

Birefringence dispersions of liquid crystals

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The origins of liquid-crystal birefringence were investigated. Theory on the quantitative birefringence dispersions of liquid crystals was developed and found to have excellent agreement with experimental results throughout the entire visible and infrared spectral regions. New guidelines for selecting or synthesizing the liquid crystals with the desired birefringence are established. Novel applications of liquid crystals in the infrared region are foreseeable.

I. INTRODUCTION

When a dielectric is introduced into an electric field, its constituent molecules, in general, become polarized and tend to line up with the resultant field. The extent to which this alignment takes place is determined by the strength of the dielectric constant. For normal gases and liquids the dielectric constant correlates with mean molecular polarizability and is described by the well-known Clausius-Mossotti equation at low frequencies and by the Lorentz-Lorenz equation at optical frequencies.¹ For liquids whose molecules have dipole moments, the low-frequency dielectric constant is usually much greater than the corresponding value at optical frequencies. The large static value is attributed to the orientation of the permanent dipole moments, but the rotational inertia of the molecules is much too large for any significant response at optical frequencies. At optical frequencies the motion of electrons in a molecule is displaced relative to the center of the nucleus and polarization is induced when an external field is applied. The electric field of the incident electromagnetic wave causes the induced dipoles to oscillate at the same frequency. The resultant motion of charge, in turn, re-emits an electromagnetic wave, also at the same frequency. For the efficiency with which the dipoles of a given medium oscillate generally varies with the frequency of the incident wave and the temperature of the medium, resulting in dispersions of the refractive index.

Nematic liquid crystals (LC's) consist of rodlike molecules which on the average line up parallel to a preferred direction, specified as the director. The dielectric constants of liquid crystals are anisotropic. When a linearly polarized monochromatic light wave propagates through a homogeneously aligned LC cell with its polarization axis at an angle of 45° to the director, the extraordinary and ordinary rays in the outgoing light will have experienced a phase difference due to the different propagating speeds in the liquid crystal. Unlike normal gases or liquids, molecules in liquid crystals are spatially correlated at the temperatures below the isotropic state. Therefore, no straight extension of those equations describing the dispersions of normal gases and liquids can be utilized for liquid crystals. Analogous to the Clausius-Mossotti equation and the Lorentz-Lorenz equation discussed above, the relationship between the dielectric constant and the molecular

polarizability of liquid crystals has been described by the Maier-Meier equations² and by the modified Lorentz-Lorenz equation (the Vuks equation³) for low frequencies and optical frequencies, respectively. Based on the Vuks equation, equations describing the wavelength and temperature dependence of LC birefringence are derived in Sec. II. The experimental results are presented in Sec. III. Very good agreement between theory and experiment is found throughout the entire visible and infrared (2–16 μm) spectral regions. New physical insights into the origins of the visible and infrared birefringence of liquid crystals are obtained. Guidelines for selecting or synthesizing LC materials with the desired birefringence are established and discussed in Sec. IV.

II. THEORY

Vuks's equation relates the microscopic structures (the molecular polarizability α) of LC molecules to the macroscopic observable (the index of refraction) as follows:

$$\frac{n_i^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N \alpha_i, \quad (1)$$

where n_i stands for $n_{||}$ or n_{\perp} , the refractive index of the extraordinary or ordinary ray, $\langle n^2 \rangle = (n_{||}^2 + 2n_{\perp}^2)/3$ is the average value of the refractive indices in the nematic phase, N is the number of molecules per unit volume, and α_i represents the principal polarizability of the nematic medium, normalized to one molecule. From Eq. (1), the birefringence ($\Delta n = n_{||} - n_{\perp}$) of liquid crystals is derived:

$$\Delta n = \frac{4\pi}{3} \frac{\langle n^2 \rangle + 2}{n_{||} + n_{\perp}} N (\alpha_{||} - \alpha_{\perp}). \quad (2)$$

In addition, since liquid crystal is a state of matter with its properties lying between those of a perfect crystal and an isotropic liquid, the differential molecular polarizability of liquid crystals is related to that of a perfect crystal by⁴

$$\alpha_{||} - \alpha_{\perp} = S(\gamma_{||} - \gamma_{\perp}). \quad (3)$$

Here, $\gamma_{||}$ and γ_{\perp} represent the longitudinal and transverse components of the perfect molecular polarizability tensor and S , the order parameter⁵ of liquid crystals, describes the degree of order of the liquid crystals. In a perfect

crystal $S=1$, whereas in an isotropic phase $S=0$. The value of S , to the first order of approximation, only depends on the temperature of material and its composition.⁵ According to the quantum-mechanical theory of dispersion,⁶ the polarizability of a molecule in the ground state (m) at frequency ω is proportional to the sum over all possible quantum transitions (n):

$$\gamma_m \propto \sum_n \frac{Zf_{mn}}{\omega_{mn}^2 - \omega^2}, \quad (4)$$

where Z is the number of active electrons per molecule (related to the molecular composition) and f_{mn} is the oscillator strength (proportional to the absorption or transition probability) at the transition frequency ω_{mn} . For liquid-crystal mixtures, the electronic absorption bands in the uv or near-uv region usually consist of either a single band or two closely overlapped bands. For liquid crystals with a single absorption band, the sum in Eq. (4) contains only one term. For liquid crystals exhibiting more than two electronic transition absorption bands, the situation is more complicated. From Eq. (4), the band with the highest oscillator strength and the longest resonance wavelength will make the largest contribution to the molecular polarizability. However, for liquid crystals having two closely separated bands (assume λ_1, λ_2 are the two resonance wavelengths and f_1, f_2 are the corresponding oscillator strengths) and at a wavelength far from resonance (i.e., $\lambda \gg \lambda_1$ and λ_2), Eq. (4) can still be simplified to a single term by introducing an effective oscillator strength (f^*) at the mean resonance wavelength (λ^*) which satisfies the following relation:

$$f_1 \lambda_1^2 + f_2 \lambda_2^2 = f^* (\lambda^*)^2. \quad (5)$$

When $f_1 \approx f_2$ and $\lambda_1 \approx \lambda_2$, the effective oscillator strength is $f^* \approx 2f_1$ and the mean resonance wavelength is $\lambda^* \approx [(\lambda_1^2 + \lambda_2^2)/2]^{1/2}$. In this single-band approximation, Eq. (4) is reduced to

$$\gamma_{\parallel, \perp} \propto Zf_{\parallel, \perp}^* \frac{\lambda^2 (\lambda^*)^2}{\lambda^2 - (\lambda^*)^2}. \quad (6)$$

Substituting Eqs. (3) and (6) into Eq. (2), the birefringence dispersions of liquid crystals at nonresonant optical frequency regions are obtained:

$$\Delta n(\lambda, T) = gNZS(T)(f_{\parallel}^* - f_{\perp}^*) \frac{\lambda^2 (\lambda^*)^2}{\lambda^2 - (\lambda^*)^2}, \quad (7)$$

where g is a constant which contains the proportionality constant as indicated in Eq. (6) and the first two terms in Eq. (2). The term $(\langle n^2 \rangle + 2)/(n_{\parallel} + n_{\perp})$ in Eq. (2) is found to be remarkably insensitive to wavelength, temperature, and liquid-crystal composition, and is merged into g as a constant. For nematic liquid crystals, the value of n_{\parallel} typically ranges from about 1.5 to 1.9, and n_{\perp} from about 1.4 to 1.6. Nevertheless, the ratio of $(\langle n^2 \rangle + 2)/(n_{\parallel} + n_{\perp})$ remains in the region of 1.40 ± 0.03 and is very insensitive to liquid-crystal composition, wavelength, and temperature.

From Eq. (7) the origins of LC birefringence can be understood. The birefringence of a liquid crystal is determined by (i) the available molecules per unit volume (i.e.,

the packing density of LC molecules), (ii) the available electrons per molecule, (iii) the degree of order, (iv) the resonance anisotropy of electronic transitions, and (v) the wavelength. Since N , S , and $(f_{\parallel}^* - f_{\perp}^*)$ are temperature dependent but wavelength independent, Eq. (7) can be further simplified:

$$\Delta n(T, \lambda) = G(T) \frac{\lambda^2 (\lambda^*)^2}{\lambda^2 - (\lambda^*)^2}, \quad (8)$$

where $G(T) = gNZS(f_{\parallel}^* - f_{\perp}^*)$. In the infrared, $\lambda \gg \lambda^*$, and Eq. (8) is reduced to

$$\Delta n(T, \lambda) \xrightarrow{\text{IR}} G(T) (\lambda^*)^2. \quad (8')$$

At a given temperature, Eq. (8') indicates that the liquid-crystal birefringence in the ir region is remarkably independent of wavelength (neglecting the contributions of molecular vibrational bands) and is primarily determined by the electronic transition behaviors of LC in the uv region and the individual LC material parameters, such as N , Z , S , and $f_{\parallel}^* - f_{\perp}^*$. In the vicinities of molecular vibrational bands which exist in the ir region, the birefringence dispersion has been discussed by Charney and Halford⁷ for the electro-optic Kerr materials and can be modified for describing liquid crystals:

$$\Delta n(T, \omega) = G(T) \left[\frac{4\pi^2 C^2}{(\omega^*)^2} + [(\mu_{\parallel})_K^2 - (\mu_{\perp})_K^2] \times \frac{\omega_K^2 - \omega^2}{(\omega_K^2 - \omega^2)^2 + \Gamma_K^2 \omega^2} \right], \quad (8'')$$

where C is the speed of light. The first term in the large parentheses is the same as that described in Eq. (8'), representing the persistent electronic contribution to the ir birefringence. The second term is the contribution from molecular vibrational bands: $(\mu_{\parallel, \perp})_K^2$, which is proportional to the oscillator strength, or transition probabilities, represents the value of the induced-dipole-moment matrix element for the extraordinary (or ordinary) ray of the K th molecular vibrational absorption band (with frequency ω_K and linewidth Γ_K).

III. EXPERIMENTAL

To verify theory, the birefringence of three nematic liquid crystals [two positive dielectric anisotropic LC's, British Drug House E-7 (cyano-biphenyl mixtures) and Merck ZLI-1132 (cyano-phenyl-cyclohexanes mixtures), and one negative dielectric anisotropic LC, Merck nematic phase-5 or NP-5 (eutectic mixture of azoxy compounds)] were measured in the visible and ir regions at room temperature. For the measurements in the visible region, several discrete Ar⁺ laser lines and a He-Ne laser were used. However, for the measurements in the ir (2–16 μm) region, a computer-controlled Fourier-transform spectrometer was used. The phase difference measurement technique developed by Wu *et al.*^{8,9} was used for the birefringence measurements in both spectral regions. Results are shown in Figs. 1(a), 1(b), and 1(c) for

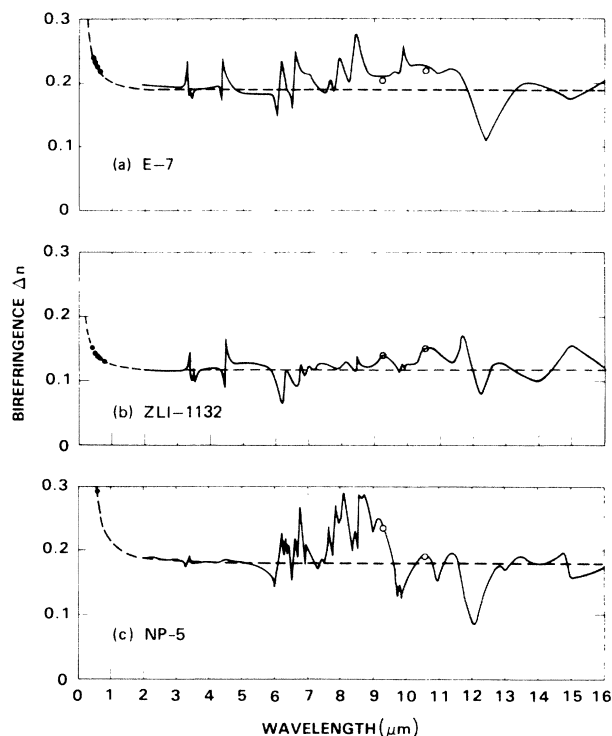


FIG. 1. Wavelength-dependent birefringence of liquid crystals: (a) E-7, (b) ZLI-1132, and (c) NP-5. Dots represent data obtained at some discrete Ar^+ and He-Ne laser wavelengths, solid lines represent the ir birefringence (the ir birefringence data for E-7 and ZLI-1132 have been reported in Ref. 9), and open circles represent the data measured at 9.27 and 10.59 μm CO_2 laser wavelengths. The dashed lines represent the theoretical calculations using Eq. (8). The parameters used for the calculations are listed in Table I.

the liquid crystals E-7, ZLI-1132, and NP-5, respectively. Dots represent the birefringence data for the visible wavelengths, solid lines the ir wavelengths (the ir birefringence data for E-7 and ZLI-1132 have been reported in Ref. 9), and open circles the two CO_2 laser lines, 9.27 and 10.59 μm . More detailed birefringence results in the visible region are shown in Fig. 2 for liquid crystals E-7 and ZLI-1132. Generally, the birefringence of liquid crystals declines as the wavelength increases in the visible region and remains approximately constant throughout the ir region except for the resonance effects in the vicinity of molecular vibrational bands.⁹

Due to the existence of molecular vibrational bands in the ir region, two types of resonance dispersion (positive and negative) are observed. For those vibrational bands with $\mu_{\parallel}^2 > \mu_{\perp}^2$, i.e., the absorption of the extraordinary ray more pronounced than that of the ordinary ray, the dispersion is positive [refer to the positive sign in Eq. (8')]. On the other hand, when the ordinary ray is the preferred absorption, the birefringence dispersion in the vicinities of those vibrational bands become negative. Examples of positive dispersion are the $\text{C}\equiv\text{N}$ bonds (centered at 4.5 μm) of the E-7 and ZLI-1132 liquid crystals, and the $\text{C}-\text{H}$ bond (centered at 3.4 μm) of the NP-5 liquid crystal, as shown in Figs. 1(a), 1(b), and 1(c), respectively. The

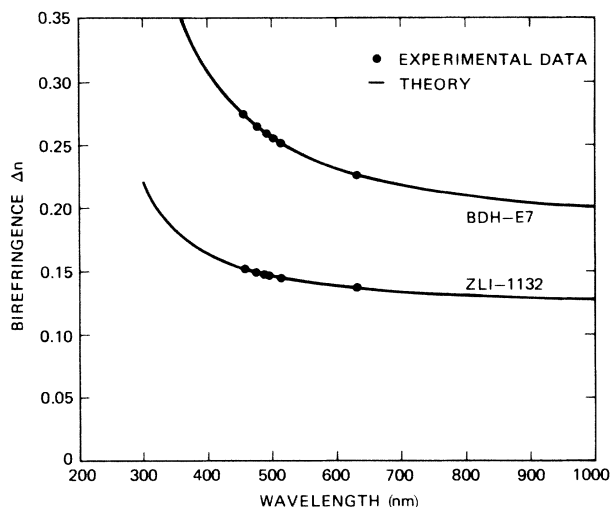


FIG. 2. Wavelength-dependent birefringence of liquid crystals E-7 and ZLI-1132 in the visible spectral region. Dots are the experimental results and solid lines are the theoretical results, calculated from Eq. (8) using parameters listed in Table I.

$\text{C}-\text{H}$ bonds of the E-7 and ZLI-1132 liquid crystals, however, behave with negative birefringence dispersion. The magnitude of the resonance-enhanced birefringence in the vicinities of molecular vibrational bands depends on the available electrons per unit volume, degree of order of the liquid crystal, polarization anisotropy, line shape of the vibrational bands, and wavelength. However, since the oscillator strength and, in turn, the absorption anisotropy of molecular vibrational bands are not as strong as the electronic transitions in the uv region, their enhancements to the LC birefringence are short ranged in wavelength; i.e., the influence is limited to the vicinities of the resonance bands.

The dashed lines shown in Fig. 1 represent the theoretical calculations using Eq. (8). Excellent agreement between theory and experiment is found throughout the visible and ir spectral regions (without taking molecular vibrational bands into account) for all three liquid crystals. The values of G and λ^* for each liquid crystal can be calculated from the measured birefringence at two discrete wavelengths. Table I shows the values of G and λ^* used in the calculations for three liquid crystals under study. Note that the G values for E-7 and ZLI-1132 are about the same; nevertheless, due to the shorter λ^* for ZLI-1132, its birefringence is lower than E-7's in both the visible and the ir regions, as shown in Figs. 1(a) and 1(b).

The mean resonance wavelength λ^* obtained from birefringence data, can also be verified directly from the

TABLE I. Parameters used for the birefringence calculations [Eq. (8)] of three nematic liquid crystals.

Liquid crystals	λ^* (nm)	G (nm^{-2})
E-7 ^a	250	3.06×10^{-6}
ZLI-1132 ^b	198	3.15×10^{-6}
NP-5 ^b	350	1.46×10^{-6}

^aBDH chemicals, England.

^bE. Merck Chemicals, Germany.

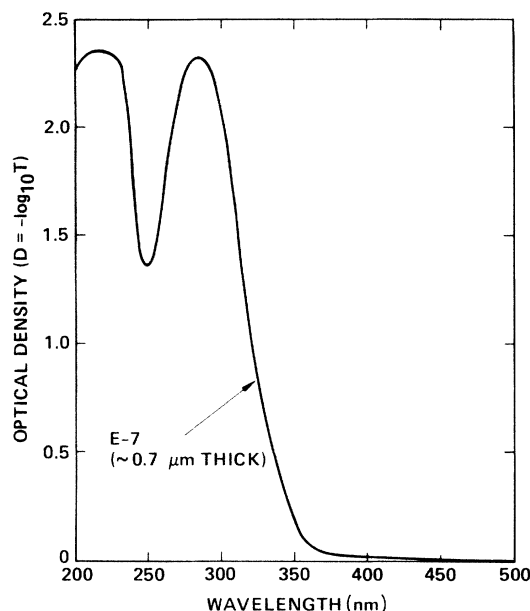


FIG. 3. Optical density measurements of liquid crystal E-7. The unpolarized uv light source used in the experiments was generated from a Cary-14 spectrometer. The rubbed KCl windows were used as LC substrates. The LC layer thickness was estimated from the transmitted color of the cell sitting between two crossed polarizers.

absorption spectrum of liquid crystals. Figure 3 shows the optical density measurement (equal to $-\log_{10} T$; T is the transmission) for liquid-crystal E-7 in the uv region. From Figure 3, two superimposed absorption bands in the liquid crystal E-7 are found—the first one centered at $\lambda_1 \sim 280$ nm and the second at $\lambda_2 \sim 220$ nm. These two bands have about equal optical density so that the condition $f_1 \approx f_2$ holds and the mean resonance wavelength λ^* can be evaluated from $[(\lambda_1^2 + \lambda_2^2)/2]^{1/2}$. The calculated λ^* is equal to 252 nm, in very good agreement with the deduced result ($\lambda^* = 250$ nm) from the birefringence data.

The temperature-dependent birefringence of liquid crystals is characterized by $G(T)$. In order to illustrate the functional dependence of $G(T)$, the temperature-dependent birefringence of E-7 liquid crystal was measured until the nematic-isotropic phase transition occurred ($T \approx 60^\circ\text{C}$). Results are shown in Fig. 4. Since $G(T)$ is a

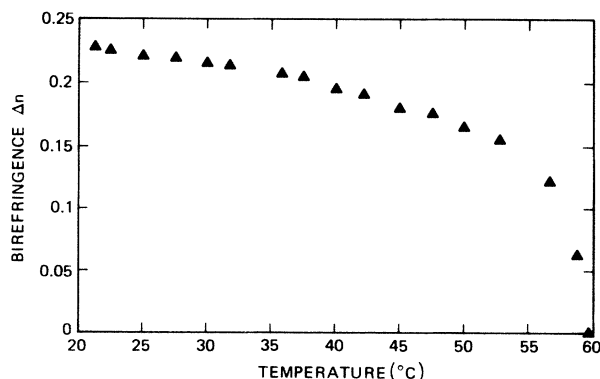


FIG. 4. Temperature-dependent birefringence of the E-7 liquid crystal at $0.633 \mu\text{m}$ wavelength.

combinational function of $gNZS(f_{\parallel}^* - f_{\perp}^*)$, where g is very insensitive to temperature, Z is a constant for a given LC molecule, and N and $(f_{\parallel}^* - f_{\perp}^*)$ are weakly dependent on the temperature, so the temperature-dependent birefringence is primarily determined by the order parameter of the liquid crystal. The degree of order of nematic liquid crystals decreases gradually as the temperature rises due to the thermal agitation of LC molecules. When the nematic-isotropic phase transition temperature is reached, liquid crystals become isotropic and their birefringence vanishes.

IV. DISCUSSION

For the electro-optic modulation of light (particularly in the infrared region) employing liquid crystals, such as an infrared liquid-crystal light valve,¹⁰ high birefringence enables a thin LC layer to be used for achieving a high modulation efficiency and, in the mean time, maintain fast response times. Intuitively, a general guideline for anticipating high-birefringent LC materials in the ir region is to select those showing high birefringence in the visible region. However, this guideline is not always reliable. As shown in Figs. 1(a) and 1(c), NP-5 has higher birefringence than E-7 in the visible region, but this superiority is reversed in the ir region. The higher birefringence of the NP-5 liquid crystal in the visible region is attributed to its longer resonance wavelength (see Table I) of the electronic transition absorptions. However, due to its lower value of G , the birefringence of NP-5 liquid crystal becomes lower than that of E-7 in the ir region. As discussed above, the value of G is proportional to the packing density, available electrons per molecule, degree of order, and electronic transition absorption anisotropy of the liquid crystal. The LC mixtures exhibiting large G value and long λ^* will produce high birefringence in both visible and ir spectral regions.

V. CONCLUSION

A quantitative study of the birefringence dispersions of liquid crystals was carried out. The electronic absorption anisotropy in the uv region plays a fundamental role in producing the birefringence of liquid crystals at optical frequencies. The contribution of molecular vibrational absorption bands to the birefringence is limited to the vicinities of these resonance bands. Very good agreement between theory and experiment on LC birefringence is found throughout the visible and ir regions. New guidelines for selecting or synthesizing high-birefringent liquid crystals are established. Novel applications of liquid crystals in the ir region are foreseeable.

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