarizability or—more specifically—the moment of a vibrational bond of the molecule lies at an angle to the major axis of the molecule, then this case may not be covered in such an analysis. We therefore extend the analysis in this paper to include the treatment of molecules as prolate spheroids having both axial $a_0$ and transverse $a_1$ polarizabilities measured with reference to the principal axes. This means that if in an actual system the polarizability were out of the plane to which the incident light is directed normally, then due to the symmetry of the distribution, the absorbance measurement would not depend on birefringence of the sample but may depend on the precise method of absorbance measurement and on effects at the surface of the cell containing the liquid crystal under test.
\[ p_{3,1} = \chi_{3,1} \epsilon_1 e_1 \]
\[ = N \frac{V}{e_1} \left( \alpha_0 (\sin \beta \cos \gamma) - \alpha_\perp (\sin \beta \cos \gamma) \right), \]
\[ \quad (6) \]

\[ p_{1,2} = \chi_{1,2} \epsilon_2 e_2 \]
\[ = N \frac{V}{e_2} \left( \alpha_0 (\sin^2 \beta \sin \gamma \cos \gamma) + \alpha_\perp (\sin^2 \beta \sin \gamma \cos \gamma) \right) \]
\[ + \alpha_\perp (\cos^2 \beta \sin \gamma \cos \gamma - \sin \gamma \cos \gamma) \]
\[ = N \frac{V}{e_2} \left( \alpha_0 (\sin^2 \beta \sin \gamma \cos \gamma) \right) \]
\[ + \alpha_\perp (\sin^2 \beta \sin \gamma \cos \gamma), \]
\[ \quad (7) \]

\[ p_{2,2} = \chi_{2,2} \epsilon_2 e_2 \]
\[ = N \frac{V}{e_2} \left( \alpha_0 (\sin^2 \beta \sin^2 \gamma) + \alpha_\perp (\cos^2 \beta \sin^2 \gamma + \sin^2 \gamma) \right) \]
\[ = N \frac{V}{e_2} \left( \alpha_0 (\sin^2 \beta \sin^2 \gamma) \right) \]
\[ + \alpha_\perp (1 - \sin^2 \beta \sin^2 \gamma), \]
\[ \quad (8) \]

\[ p_{1,3} = \chi_{1,3} \epsilon_3 e_3 \]
\[ = N \frac{V}{e_3} \left( \alpha_0 (\sin \beta \cos \beta \cos \gamma) - \alpha_\perp (\sin \beta \cos \beta \cos \gamma) \right), \]
\[ \quad (9) \]

\[ p_{2,3} = \chi_{2,3} \epsilon_3 e_3 \]
\[ = N \frac{V}{e_3} \left( \alpha_0 (\sin \beta \cos \beta \sin \gamma) - \alpha_\perp (\sin \beta \cos \beta \sin \gamma) \right), \]
\[ \quad (10) \]

\[ p_{3,3} = \chi_{3,3} \epsilon_3 e_3 \]
\[ = N \frac{V}{e_3} \left( \alpha_0 (\cos^2 \beta) + \alpha_\perp (\sin^2 \beta) \right). \]
\[ \quad (11) \]

With Eqs. (A1)–(A6) of [1], we find that
\[ p_{1,1} = \chi_{1,1} \epsilon_1 e_1 \]
\[ = N \frac{V}{e_1} \left\{ \alpha_0 \left[ \frac{1}{2} - B + \frac{3D}{2} \right] + \alpha_\perp \left[ \frac{1}{2} + B - \frac{3D}{2} \right] \right\}, \]
\[ \quad (13) \]

\[ p_{2,1} = \chi_{2,1} \epsilon_1 e_1 \]
\[ = N \frac{V}{e_1} \left( \alpha_0 \left( \frac{F}{2} - \alpha_\perp \frac{F}{2} \right) \right), \]
\[ \quad (14) \]

\[ p_{3,1} = \chi_{3,1} \epsilon_1 e_1 \]
\[ = N \frac{V}{e_1} \left( \alpha_0 \left( \frac{C}{2} - \alpha_\perp \frac{C}{2} \right) \right), \]
\[ \quad (15) \]
\[ P_{1,2} = \chi_{1,2} \epsilon_0 e_2 = \frac{N}{V} \epsilon_2 \left\{ \frac{F}{2} - \alpha_\perp \frac{F}{2} \right\}, \] \[(16)\]

\[ P_{2,2} = \chi_{2,2} \epsilon_0 e_2 \]
\[ = \frac{N}{V} \epsilon_2 \left\{ \frac{2 - 3D}{2} + \alpha_\perp \left[ 2 + B + \frac{3D}{2} \right] \right\}, \] \[(17)\]

\[ P_{3,2} = \chi_{3,2} \epsilon_0 e_2 \]
\[ = \frac{N}{V} \epsilon_2 \left\{ \frac{E}{2} - \alpha_\perp \frac{E}{2} \right\}, \] \[(18)\]

\[ P_{1,3} = \chi_{1,3} \epsilon_0 e_3 = \frac{N}{V} \epsilon_3 \left\{ \frac{C}{2} - \alpha_\perp \frac{C}{2} \right\}, \] \[(19)\]

\[ P_{2,3} = \chi_{2,3} \epsilon_0 e_3 \]
\[ = \frac{N}{V} \epsilon_3 \left\{ \frac{E}{2} - \alpha_\perp \frac{E}{2} \right\}, \] \[(20)\]

\[ P_{3,3} = \chi_{3,3} \epsilon_0 e_3 \]
\[ = \frac{N}{V} \epsilon_3 \left\{ \frac{C}{3} \left[ 1 + 2B \right] + \frac{2\alpha_\perp}{3} \left[ 1 - B \right] \right\}. \] \[(21)\]

Therefore, the components of susceptibility \( \chi_1, \chi_2, \) and \( \chi_3, \) along the axes 1, 2, and 3 are

\[ \chi_{1,1} = \frac{N}{\epsilon_0 V} \left\{ \frac{(\alpha_0 + 2\alpha_\perp)}{3} + \frac{(\alpha_0 - \alpha_\perp)}{3} \left( -B + \frac{3D}{2} \right) \right\}, \] \[(22)\]

Equations (22)–(30) can be expressed in terms of the following matrix equation:

\[
\begin{pmatrix}
\chi_{1,1} & \chi_{1,2} & \chi_{1,3} \\
\chi_{2,1} & \chi_{2,2} & \chi_{2,3} \\
\chi_{3,1} & \chi_{3,2} & \chi_{3,3}
\end{pmatrix}
\begin{pmatrix}
\tilde{\alpha} + \Delta \left( -\frac{B}{3} + \frac{D}{2} \right)
\Delta F
\Delta C
\Delta E
\tilde{\alpha} + \Delta \left( -\frac{B}{3} + \frac{D}{2} \right)
\Delta E
\tilde{\alpha} + \Delta \left( 2B \right)
\end{pmatrix}
\]

\[(31)\]

where \( \tilde{\alpha} = \frac{\alpha_0 + 2\alpha_\perp}{3} \) and \( \Delta = (\alpha_0 - \alpha_\perp). \)

Clearly we find that \( \chi_{i,j} = \chi_{j,i} \). This is of the same form as matrix (5.1) of our previous paper [1], except that the permittivity in different directions is related explicitly with the anisotropy in the polarizability \( \Delta \) and the averaged polarizability \( \tilde{\alpha} \). The matrix (31) can be used to relate the various order parameters of the distribution function to the averaged polarizability, the birefringence, and the components of the electrical susceptibilities along different axes. By using Eqs. (22) and (26), the order parameters \( B \) and \( D \) can be found from the susceptibilities by the following equations:

\[ B = \frac{3}{\Delta} \left[ \tilde{\alpha} - \frac{\epsilon_0 V}{2N} (\chi_{1,1} + \chi_{2,3}) \right], \] \[(32)\]

\[ D = \frac{\epsilon_0 V}{N\Delta} (\chi_{1,1} - \chi_{2,2}). \] \[(33)\]

The order parameters \( C, E, \) and \( F \) can similarly be found by using Eqs. (27)–(29).

\section*{III. Poynting Vector and Transmission Through the IR Cell}

Case of elliptically polarized light

In our previous analysis, we considered the incident IR beam to be plane polarized, which makes an angle \( \theta \) with the \( z \) axis. Now we extend this analysis to include elliptically polarized light.
polarized light as shown in Fig. 2 with two orthogonal components \( aE_0 \cos \omega t \) and \( bE_0 \sin \omega t \) lying in the x-z plane. The component \( aE_0 \cos \omega t \) makes an angle \( \theta \) with respect to the axis \( z \) or 3.

The elliptical polarized light incident along the axis \( y \) or 2. The component \( aE_0 \cos \omega t \) makes an angle \( \theta \) with respect to the axis \( z \) or 3.

In place of Eq. 3.7 of our previous analysis [1], we would have the total electric field vector within the sample

\[ E(t) = Re \left[ a \cos \theta + ib \sin \theta \right] e^{iut}, \]

\[ e_y = E_0 \cos \omega t \sin \theta + bE_0 \sin \omega t \cos \theta, \]

and

\[ e_z = E_0 \cos \omega t \cos \theta - bE_0 \sin \omega t \sin \theta, \]

In place of Eq. (3.4a) of our previous analysis [1], we would have the total electric field vector within the sample

\[ \mathbf{E}(t) = Re \left[ iE_0 \left( a \cos \theta - ib \sin \theta \right) F_{1,E} C_{1,H}(\omega) e^{i(\omega t - y)}, \right] \]

\[ + iE_0 \left( a \cos \theta + ib \sin \theta \right) F_{1,E} C_{1,H}(\omega) e^{i(\omega t + y)}, \]

and in place of Eq. (3.4b) [1] we have the magnetizing force vector in the sample

\[ \mathbf{H}(t) = \frac{1}{\omega \mu_0} \left[ Re \left[ E_0 \left( a \cos \theta + ib \sin \theta \right) k_{1,H}(\omega) \right] \times F_{1,E}(\omega) C_{1,H}(\omega) e^{-i\omega t} \right] \]

\[ \left( - \mathbf{F}_{1,E}(\omega) C_{1,H}(\omega) e^{i\omega t} \right) \]

If we continue the procedure of calculations as in [1], we will find the Poynting vector in the cell normal to the plane of the cell windows to be

\[ \mathbf{S}(y) = \frac{2}{\omega \mu_0} \left( \left| E_0(\omega) \right|^2 e^{-i\omega t} e^{y/2} (a^2 \cos^2 \theta + b^2 \sin^2 \theta) \right] \]

\[ \left. \times \left| F_{1,E}(\omega) \right|^2 k_{1,H}(\omega) C_{1,H}(\omega) \right| \]

\[ + e^{-i\omega t} (a^2 \cos^2 \theta + b^2 \sin^2 \theta) \left| F_{1,E}(\omega) \right|^2 k_{1,H}(\omega) C_{1,H}(\omega) \right|, \]

in place of Eq. 3.7 of [1].

We apply this analysis to an IR cell. The intensity of the IR beam is somewhat attenuated by the windows of the cell, we work out the mean power density emerging from the cell

\[ P_{out}(\omega, \theta) = \frac{1}{P_{in}(\omega, \theta)} \left[ \left| E_0(\omega) \right|^2 e^{-i\omega t} e^{y/2} (a^2 \cos^2 \theta + b^2 \sin^2 \theta) \right] \]

\[ + \left| F_{1,E}(\omega) \right|^2 k_{1,H}(\omega) C_{1,H}(\omega) \right| \]

\[ \times \cos \theta \left( a^2 b^2 + \sin^2 \theta \right), \]

which has the same form as the original Eq. (3.14) of our analysis [1]. If \( a \) and \( b \) were independent of \( \theta \), we arrive at a result similar to Eq. (1).

IV. EXPERIMENT

We show the experimental data on the absorbance of three bands as a function of the angle of polarization of the incident IR beam for a liquid-crystalline material. The molecules of the material are aligned homogeneously on the substrates, the surfaces of the latter were rubbed so as to have a planar alignment of the molecules along a specific direction. This was achieved by assembling the substrates that are parallel rubbed to form a cell with a cell spacing of 6 \( \mu m \) thickness. Fields of different constant strengths were applied across the cell. The geometrical arrangement of the experimental setup is given in Fig. 3. The compound with the chemical name \((\text{S})-4-(1\text{-methylheptyloxy} \text{carbonylphenyl}-4'-\text{tetrafluoromethylbutylcarbonyloxy})\) [biphenyl-4-carboxylate and an acronym of MHPHFFHOBC (laboratory name AH43), (chemical formula given in Ref. [11], Fig. 1) was synthesized with a partly fluorinated achiral tail in the laboratory of Goodby. The phase sequence of the compound
FIG. 4. (Color online) The absorbance $A(\theta)$ as a function of the polarization angle $\theta$ for the phenyl bands at 1525 cm$^{-1}$ (C) and 1603 cm$^{-1}$ ( ) and for the carbonyl bond at 1715 cm$^{-1}$ ( ) for MHPHFHHOBBC in a 6 $\mu$m cell at a temperature of 122 °C. Voltages applied across the cell are (a) $V_{DC}$=0 V, (b) $V_{DC}$ =160 V, and (c) $V_{DC}$=-160 V. The fitted curves shown by the continuous and dotted lines are obtained using Eq. (1). In color online: red represents the band at 1525 cm$^{-1}$, blue represents the band at 1715 cm$^{-1}$, and black represents the band at 1603 cm$^{-1}$.

When the external voltage is applied, the material is in a different state than in the absence of the field. The fitting of the experimental results to Eq. (1) is again shown by lines that join the data points. The overall conclusion is that Eq. (1) fits the data reasonably well except at the two extremities of the maximum and the minimum absorbances. This is clarified in Fig. 7, where the data of Fig. 5 are magnified both for the strongest and the weakest absorbance bands at a temperature in the SmA* (again only in the absence of the external field) for both positive and negative voltages. The discrepancy $A_{exp}(\theta)-A_{fit}(\theta)$ as a function of the angle of polarization $\theta$ for the data presented in Fig. 7 (as per one example) for the two bands are shown in Fig. 8. From Fig. 8, we find that the obtained on cooling using polarized optical microscopy and IR spectroscopy on a homogeneously aligned sample was Iso 125.3 °C SmA* 120.2 °C SmC* 115 °C SmC$_A$ 57.5 °C crystalline using polarized optical microscopy and IR spectroscopy on a homogeneously aligned sample of the compound in a cell of 6 $\mu$m thickness. For a temperature of 122 °C in the SmA* phase at zero field, the results of absorbance for the in-plane C-C stretching vibration bands at 1525 cm$^{-1}$ and 1603 cm$^{-1}$ and the carbonyl band near the chiral center of 1715 cm$^{-1}$ are shown in Fig. 4. The fitting of the data to Eq. (1) is shown by continuous, dashed, and dotted lines. The in-plane stretching vibration at 1603 cm$^{-1}$ band has higher absorbances than the other two bands. We find that the fitting of the data to the highest absorbance band is poorer than either of the other two bands. The results for temperatures in the SmC* and SmC$_A$ (phases in the zero-field condition) are given in Figs. 5 and 6.

FIG. 5. (Color online) The absorbance $A(\theta)$ as a function of the polarization angle $\theta$ for the phenyl bands at 1525 cm$^{-1}$ (C) and 1603 cm$^{-1}$ ( ) and for the carbonyl bond at 1715 cm$^{-1}$ ( ) for MHPHFHHOBBC in a 6 $\mu$m cell at a temperature of 118 °C in SmC* at zero field across the cell. Voltages applied across the cell are (a) $V_{DC}$=0 V, (b) $V_{DC}$=40 V, and (c) $V_{DC}$=-40 V. The fitted curves to Eq. (1) are shown by the continuous and dotted lines. In color online: red represents the band at 1525 cm$^{-1}$, blue represents the band at 1715 cm$^{-1}$, and black represents the band at 1603 cm$^{-1}$.

FIG. 6. (Color online) The absorbance $A(\theta)$ as a function of the polarization angle $\theta$ for the phenyl bands at 1525 cm$^{-1}$ (C) and 1603 cm$^{-1}$ ( ) and for the carbonyl bond at 1715 cm$^{-1}$ ( ) for MHPHFHHOBBC in a 6 $\mu$m cell at a temperature of 65 °C in SmC$_A$ at zero field across the cell. Voltages applied across the cell are (a) $V_{DC}$=0 V, (b) $V_{DC}$=40 V, and (c) $V_{DC}$=-40 V. Fitted curves shown by continuous and dotted lines are obtained using Eq. (1). In color online: red represents the band at 1525 cm$^{-1}$, blue represents the band at 1715 cm$^{-1}$, and black represents the band at 1603 cm$^{-1}$.

021704-5
maximum discrepancy occurs during the two extremities of maximum and minimum absorbances. Nevertheless, the maximum error in the fitting of the data to the experiment is ±5%. The possible reasons for the discrepancy are given in the next section.

V. DISCUSSION

First we find that the formula (1) is independent of the birefringence also for the two cases considered in this paper. Jang et al. [14] stated that Eq. (1) is exact only for zero birefringence and they justify it on the basis that it is almost zero in the given experiments particularly “when the eigen-modes of a dichroic medium are linearly polarized along the directions of maximum and minimum absorbances. For the vibrations polarized nearly along the optic axis of the real part of the dielectric constant, the birefringence can be ignored in a few µm thick samples.” This means that when the absorbance is maximum or minimum, the real part of the permittivity along the two axes is the same. In our view, this is very unlikely to be the case. For the case of a planarly aligned cell as is the case here, even if the light were polarized parallel to the optical axis of maximum permittivity, the biaxiality would play a role. In the given experiment, however, the angle of polarization is varied and the absorbance is studied as a function of this angle. Consequently, the birefringence experienced by the IR beam is not zero and is dependent on the angle of polarization. From the examination of Fig. 8, we find that the fitting has a maximum error of ±5% in absorbance close to the extremities of the absorbance. The error in between the theory and the experiments is somewhat higher when voltage applied is of positive polarity as compared to when the polarity is reversed. In any case, the percentage error based on the results seems to be independent of the strength of the absorbance. One can reasonably expect that the IR birefringence is higher for the band with a higher absorbance. The errors in fitting are thus found to be independent of the magnitude of birefringence. Thus, the latter playing any role in the discrepancy between the theory as given by Eq. (1) and the experimental data is ruled out. One of the reasons for the small discrepancy may possibly arise from the manner in which the absorbance is calculated. The maximum absorbance of the IR band is calculated from the definition of the absorbance,

$$A(\omega, \theta) = -\log_{10} T_{cell}(\omega, \theta),$$  

where

$$T_{cell}(\omega, \theta) = \frac{I_{out}(\omega, \theta)}{I_{in}(\omega, \theta)}.$$  

For higher absorbances, one may obtain a considerable error in calculating the exact value of the absorbance for the reason that the transmission through the cell $T_{cell}(\omega, \theta)$ is low. The error in the logarithmic value of the transmission will increase further. This could in principle alter the fitting and make it bad for higher absorbance bands in particular.

Another likely source of the error is possibly the effect due to the surfaces. The surface treatment of substrates of the cell is used to align the liquid-crystalline molecules and the relative alignment of the molecules is likely to vary in the

FIG. 7. (Color online) Fitting to Eq. (1) is shown for the data in Fig. 5 for the bands (a) 1603 cm$^{-1}$, +40 V ($\Delta$); 1603 cm$^{-1}$, −40 V ($\Delta$); 1525 cm$^{-1}$, +40 V (\(\triangledown\)); and 1525 cm$^{-1}$, −40 V (\(\triangledown\)) at a temperature of 118 °C. The experimental data points are marked, whereas the fitting to Eq. (1) is given by the continuous and dotted lines. In color online: red represents the band at 1525 cm$^{-1}$, and black the band at 1603 cm$^{-1}$.

FIG. 8. (Color online) The deviations $[A_{exp}(\theta)-A_{fit}(\theta)]$ of the experimental data in Fig. 5 for the bands at (a) 1603 cm$^{-1}$, +40 V (\(\triangleright\)); 1603 cm$^{-1}$, −40 V (\(\triangleright\)); 1525 cm$^{-1}$, +40 V (\(\bullet\)), and (b) at the band 1525 cm$^{-1}$, −40 V (\(<\)) from the fitted equation as a function of the polarization angle. This illustration corresponds to the data shown in Fig. 7. In color online: red represents the band at 1525 cm$^{-1}$, and black represents the band at 1603 cm$^{-1}$. 
bulk with the distance from the substrate. It seems very likely that the alignment throughout the bulk of the cell is not as uniform as on the surfaces.

A comparison of the theory with the experiments shows that IR birefringence as stated above plays no role in Eq. (1) for the absorbance as a function of the polarization angle of the incident IR beam. This formula (1) is also independent of whether the molecules of the liquid-crystalline system are needle shaped or ellipsoidal or whether the incident light is plane or circularly polarized.

The underlying assumption that the principal axes of the system coincide with the axes of the permittivity tensor may strictly be not valid for the liquid-crystalline systems and this problem needs to be explored further.

ACKNOWLEDGMENTS

The authors thank Uttam Manna for organizing the figures. The work was funded partly by the SFI (Grant No. 02/W1/02) and RFP ENE Grant No. 06/0039. The IR spectroscopic measurements were made using the sample synthesized in the laboratory of Professor J. W. Goodby under the European SAMPA research project (2002–2006).

APPENDIX

A few typographic errors in our previous paper [1] corrected are being listed here. Equation (5.3c) should be read as

\[ p_{3,1} = \chi_{3,1} e_0 e_1 = \frac{N}{V} \left( \alpha e_1 \cos \gamma \cos \beta \sin \beta \right) = (\epsilon_{3,1} - 1) e_0 e_1. \]  
(A1)

Equation (5.7a) should be read as

\[ p_{1,3} = \chi_{1,3} e_0 e_3 = \frac{N}{V} \left( \alpha e_3 \cos \gamma \sin \beta \cos \beta \right) = (\epsilon_{1,3} - 1) e_0 e_3. \]  
(A2)

Equation (5.7b) should be read as

\[ p_{2,3} = \chi_{2,3} e_0 e_3 = \frac{N}{V} \left( \alpha e_3 \sin \gamma \sin \beta \cos \beta \right) = (\epsilon_{2,3} - 1) e_0 e_3. \]  
(A3)

Equation (5.7c) should be read as

\[ p_{3,3} = \chi_{3,3} e_0 e_3 = \frac{N}{V} \left( \alpha e_3 \cos^2 \beta \right) = (\epsilon_3 - 1) e_0 e_3. \]  
(A4)