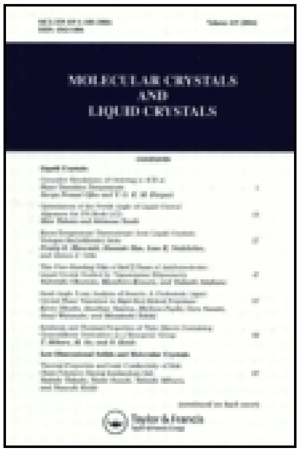

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INTRINSIC BAND SPLITTING IN OPTICAL SPECTRA OF LIQUID CRYSTALS

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Abstract The intermolecular interaction effect on the light propagation in uniaxial liquid crystals is studied by Green function method. It is shown that dipole-dipole resonant interaction causes the splitting and the shape deformation of intrinsic bands.

INTRODUCTION

The study of intrinsic absorption bands provides the useful information on the internal structure and dynamics of molecular systems. Optical properties of liquid crystals (LC) are widely used[1], however the spectroscopy of LC is poorly investigated yet.

This work deals with the peculiarities of intrinsic absorption bands, that are caused by intermolecular interaction. Intermolecular interaction consists of two terms: static interaction which changes molecular excitation energy and resonant one associated with excitation transfer between molecules. The dipole-dipole term of the resonant interaction is long-range ($\sim R^{-3}$) and the contribution of distant molecules is essential. Calculation by Green function method within the adiabatic approximation showed that intrinsic band splitting should be observed in uniaxial LC[2] (that is an analog of Davydov splitting in molecular crystals).

DISPERSION OF PERMITTIVITY

Let us consider electromagnetic wave propagation in uniaxial LC. We shall suppose that the system may be divided into two subsystems: one quantum, including the electronic excitations and the intramolecular vibrations, and one classical, including the translational and rotational molecular motion. The Hamiltonian of the quantum subsystem in the adiabatic approximation may be written

$$H = \sum_{n,f} E_{nf} B^{+}_{nf} B_{nf} + \frac{1}{2} \sum M^{fg}_{nm} (B^{+}_{nf} + B_{nf})(B^{+}_{mg} + B_{mg}) \quad (1)$$

where B^{+}_{nf} and B_{nf} are, respectively, the creation and annihilation operators for an excitation of type f at the molecule n, E_{nf} is the energy of that excitation. The matrix element of the resonant interaction is approximated by dipole-dipole term

$$M^{fg}_{nm} = d^{\alpha}_{nf} T^{\alpha\beta}_{nm} d^{\beta}_{mg} , \qquad T_{nm} = \frac{R^{2}_{nm} \delta_{\alpha\beta} - 3 \cdot R^{\alpha}_{nm} R^{\beta}_{nm}}{R^{5}_{nm}} \quad (2)$$

$\underline{d}_{nf}$ is the dipole moment of the transition of molecule n into excited state f, and $\underline{R}_{nm}$ is the vector from molecule n to molecule m, The quantities E_{nf} and M^{fg}_{nm} depend on the variables of the classical subsystem.

The propagation of an electromagnetic wave with vector $\underline{Q}$ and frequency w may be described by means of the transverse permittivity tensor, whose components are given in terms of Fourier transform of the retarded Green function by

$$\varepsilon^{\perp}_{\alpha\beta} = \delta_{\alpha\beta} - \langle G_n^{\alpha\beta}(w,\underline{Q})\rangle , \tag{3}$$

where the brackets $\langle \ldots \rangle$ denote averaging over the classical variables.

The expression for $\varepsilon^{\perp}_{\alpha\beta}$ is somewhat different from those generally used,[3] since a different definition of Green function is more suitable here, whereby it satisfies the equation

$$G_n^{\alpha\beta}(w,\underline{Q}) = -U_n^{\alpha\beta}(w) - \frac{v}{4\pi} U_n^{\alpha\xi}(w) \sum_{m\neq n} T_{nm}^{\xi\mu}(\underline{Q}) G_m^{\mu\beta}(w,\underline{Q}) \tag{4}$$

with

$$U_n^{\alpha\beta}(w) = -\frac{4\pi}{v} \sum_f \frac{2\cdot E_{nf}}{h^2 w^2 - E_{nf}^2} d_{nf}^{\alpha} d_{nf}^{\beta} \tag{5}$$

$$T_{nm}^{\xi\mu}(\underline{Q}) = T_{nm}^{\xi\mu} \exp(-i\cdot\underline{Q}\cdot\underline{R}_{nm}) \tag{6}$$

v being the volume for one molecule.

Assuming that the main contribution to the sum over m in Eq.(4) comes from molecules at a distance exceeding the correlation radius, one can average independently the quantities depending on n and m. One then obtains

$$\langle G_n^{\alpha\beta}(w,\underline{Q})\rangle = -\langle U_n^{\alpha\beta}(w)\rangle - \langle U_n^{\alpha\xi}(w)\rangle W^{\xi\mu}(\underline{Q}) \langle G_n^{\mu\beta}(w,\underline{Q})\rangle \tag{7}$$

where

$$W^{\xi\mu}(\underline{Q}) = \left\langle \frac{v}{4\pi} \sum_{m} T^{\xi\mu}_{nm}(\underline{Q}) \right\rangle = \frac{Q^{\xi} Q^{\mu}}{Q^{2}} - L^{\xi\mu} \qquad (8)$$

and $L^{\xi\mu}$ are the components of Lorentz tensor.

The method of frequency moments was used[4] and the diagram technique was developed[5] to take correlations into account. Diagram summations resulted in a convergent series. The first term of this series coincides with the solution of Eq.(7).

INTRINSIC ABSORPTION BAND SPLITTING

We shall consider the optical properties of LC at frequencies close to an isolated absorption band of Lorentzian form, for which the dipole moment $\underline{d}_p$ of the corresponding transition is parallel to the long molecular axis. If the contribution of the other levels is assumed independent of frequency in the absorption region, we derive expressions for the diagonal components of the tensor $\bar{U}(w) = \langle U_n(w) \rangle$:

$$\bar{U}_{\perp,\parallel}(w) = U^{o}_{\perp,\parallel} - \frac{A^{o}_{\perp,\parallel}}{w - w^{o}_{\perp,\parallel} + i\gamma} \qquad (9)$$

$$A^{o}_{\perp} = \frac{1-S}{3} A, \qquad A^{o}_{\parallel} = \frac{2\cdot S+1}{3} A, \qquad A = \frac{4\pi d_p^{2}}{\hbar \cdot v} \qquad (10)$$

and S is the order parameter.

The difference between $w^{o}_{\perp}$ and $w^{o}_{\parallel}$ is due to the orientation dependence of the static and dispersive interactions[6].

Using Eqs. (3) and (7), we easily find the diagonal components $\varepsilon_{\perp}(w)$ and $\varepsilon_{\parallel}(w)$ of the permittivity tensor, which are the same as those of the transverse tensor if the wave vector is perpendicular to the director

$$\varepsilon_{\perp,\parallel}(w) = \varepsilon^{o}_{\perp,\parallel} - \frac{A_{\perp,\parallel}}{w - w_{\perp,\parallel} + i\gamma} \qquad (11)$$

where

$$\varepsilon^{o}_{\perp,\parallel} = 1 + \frac{U^{o}_{\perp,\parallel}}{1 - U^{o}_{\perp,\parallel} L_{\perp,\parallel}} \qquad (12)$$

$$A_{\perp,\parallel} = A^{o}_{\perp,\parallel} \left[1 + (\varepsilon^{o}_{\perp,\parallel} - 1)L_{\perp,\parallel}\right]^{2} \qquad (13)$$

$$w_{\perp,\parallel} = w^{o}_{\perp,\parallel} - A^{o}_{\perp,\parallel} L_{\perp,\parallel} \left[1 + (\varepsilon^{o}_{\perp,\parallel} - 1)L_{\perp,\parallel}\right] \qquad (14)$$

As follows from Eq.(14), the absorption maxima mismatch in two polarizations (Fig. 1). The physical nature of this splitting may be explained in the following way. The main contribution to the ordinary wave absorption is given by the molecules which are strongly disoriented relative to the director, whereas the weakly disoriented molecules interact with the extraordinary wave. Since the excitation transfer interaction depends on the molecular orientation, the absorption band shifts differ in the two polarizations. The splitting value is proportional to the oscillator strength and depends on the order parameter and Lorentz tensor. It is obvious that this splitting disappears in the isotropic phase.

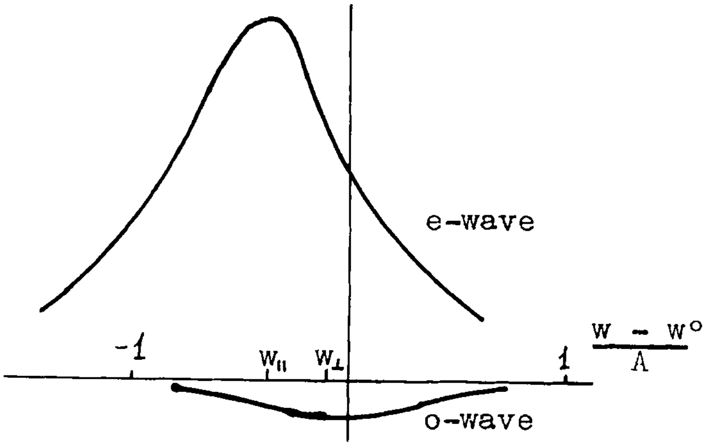

FIGURE 1. Absorption band splitting in uniaxial liquid crystals due to resonant interaction. $w_{\perp}^{o}=w_{\parallel}^{o}=w^{o}$, $\varepsilon_{\perp}^{o}=\varepsilon_{\parallel}^{o}=2.5$, S=0.75, $L_{\perp}=L_{\parallel}=1/3$, $A=2\gamma$.

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