Spectral and kinetic properties of doped liquid crystals upon electron excitation energy transfer

D. V. Baradulin, V. A. Kizel', V. A. Sklyaruk, and D. D. Toptygin

Moscow Engineering Physics Institute

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Electron excitation energy transfer in an anisotropic liquid crystal (LC) medium is investigated based on the kinetics and the luminescence spectra of the impurity molecules. The transition of a liquid crystal from the anisotropy to the anisotropic state is accompanied by a change in the luminescence anisotropy of the acceptor and the damping kinetics of the donor and acceptor, which allows determination of the presence and efficiency of energy transfer. The transition itself is related to the orientational ordering of the LC molecules. The change in phase state also causes a change in energy transfer efficiency, in which the ratio of the lifetime of the molecule in its excited state to its rotational relaxation time plays an important role. Local high order in the liquid crystal is determined to exist. We report an investigation of electron excitation energy transfer in a liquid crystal (LC) matrix. This problem has only begun to be analyzed for a number of reasons, not the least of which is the complexity of the required experimental techniques.[1,2]

1. EXPERIMENTAL TECHNIQUE AND SPECIMEN SELECTION

An experimental set-up[3] that makes it possible to carry out measurements with a higher degree of accuracy compared to experiments using other techniques was employed for measurement of the spectral characteristics of the LC specimens and impurities. The measurement geometry is shown in Fig. 1. An "ORTEC" spectrofluorimeter was used for the kinetic measurements; the measurement technique is described in Ref. 4, 5. The absorption spectra were measured on an "Hitachi-330" spectrophotometer. The specimen temperature-control and fabrication techniques are discussed in Ref. 6, 7.

An N106 nematic LC (NLC) transparent to radiation to 250 nm was used as the orienting LC matrix. A substantial number of dichroic dyes were tested for use as the oriented impurities introduced into the LC matrix. Three donor-acceptor pairs were selected from this group based on spectral properties and their "embeddability" in the LC: CD-8 (a naphthalamide derivative) + CV (cresyl-violet), C_2 (a coumarin derivative) + CD-8 and CD-8 + "12". One of the few luminescing LCs—namely, LC 549 (4-hexyloxy-4-cyanobiphenyl)—forms excimers[8,9] and hence is unsuitable for our investigations.

The absorption spectra of these dyes in various solvents reveal that no substantial spectral dependence on the nonpolar solvent is observed, while the moderate bathochromic shift is due to the high refractive index of the NLC (as demonstrated by calculations in accordance with Ref. 10); the same situation is observed in the luminescence spectra (Fig. 1). The lack of associate formation for these substances is confirmed by the fact that analysis revealed no concentration dependence of the absorption spectra with the concentration ranging from 10^{-3} to 10^{-8} M. No concentration dependence in the luminescence spectra was observed with identical concentrations for these dyes, which suggests the absence of excimer complex formation. The reverse influence of the impurity on the degree of order of the liquid crystal is insignificant[11] and the effect of the two impurities is additive.[12] The absence of chemical interactions between the partners is tested experimentally and confirmed by the fact that the absorption spectrum of the substances in the pair is the additive sum of their separate spectra. The results obtained for all substance pairs are qualitatively analogous across the entire spectrum of chemical formulae. This suggests that the results and conclusions provided below for one to two pairs have a high degree of generality.

2. STATIC MEASUREMENT RESULTS

The polarization luminescence technique was used to investigate the structure and characteristics of the LCs. The experiment measured the luminescence polarization anisotropy

$$r=(I_{\parallel}-I_{\perp})/(I_{\parallel}+2I_{\perp}),$$

where $I_{\parallel}$ and $I_{\perp}$ are the parallel and perpendicular radiation components, respectively, for the case of excitation of the specimen by linearly-polarized light parallel to the "director" of the NLC (the direction of preferred orientation), together with the anisotropy r' with excitation polarization perpendicular to the director. The degree of orientation order of the LC molecules was determined on this basis.[13,14]

Figure 1 shows the luminescence anisotropy measurement results for CD-8 and CV dyes dissolved in liquid crystals as a function of luminescence wavelength. It is clear from these relations as well as measurements of the linear dichroism of these dyes that their luminescence bands and long-wavelength absorption bands are accurately simulated by a single oscillator (traces of the vibrational structure are clear for the hexane solution) oriented along the long axis of the molecule and no changes in molecular conformation occurred under excitation. This was established for other substances as well. This conclusion was also confirmed by measurements of the anisotropy kinetics described in Ref. 4, 5.

Measurements of the intensity and anisotropy of the donor and acceptor radiation were carried out from 20 to 70 °C, i.e., for both the anisotropic and the isotropic states of the LC matrix (the nematic liquid crystal N106 makes the transition from the anisotropic to the isotropic state at $T = 58.5$ °C). Luminescence was excited at the absorption wavelength of the donor which was selected to avoid direct luminescence excitation of the acceptor molecules (for the CD-8 + CV pair: $\lambda_{\text{exc}} = 416$ nm), and sensitized lumines-

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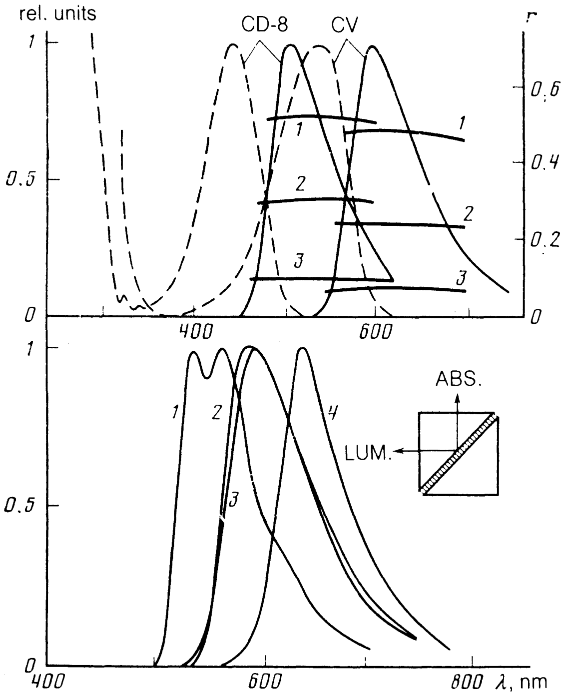

FIG. 1. Above: Absorption spectrum D (dashed curves) and luminescence spectrum I (solid curves) for CD-8 and CV; luminescence anisotropy $r(\lambda)$ for the CD-8 + CV pair at: 1—22 °C, 2—55 °C; 3—67 °C. Below: Luminescence spectra of CV dye: 1—In hexane; 2—in benzene; 3—in NLC; 4—in ethanol. Insert: Measurement geometry.

cence of the acceptor molecules from dipole-dipole energy transfer observed.

The possibility of luminescence excitation directly from the source was evaluated. The acceptor was therefore excited at its absorption wavelength, i.e., in conditions where the donor does not absorb (for the CD-8 + CV pair: at $\lambda = 540$ nm, see Fig. 1) and the acceptor luminescence intensity I_{A2} was also measured. The acceptor luminescence intensities I'_{A1} and I'_{A2} were initially measured without the donor (the indices 1 and 2 refer to the excitation wavelength in the absorption band of the donor and acceptor, respectively). The level of direct acceptor excitation within the pair can then be determined as

$$I_{A_1} = I_{A_2}\frac{I'_{A_1}}{I'_{A_2}}(1-\alpha),$$

where α is determined by donor absorption at the excitation wavelength. Estimates reveal that the luminescence sensitized due to electron excitation energy transfer makes the principal (90–95%) contribution to acceptor luminescence.

Thin crystal specimens ($d \sim 10\,\mu$m) were used for measurements of the spectral luminescence characteristics of the donor and acceptor in order to avoid the error associated with possible reabsorption of radiation (concentration 10^{-4} M).

Since light linearly polarized along the LC director was used for excitation it is clear that the fraction of absorbed light diminishes as the angle θ by which the molecular axes deviate from the director increases; such deviations grow with temperature. A calculation using data on the temperature dependence of the degree of orientational ordering of the liquid crystal reveals that the change in luminescence intensity as a function of T (Fig. 2) can be attributed specifically to the increasing deviation of the molecules from the LC director, i.e., to the change in the distribution function $f(\theta)$, while the temperature luminescence quenching is negligible (it is independent of the orientation). As we know

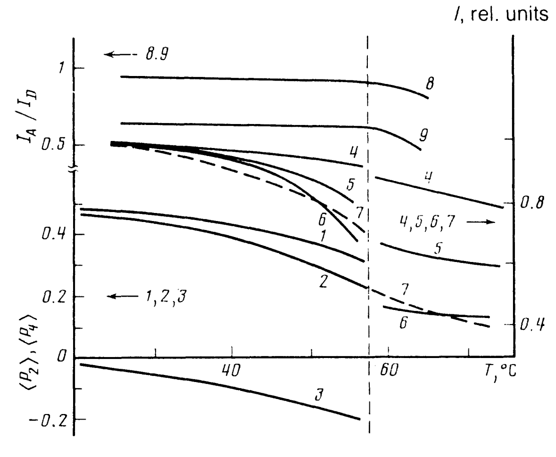

FIG. 2. Parameters of the orientation distribution function for CD-8 dye: 1—$\langle P_2\rangle$, absorption dichroism; 2—$\langle P_2\rangle$, luminescence, 3—$\langle P_4\rangle$, luminescence. The total luminescence intensity ($I = I_\parallel + 2I_\perp$) for the dyes; 4—CV; 5—CD-8; 6—C_2; 7—theoretical calculation for CD-8. The ratio I_A/I_D for the CD-8 + CV pair at CV concentrations; 8—$1.5\cdot 10^{-4}$ M; 9—$1.0\cdot 10^{-4}$ M.

$$f(\theta) = \sum_n \frac{2n+1}{2} P_{2n}(\cos\theta)\langle P_{2n}(\cos\theta)\rangle,$$

where P_{2n} are the Legendre polynomials of degree $2n$. The polynomial $\langle P_2\rangle$ is normally designed S and is called the order parameter.

These measurements of the radiation anisotropy of the "donor + acceptor" pair revealed the following. As was the case for the radiation anisotropy of each separate substance, no dependence of the anisotropy on the luminescence recording wavelength was observed nor was any diminishing anisotropy with increasing LC matrix temperature identified.

The temperature dependence of the luminescence anisotropy of the donors and acceptors reveals that the luminescence anisotropy of the donor remains unchanged when the acceptor is present, while the sensitized luminescence anisotropy of the acceptor is 10–15% below the anisotropy measured for the acceptor in the absence of the donor under direct excitation. Depolarization of acceptor luminescence is observed when the donor is present (Fig. 3): $r(T)$ diminishes, while $r'(T)$ grows compared to $r(T)$ and $r'(T)$ of the acceptor without the donor.

A comparison of the curves in Fig. 3 shows that the luminescence anisotropy of the CD-8 donor remains unchanged from its value with a zero acceptor concentration (curves 7, 8 and 11, 12) or varies little (curves 3, 4). If the CD-8 is an acceptor, its radiation anisotropy will drop substantially compared to measurements performed without the donor (curves 5, 6). Analogous changes (drops) in the radiation anisotropy compared to measurements performed without the donor were observed for the CV acceptor and acceptor "12," while the luminescence anisotropy of the C_2 donor generally remains unchanged in the presence of the CD-8 energy acceptor.

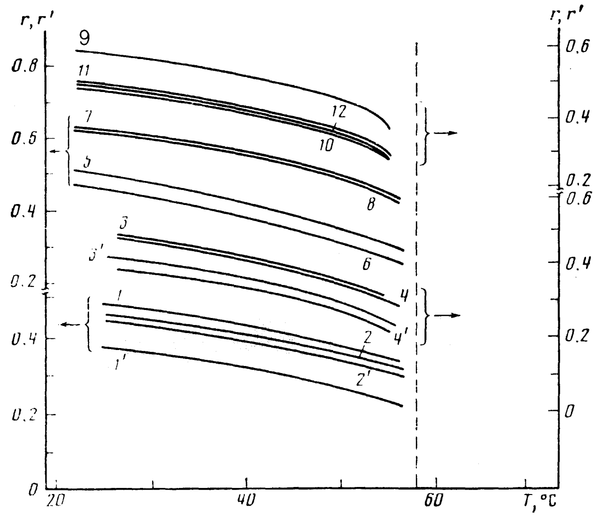

FIG. 3. Luminescence anisotropy of the donor (D) and acceptor (A) for the case of luminescence excitation by light parallel to the director [$r(T)$, curves 1–12] and perpendicular to the director [$r'(T)$, curves 1'–4']. CD-8 + CV pair: 1, 1'—A without D; 2, 2'—with D; 3, 3'—D without A; 4, 4'—with A. The C_2 + CD-8 pair; 5—A without D; 6—with D; 7—D without A; 8—with A. The CD-8 + "12" pair; 9—A without D; 10—with D; 11—D without A; 12—with A.

The effect of electron excitation energy transfer on the luminescence anisotropy of the acceptor has been considered previously for liquid solutions. It has been demonstrated[15] that the radiation anisotropy of the acceptor is given by $r_A = 0.016$ in such a system for the case of donor excitation by linearly polarized light, i.e., the radiation is nearly depolarized after a single transfer event due to the isotropic orientation distribution of the molecules. The low anisotropy obtained for such systems suggests that the excitation probability of the acceptors is generally independent of their orientation.

As discussed previously the orientations of the donor and acceptor molecules are determined by the distribution function $f(\theta)$ for the anisotropic state of the liquid crystal matrix which produces a sensitized luminescence anisotropy of the acceptor molecules that differs from the anisotropy in solutions.

As demonstrated in Ref. 4 the lifetime of a molecule in its excited state is comparable to but greater than the rotational relaxation time (see Ref. 16). Hence during the excitation process the acceptor molecules undergo many changes in spatial position, thereby resulting in radiation depolarization. The polarization is not complete as in the case of isotropic solutions, however, but only to a point corresponding to the order parameter $S = \langle P_2 \rangle$ which is determined from linear dichroism measurements. The observed drop in sensitized luminescence anisotropy of the acceptor is therefore due to the relaxation of the orientations of the excited molecules due to electron excitation energy transfer.

The luminescence intensity of the donor molecules alone diminishes when energy is transferred due to the excitation of the acceptor molecules, while no changes in donor radiation anisotropy occur. The radiation anisotropy of the donor will drop due to the increasing probability of energy transfer between the nearly parallel donor and acceptor molecules (see below) only in the case of very high orientational ordering of both the donor molecules and the acceptor molecules.

Energy transfer therefore has a substantial influence on the radiation anisotropy of the acceptor and measurements of such anisotropy can be used to determine the existence of energy transfer. We note that our calculations neglected diffusion anisotropy which is quite complex for nematic liquid crystals[13,17] as well as the local field anisotropy since such factors have little influence on energy transfer in liquid crystals. It is, however, important to note that all existing theories of luminescence polarizations are based on an expression for the absorption or radiation indicatrix of a dipole oscillator in an isotropic configuration. In an anisotropic medium such as a liquid crystal the indicatrix has substantially more complex angular dependence (see Ref. 18, 19 and Ref. 20 for nematic crystals). Such concepts are important for a critical evaluation of derived results.

3. KINETIC MEASUREMENT RESULTS

A number of studies devoted to the energy transfer kinetics in liquid solutions exist today (see Ref. 15 and the references contained therein), while the study of this same phenomenon in liquid crystal is only beginning to develop.[1,2] Given below are results from an analysis of energy transfer in liquid crystals using kinetic techniques: Studies of the decay of the polarization luminescence components of the donor and acceptor for two pairs, CD-8 (donor) + CV (acceptor) and C_2 (donor) + CD-8 (acceptor); these pairs have significant spectral overlapping (Fig. 1). The Foerster transfer radius R_0 determined from the overlapping spectra for these pairs are 46 ± 5 and 32 ± 5 Å, respectively.

Energy transfer causes the decay law of the donor to go from exponential

$$I(t)=I_0 \exp(-t/\tau_F), \qquad (1)$$

where τ_F is the donor lifetime in the excited state to nonexponential,

$$I(t)=I_0 \exp\left[-t/\tau_F-2q(t/\tau_F)^{1/2}\right], \qquad (2)$$

where q is the coefficient representing the energy transfer efficiency[15]; this coefficient is determined by the relative position of the donor and acceptor molecules. Figure 4 shows a characteristic experimental luminescence decay curve for the donor together with a comparison to decay laws (1) and (2). Clearly (2) matches the experimental curve within the 95% confidence range. Figure 4 shows calculated $I(t)$ curves for the transition of the decay law from (1) to (2). It turned out that τ_F was identical for anisotropic and isotropic liquid crystal states and amounted to 10.9 ± 0.1 ns. The rotational relaxation time τ_R was of the order of 2.7 ± 0.1 ns[4] (compare with Ref. 21, 22 as well).

If energy transfer causes the decay law of the donor to go from (1) to (2), the decay law of the acceptor will go from an exponential law to a complicated nonexponential relation that is difficult to analyze. However the luminescence decay curves of the acceptor suggest an effective increase in the acceptor lifetime due to the nonsimultaneous excitation of the acceptor molecules during energy transfer from the donor molecules (Fig. 5).

It was determined using formula (2) for the CD-8 + CV pair that $q = 0.5 \pm 0.02$ in the isotropic phase for the selected acceptor concentration while q increased 11–

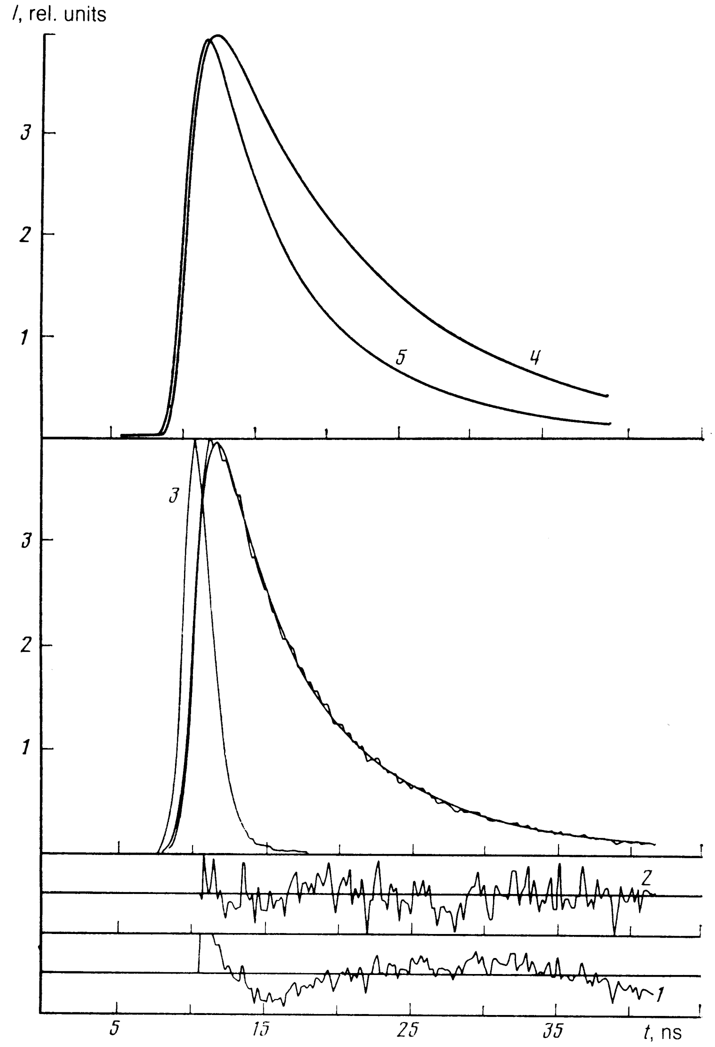

FIG. 4. Below: Experimental and calculated [by (2), smooth curve] luminescence decay curves of CD-8 in N106. RMS deviation: 1—Approximation of experimental curve by formula (1); 2—approximation of experimental curve by formula (2); 3—excitation plane. Above: Change in luminescence kinetics of CD-8 without (4) and with (5) energy transfer to the CV.

16% in the liquid crystal phase for the various specimens. An 8–12% growth in q was obtained for the C_2 + CD-8 pair in this transition.

The average value of the parameter q is determined by the expression

$$q=c_AR_0^6\left(\frac{2}{3}\right)^{1/2}\pi^{3/2}\frac{1}{(4\pi)^3}\iiint f_A(\mathbf{e}_A)f_D(\mathbf{e}_D)\times[\chi^2(\mathbf{e}_A,\mathbf{e}_D,\mathbf{e}_R)]^{1/2}\,d\Omega_A\,d\Omega_D\,d\Omega_R, \qquad (3)$$

where c_A is the acceptor concentration, and f_A, f_D are the acceptor and donor orientation distribution functions.

The coefficient χ accounting for the relative partner orientation is determined by the following relation:

$$\chi(\mathbf{e}_A,\mathbf{e}_D,\mathbf{e}_R)=\mathbf{e}_A\mathbf{e}_D-3(\mathbf{e}_A\mathbf{e}_R)(\mathbf{e}_D\mathbf{e}_R), \qquad (4)$$

where the vector $\mathbf{R}$ links the dipoles, $\mathbf{e}_A$, $\mathbf{e}_D$ are the unit vectors running along the dipole moments of the partners, and $\mathbf{e}_R$ is the unit vector in the direction of $\mathbf{R}$.

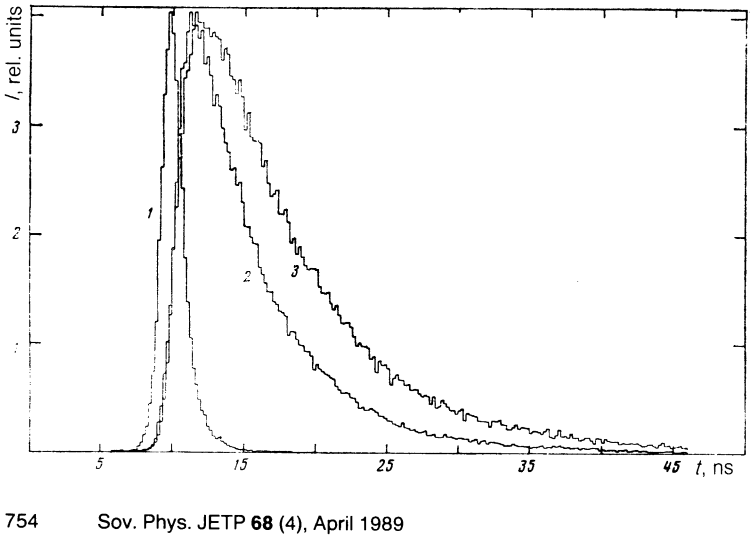

FIG. 5. Change in luminescence kinetics of CV acceptor without the CD-8 donor (curve 2) and with the CD-8 donor (curve 3). 1—Excitation pulse.

A calculation using (3) and assuming that the molecules do not move in the transition from the isotropic phase (IP) to the liquid crystal phase yields a change in q of $\approx 2\%$. The order parameter in this case was calculated for 22 °C using the data from Fig. 2 and here was ≈ 0.45 for the CD-8 + CV pair and ≈ 0.6 for C_2. The same calculation assuming free molecular rotation yielded values of q 18% higher than in the preceding case, although the change in q from the isotropic phase-to-liquid crystal transition was only $\approx 0.2\%$ (which seems natural), i.e., molecular rotation has a significant effect in both phases, yet does not explain the differences between them.

In reality there is, of course, no free rotation but rather high amplitude (of the order of 30°) rotational pumping.[4,16,23] However, accounting for this phenomenon will obviously cause a difference in q between the IP and LC ranging from 0.2–2%. In the case of fixed molecules and a partner group for the isotropic medium sufficiently large for averaging (ideal disorder, $S = 0$) $\langle \chi^2 \rangle$ is, as we know,[1] equal to 10/15. A calculation for fixed molecules with an ideally parallel orientation ($S = 1$, $\theta \sim 0$) yields $\langle \chi^2 \rangle = 12/15$, i.e., $\langle \chi^2 \rangle^{1/2}$ changes by $\approx 14\%$ in the transition from the isotropic medium to ideal ordering. This is relatively close to the change in q obtained experimentally.

It appears that molecular orientations are completely correlated ($S_{\text{loc}} = 1$) in liquid crystals at distances of the order of the Foerster radius (~ 50 Å), while the rotational relaxation time τ_R is the specimen average, as is the case with the indicated angles of rotation.

The present study has therefore employed static and kinetic techniques to analyze electron excitation energy transfer between impurity molecules in a liquid crystal matrix and has demonstrated the substantial effect of this process on the radiation anisotropy of the acceptor. It has also been demonstrated that the ratio between the lifetime of the molecule in the excited state and the rotational relaxation time is important in determining the change in energy transfer efficiency in the transition when the liquid crystal goes from an isotropic to an anisotropic state.

The kinetic and static methods allow determination of the existence and effectiveness of energy transfer in a liquid crystal medium, while the rate of change in the liquid crystal phase state establishes new possibilities both for investigating the energy transfer phenomenon and for further investigation of the structure and properties of the liquid crystal medium.

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