

Giant spectral response of impure nematic liquid crystal to applied field at Fréedericksz transition

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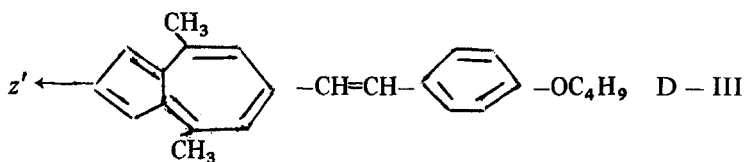
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The restructuring of the position of the maximum ν_e of the polarized absorption band of a dye in a nematic-liquid-crystal matrix at the Fréedericksz transition in an electric field is characterized by a giant response $d\nu_e/dE$, which is 10^5 times the response in the case of the Stark effect in molecular liquids and crystals.

1. The shift and splitting of the spectral bands of condensed molecular media during the application of fields are of scientific and applied interest, for data storage and processing,¹ for laser systems, and for devices in which there is a modulation of spectral parameters. In the case of the Stark effect and in the electronic spectra of molecular liquids and crystals, the derivative $d\nu/dE$, which is the spectral response of the medium to the applied field, is typically¹ $10^{-5} \text{ cm}^{-1}/(\text{V/cm})$. This response may increase substantially when three conditions are met simultaneously: (a) An anisotropic molecular medium, in which the position of a spectral band depends on the polarization of the observed light, is used. (b) The optic axis of the medium undergoes a reorientation in an external field E . (c) This reorientation is of the nature of a second-order phase transition in the field E , with an anomalous increase in the susceptibility near a threshold E_t . All these conditions are satisfied by a nematic liquid crystal at the Fréedericksz transition, which is used as an anisotropic matrix for impurity molecules with a tunable spectral band. In the present letter we report an experimental realization of this idea for intensifying the spectral response of a medium to an external field.

2. As the nematic matrix we used 4-n-pentyl-4'-cyanobiphenyl (5CB), and as the impurity we used the dye D-III, with a known electronic structure² (at a concentration of 0.16 M). Experiments were carried out at $\Delta T = T_c - T = 4.5^\circ$, where T_c is the temperature of the nematic-(isotropic liquid) transition. The thickness of the layer of liquid crystal was $d = 100 \mu\text{m}$. The reorientation of the liquid crystal at the Fréedericksz transition, from the original planar orientation, was carried out with an alternating electric field at a frequency of 400 Hz.



The long-wavelength electronic absorption bands for III, with peaks at $\lambda_i = 407$

and 580 nm in the isotropic phase, lie in the transmission region of 5CB. Polarized absorption spectra for III in various matrices are given in Ref. 2. The symmetric band with $\lambda_i = 580$ nm has a nonuniform polarization, since it is formed by overlapping vibron bands of the first electronic transition, with different values of the parameter $S_\beta = (3\cos^2\beta - 1)/2$, where β is the angle between the direction of the dipole moment of the vibron transition and the longitudinal axis (z') of the azulene fragment. As a result, within the symmetric envelope the quantity $S_\beta(\nu)$ varies continuously, while near the maximum ν_i the function $S_\beta(\nu)$ is linear.² This inhomogeneous polarization of the absorption bands, which is typical of dye molecules, leads to their splitting into two components, $\nu_{\parallel, \perp}$, which are polarized parallel to and perpendicular to the optic axis of the liquid crystal. The difference $\Delta\nu = \nu_{\parallel} - \nu_{\perp}$ can reach 10^3 cm^{-1} .

Under the experimental conditions, a light wave incident along the normal (z) to the cell walls was polarized along the optic axis (x) of the liquid crystal, and the maximum of the impurity absorption band, ν_e , coincided with ν_{\parallel} . If the voltage applied to the cell, U , exceeds the threshold U_t , the reorientation of the director in the xz plane, which occurs as a result of the Fréedericksz transition, leads to a shift of the absorption maximum for the extraordinary wave, $\nu_e(U)$, toward ν_{\perp} . A PYE UNICAM 8800 spectrophotometer was used to record the spectra and to automatically record the position of $\nu_e(U)$. For the band at $\lambda_i = 580$ nm, the angle $\beta(\nu_i) = 42^\circ$ is close to the magic angle $\beta_M = 54.7^\circ$, so the dichroism for this band is small, $N \lesssim 1.4$.

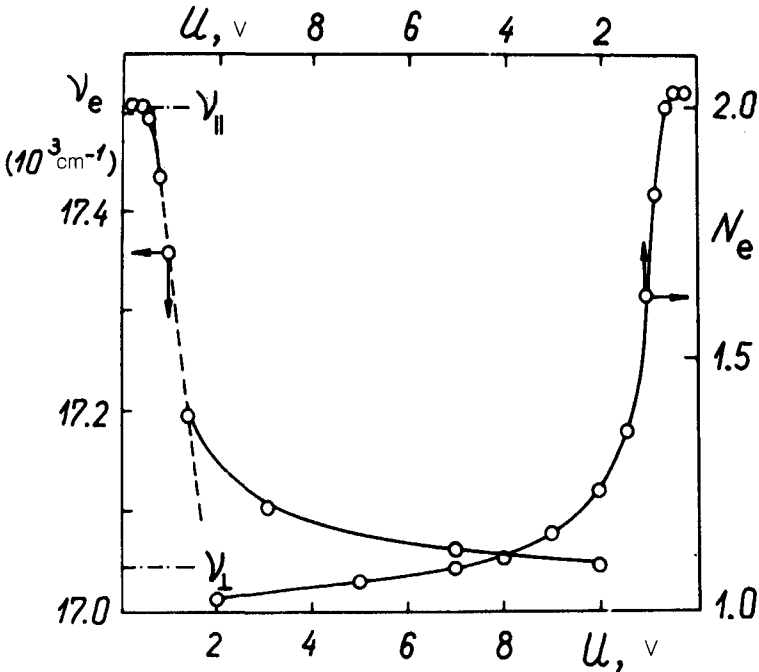


FIG. 1. Lower left: Field dependence of ν_e , the maximum of the absorption band of the dye D-III, with $\lambda_i = 580$ nm, in a 5CB nematic matrix. Open circles—Experimental; solid line—calculated from (1) and (2). Upper right: Field dependence on the dichroism $N_e = D_e/D_l$ measured at $\lambda = 465$ nm on the long-wavelength wing of the absorption band of the dye-III, with $\lambda_i = 407$ nm. Solid line—Interpolation.

Figure 1 shows $\nu_e(U)$. At $0.8 \leq U \leq 1.4$ V, this dependence has a linear region. An extrapolation of this linear region (the dashed line in the figure) to $\nu_e = \nu_{\parallel}$ gives us the effective threshold, $U_{\text{eff}} = 0.65$ V, which agrees with an estimate found from the expression³ $U_i = \pi(4\pi K_{11}/\Delta\epsilon)^{1/2} = 0.68$ V, with $K_{11} = 0.47 \times 10^{-6}$ dyn and $\Delta\epsilon = 11.46$ (Ref. 4). The difference between these values and the experimental value $U_i = 0.4$ V may result from a small deviation ($\sim 1-2^\circ$) of the director from the x axis at the surface of the cell.³ In the linear region of $\nu_e(U)$, the value $d\nu_e/dU = -390$ cm^{-1}/V corresponds to the value $d\nu_e/dE = 4$ $\text{cm}^{-1}/(\text{V}/\text{cm})$, which is 10^5 times that in the case of the Stark effect in molecular liquids or crystals.¹ For the particular system studied, and for these particular experimental conditions, we have $\Delta\nu = 460$ cm^{-1} . As this quantity is lowered, even by a factor of 100, for narrow electronic absorption bands, i.e., as it is lowered to the typical values of $\Delta\nu$ in Stark spectroscopy,¹ the method proposed here leads to a value of $d\nu_e/dE$ which is still 10^3 times that under ordinary conditions.

3. For the case under consideration here, of nonuniformly polarized impurity bands, the dependence of ν_e on the average $\overline{\cos^2\theta}$, over the cell thickness, is¹

$$\nu_e = \nu_i + \frac{aS[(2+c)\overline{\cos^2\theta} - c]}{c(1-bS) + [1-c + (2+c)bS]\overline{\cos^2\theta}}, \quad (1)$$

where θ is the angle between local directions of the vector $\mathbf{E}(z)$ of the extraordinary light wave and the director $\mathbf{r}(z)$, S is the orientational order parameter of the impurity subsystem, $b = S_\beta(\nu_i)$, $a = S'_\beta(\nu_i)/\alpha$, $\alpha = |D''_i(\nu_i)|/D_i(\nu_i)$, $D_i(\nu)$ is the spectrum of the optical density of the impurity band in the isotropic phase, ν_i is the maximum of the band $D_i(\nu)$, $c = (f_{\perp}/f_{\parallel})^2$, and $f_{\parallel,\perp}$ are components of the local field tensor of the light wave for the matrix liquid crystal in the region of the impurity band.

We determine $\overline{\cos^2\theta}$ from the expressions¹

$$\overline{\cos^2\theta} = \frac{N_e g_e - 1}{N_g - 1}, \quad g_e = 1 + \frac{g - 1}{N - 1} (N_e - 1), \quad (2)$$

making use of the dichroism $N_e(U)$ (Fig. 1) measured at $\lambda = 465$ nm on the long-wavelength wing of the absorption band for III ($\lambda_i = 407$ nm). The position of this band does not depend on U , and the dichroism $N(\lambda) = D_{\parallel}(\lambda)/D_{\perp}(\lambda)$ does not depend on λ . Here $N = N_e(U \leq U_i)$, $g = n_{\parallel}/n_{\perp} = 1.12$, and $n_{\parallel,\perp}$ are the refractive indices of the liquid-crystal matrix in the impurity absorption region. For the impurity system which we are discussing here, the experimental values of the parameters in (1), $S(\Delta T = 4.5^\circ) = 0.425$, $\alpha = 398$ cm^{-1} , $b = 0.326$, and $c = 1.26$, were taken from Refs. 2 and 5, respectively. A calculation of $\nu_e(U)$ from (1) and (2) over the entire range of U leads to results which agree well with the experimental data. Analysis shows that the approximation $c = 1$ causes only a slight degradation of this agreement.

4. At small values of $h = (U - U_{\text{eff}})/U_{\text{eff}}$, we can ignore the deviation of the angle θ from θ' , which is the angle between the x axis and $\mathbf{r}(z)$. Setting $c = 1$, and substituting the relationship³

$$\overline{\sin^2\theta'} = 2h \left(\frac{K_{33}}{K_{11}} + \frac{\Delta\epsilon}{\epsilon_1} \right)^{-1}$$

into (1), we find the response from (1):

$$\left(\frac{dv_c}{dh}\right)_{h=0} = -\frac{6aS}{(1+2bS)^2} \left(\frac{K_{33}}{K_{11}} + \frac{\Delta\epsilon}{\epsilon_{\perp}}\right)^{-1}.$$

We see that the giant spectral response observed here for this system is not a record high value. It could be increased significantly by selecting liquid-crystal matrices with higher values of S and smaller values of the parameters K_{33}/K_{11} and $\Delta\epsilon/\epsilon_{\perp}$. Another possibility for increasing dv/dE would be to use the Fréedericksz transition with a B deformation of the director field in a liquid crystal and also in twist and supertwist cells.

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¹The derivation of Eqs. (1) and (2) will be published separately.

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³L. M. Blinov, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals*, Wiley, New York, 1983.

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⁵E. M. Aver'yanov *et al.*, *Zh. Eksp. Teor. Fiz.* **86**, 2111 (1984) [*Sov. Phys. JETP* **59**, 1227 (1984)].

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