

Stationary polarized-fluorescence spectrum from an impure liquid crystal

E. M. Aver'yanov

L. V. Kirenski Institute of Physics, Siberian Branch, Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

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The stationary polarized-fluorescence spectrum from an impure nematic liquid crystal is investigated by a statistical molecular approach. For uniaxial molecules it is shown that the positions ν_{ij} of the centers of gravity of the bands $J_{ij}(\nu)$ are related to the electronic structure of the molecules (the orientation of the absorption and emission transition dipole moments), the parameters of their orientational ordering in the ground and excited states, and the characteristics of the orientational molecular dynamics and of the anisotropic interactions between the impurity and the matrix. The known experimental features of the spectrum ν_{ij} are explained. It is shown that data on the intensities and positions of the polarized absorption and fluorescence bands of the impurity can be used together to determine the parameters characterizing the relaxation of the environment surrounding excited impurity molecules in the nematic phase.

1. INTRODUCTION

The polarized fluorescence of impurity molecules in liquid crystals (LCs) and other anisotropic statistically ordered molecular media is a traditional method for studying the electronic structure of these molecules and their orientational ordering and dynamics.¹ The information obtained in this manner is limited primarily by the use of the intensities of the polarized impurity fluorescence bands, which are interpreted in the oriented molecular gas approximation.^{1–3} The experimental data show, however, that in several respects this approximation is quite limiting. For example, neglecting the anisotropy of the local field of the light wave acting on an impurity molecule can have unphysical experimental consequences, even for anisotropic matrices with weak birefringence,^{4,5} and neglecting the change induced in the impurity–matrix anisotropic interaction energy by electronic excitation of an impurity molecule contradicts observations^{6–10} showing that in liquid crystals and anisotropic polymer films,^{3,11} the positions ν_{ij} of the maxima of the stationary impurity-fluorescence bands $J_{ij}(\nu)$ depend on the polarization of the absorbed (i) and emitted (j) light.

The dependence of the impurity–matrix interaction energy on the electronic state of the impurity leads to two new processes: relaxation of the orientational ordering of the impurity subsystem^{12,13} and structural relaxation of the environment of fluorescent molecules over their lifetime in the excited state.¹² Together with orientational diffusion of the excited molecules, these processes determine the kinetics of the positions of the maxima (or centers of gravity) $\nu_{ij}(t)$ of the polarized components $J_{ij}(\nu, t)$ of the fluorescence of an impurity in a liquid crystal under pulsed excitation.^{12,14,15} Taking into account the relaxation of the orientational ordering of excited fluorescent molecules in the interpretation of the impurity-fluorescence intensity¹² has made it possible to remove the long-standing inconsistencies in these methods of kinetic and stationary fluorescence spectroscopy both with one another and with the results of independent measurements.^{13,16}

The characteristics of the relaxation of the environment surrounding excited molecules in liquid crystals and other anisotropic media are still not clear, in spite of their importance for the development of optical recording and information processing systems based on impurity molecules. In this respect the isotropic solutions using kinetic and stationary fluorescence have been investigated in detail.^{17–19} Even for them, however, the stationary polarized impurity-fluorescence spectrum is distinguished from the kinetic spectrum by a number of interesting features.²⁰ For this reason, used together, the data on the intensities and positions of the polarized fluorescence bands of an impurity could offer new possibilities for studying the relaxation of the environment surrounding fluorescent molecules in liquid crystals.

Our objective in the present paper is to determine the characteristics of the stationary fluorescence spectrum of an impurity in a liquid crystal and to determine whether they can be used to study the relaxation of the environment surrounding excited impurity molecules. In Sec. 2 a general expression is derived for the components of the spectrum ν_{ij} of impurity molecules, having arbitrary symmetry, in a nematic liquid crystal. The dependence of ν_{ij} on the electronic structure of molecules, orientational ordering of the impurity subsystem and liquid-crystal matrix, relaxation of this ordering, and anisotropic intermolecular interactions are investigated for the special case of uniaxial impurity molecules. An explanation is given for the experimentally observed features of the spectrum ν_{ij} .^{6–10} In Sec. 3 it is shown that the intensity data can be used together with data on the positions of the polarized absorption and fluorescence bands of the impurity to determine the parameters characterizing the above-noted relaxational processes. The existing experimental data are used to show that in nematic liquid crystals, the environment surrounding excited fluorescent molecules undergoes structural relaxation. In Sec. 4 the basic results of this work are briefly summarized.

2. STATIONARY POLARIZED FLUORESCENCE SPECTRUM FROM AN IMPURE NEMATIC

Consider a uniformly oriented nematic liquid crystal with a low concentration of impurity molecules which absorb and emit light in the transmission range of the matrix. Assume also that the ground and excited (emitting) states of the impurity are nondegenerate and that the conformation of the molecules does not change with excitation. In the laboratory coordinate system (x, y, z) with the director \mathbf{n} oriented parallel to the z axis, the electric vector of the exciting light (\mathbf{e}_i) and the electric vector of the analyzed light (\mathbf{e}_j) are oriented along the axes of this system. The directions of the molecular transition dipole moments associated with light absorption and emission are fixed by the unit vectors $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_e$, respectively. In the absence of nonlinear effects and reabsorption, the intensity of stationary fluorescence per impurity molecule is given by the expression

$$J_{ij}(\nu) = J_i(\nu_a) K_{ij} \int_0^\infty dt F(t) \langle I_{ij}(\Omega_0, \Omega_t) \rho(\nu, \Omega_t, t) \rangle, \quad (1)$$

$$I_{ij}(\Omega_0, \Omega_t) = [\mathbf{e}_i \boldsymbol{\mu}_a(\Omega_0)]^2 [\mathbf{e}_j \boldsymbol{\mu}_e(\Omega_t)]^2,$$

where the constant isotropic coefficients have been dropped. Here, $J_i(\nu_a)$ is the intensity of the exciting light flux; K_{ij} are corrections to the anisotropy of the local field of the light wave and the birefringence of the liquid crystal,^{4,21} and their dispersion within the band $J_{ij}(\nu)$ in the transmission range of the matrix can be neglected; $F(t) = \exp(-t/\tau_F)/\tau_F$, where τ_F is the effective fluorescence lifetime; the Euler angles Ω_0 and Ω_t characterize the orientation of the molecule in the laboratory coordinate system at the times $t=0$ and t when light is absorbed and emitted. The intramolecular relaxation time from the absorbing into the emitting level is assumed to be much shorter than the characteristic times over which the spatial coordinates of the molecules change during thermal motion. The brackets $\langle \dots \rangle$ indicate statistical averaging over the orientations of the excited impurity molecules with the nonequilibrium single-particle distribution function

$$f_e^{(n)}(\Omega_t) = \int d\Omega_0 f_g^{(eq)}(\Omega_0) P(\Omega_0 | \Omega_t), \quad (2)$$

which at $t=0$ is identical to the equilibrium distribution function $f_e^{(eq)}(\Omega_t)$ of the impurity molecules in their ground state. Here $P(\Omega_0 | \Omega_t)$ is the conditional probability distribution that a molecule whose orientation at time $t=0$ is Ω_0 has the orientation Ω_t at time t .

The shape of the fluorescence band $\rho(\nu, \Omega_t, t)$ of an individual impurity molecule is determined by intramolecular relaxation processes and, just as in the case of isotropic solutions,¹⁷⁻¹⁹ it is assumed to be independent of the phase state of the matrix and the orientation Ω_t of the molecule relative to the director \mathbf{n} . However, the position of the center of gravity $\nu_f(\Omega_t, t)$ of the band $\rho(\nu, \Omega_t, t)$ depends on the difference of the impurity-matrix anisotropic interaction energies in the nonequilibrium Franck-Condon excited state $E_e^{(n)}(t)$ and the ground state $E_g^{(n)}(t+0)$. A consequence of this is that ν_f depends on Ω_t and t .¹² In a uniaxial nonpolar nematic phase the general form of the function $\nu_f(\Omega_t, t)$ for molecules of arbitrary symmetry has the form¹²

$$\nu_f(\Omega_t, t) = \nu_0(t) - \sum_{Lk} \varepsilon_{Lk}(t) D_{0k}^L(\Omega_t), \quad (3)$$

where the summation over the Wigner D -functions $D_{0k}^L(\Omega_t)$ is restricted to even values of $L \geq 2$, and the isotropic term with $L=0$ is included in the center of gravity $\nu_0(t)$ of the impurity fluorescence band $J_{ij}(\nu, t)$ of the liquid crystal isotropic phase. The values of the index K are restricted by the operations of the point symmetry group of the impurity molecule. The time dependence of the parameter $\varepsilon_{Lk}(t)$ is due to the relaxation of the environment surrounding the impurity molecules while they occupy the excited state, and to the associated change in the impurity-matrix anisotropic interaction energy in both states $E_e^{(n)}(t)$ and $E_g^{(n)}(t+0)$.

Since the area under the curve $\rho(\nu, \Omega_t, t)$ is independent of $\Omega_{0,t}$ and t , the position of the center of gravity

$$\nu_{ij} = \int \nu J_{ij}(\nu) d\nu / \int J_{ij}(\nu) d\nu \quad (4)$$

of the components $J_{ij}(\nu)$ (1) assumes the form

$$\nu_{ij} = \frac{1}{I_{ij}} \int dt F(t) \left\{ \nu_{cg}(t) I_{ij}(t) - \sum_{Lk} \varepsilon_{Lk}(t) \times [\langle I_{ij}(\Omega_0, \Omega_t) D_{0k}^L(\Omega_t) \rangle - I_{ij}(t) \langle D_{0k}^L(\Omega_t) \rangle] \right\}. \quad (5)$$

Here $I_{ij}(t) = \langle I_{ij}(\Omega_0, \Omega_t) \rangle$ and

$$I_{ij} = \int I_{ij}(t) F(t) dt. \quad (6)$$

The expression

$$\nu_{cg}(t) = \nu_0(t) - \sum_{Lk} \varepsilon_{Lk}(t) \langle D_{0k}^L(\Omega_t) \rangle \quad (7)$$

gives the position of the center of gravity of the multiplet $\nu_{ij}(t)$ of all nine polarized components $J_{ij}(\nu, t)$ of the kinetic fluorescence spectrum excited by a pulse at time $t=0$. Since the expression for the maximum $\nu_j^{(m)}(\Omega_t, t)$ of the band $\rho(\nu, \Omega_t, t)$ is given by the same formula (3) with $\nu_0(t)$ replaced by $\nu_0^{(m)}(t)$, it can be shown by analogy to Ref. 12 that to a first approximation the position of the maximum $\nu_j^{(m)}$ of the band $J_{ij}(\nu)$ is given by the same formula (5). This explains the relative displacement of the bands $J_{ij}(\nu)$ as a whole relative to one another, for different values of the indices i, j , without any appreciable change in shape.¹⁰

For uniaxial impurity molecules the index $k=0$ in Eqs. (3), (5), and (7), and the expressions given in Ref. 12 for $I_{ij}(t)$ and the correlation functions $I_{ij}^L(t) = \langle I_{ij}(\Omega_0, \Omega_t) D_{00}^L(\Omega_t) \rangle$ can be used:

$$I_{ij}(t) = \frac{1}{9} \left\{ 1 + f_{ij} S_{\beta a} S_g + g_{ij} S_{\beta e} S(t) + \sum_n D_{n0}^{2*}(0, \beta_a, 0) D_{n0}^2(\alpha_e, \beta_e, 0) [h_{ij} \Phi_{0n}(t) + q_{ij} \Phi_{2n}(t)] \right\}, \quad (8)$$

$$\begin{aligned}
I_{ij}^L(t) = & \frac{1}{9} \left\{ \langle P_L(t) \rangle + f_{ij} S_{\beta_a} \langle P_2(0) P_L(t) \rangle \right. \\
& + g_{ij} S_{\beta_e} \langle P_2(t) P_L(t) \rangle \\
& + \sum_n D_{n0}^{2*}(0, \beta_a, 0) D_{n0}^2(\alpha_e, \beta_e, 0) \\
& \times [h_{ij} \langle D_{0n}^2(\Omega_0) D_{0n}^{2*}(\Omega_t) D_{00}^L(\Omega_t) \rangle \\
& \left. + q_{ij} \langle D_{2n}^2(\Omega_0) D_{2n}^{2*}(\Omega_t) D_{00}^L(\Omega_t) \rangle \right\}. \quad (9)
\end{aligned}$$

Here the angles β_a , α_e , and β_e specify the orientation of the unit vectors $\mu_a(\sin \beta_a, 0, \cos \beta_a)$ and $\mu_e(\sin \beta_e \cos \alpha_e, \sin \beta_e \sin \alpha_e, \cos \beta_e)$ in the molecular coordinate system, where the $\beta_{a,e}$ are the angles between $\mu_{a,e}$ and the long axis of the molecule, and $S_\beta = (3 \cos^2 \beta - 1)/2$; $P_L(t) = P_L(\cos \theta_t)$ are Legendre polynomials; θ_t is the angle between the long axis of the excited molecule and the director \mathbf{n} at time t ; $S_g = \langle P_2(\cos \theta) \rangle$ is the equilibrium orientational order parameter of the unexcited impurity molecules; $S(t) = \langle P_2(\cos \theta_t) \rangle$ is the nonequilibrium order parameter of the excited impurity molecules. At $t=0$ it equals S_g , and at $t=\infty$ it relaxes to the equilibrium value S_e . The functions $\Phi_{mn}(t) = \langle D_{mn}^2(\Omega_0) D_{mn}^{2*}(\Omega_t) \rangle$ are the orientational correlation functions.

The intensity $I_{ij}(t)$ has five independent components with $ij=zz, zx, xz, xx$, and xy , and the coefficients $(f, g, h, q)_{ij}$ assume the values

$$\begin{aligned}
f_{zz} = f_{zx} = g_{zz} = g_{xz} = h_{zz}/2 = -h_{zx} = -h_{xz} = 2, \\
f_{xx} = f_{xy} = f_{xz} = g_{xx} = g_{xy} = g_{zx} = -h_{xx} = -h_{xy} = -1, \\
q_{zz} = q_{zx} = q_{xz} = 0, \quad q_{xx} = -q_{xy} = 3. \quad (10)
\end{aligned}$$

We shall consider the cases $\beta_e=0$ and $\beta_a=0$, for which the index $n=0$ in Eqs. (8) and (9). It is convenient to start our analysis of the characteristic features of the spectrum ν_{ij} with the isotropic phase of the liquid crystal.

2.1. Isotropic phase of the liquid crystal

In this phase $S_g = S(t) = \varepsilon_{Lk}(t) = 0$, and the correlation functions $\Phi_{m0}(t) = 0.2 \exp(-t/\tau_R)$ with $m=0$ and 2 relax with the same relaxation time τ_R . The two independent components $I_{VV}(t)$ and $I_{VH}(t)$ with vertical (V) and horizontal (H) polarization of the radiation are given by

$$\begin{aligned}
I_{VV}(t) = 1 + \frac{4}{3} S_\beta \exp(-t/\tau_R), \\
I_{VH}(t) = 1 - \frac{2}{3} S_\beta \exp(-t/\tau_R). \quad (11)
\end{aligned}$$

In this case it is not important which moment μ_a or μ_e tilts away from the long axis of the molecule by the angle β . The centers of gravity ν_{VV} and ν_{VH} of the bands $J_{VV}(\nu)$ and $J_{VH}(\nu)$ are given by expressions which follow from Eqs. (5) and (11):

$$\begin{aligned}
\nu_{VV} = \nu_0 + \frac{4}{5} S_\beta \delta_{\nu R} \left[1 + \frac{4}{5} S_\beta \tau_R / (\tau_R + \tau_F) \right]^{-1}, \\
\nu_{VH} = \nu_0 - \frac{2}{5} S_\beta \delta_{\nu R} \left[1 - \frac{2}{5} S_\beta \tau_R / (\tau_R + \tau_F) \right]^{-1}, \quad (12)
\end{aligned}$$

where

$$\begin{aligned}
\nu_0 = \int dt F(t) \nu_0(t), \\
\delta_{\nu R} = \int dt F(t) \nu_0(t) \exp(-t/\tau_R) - \nu_0 \tau_R / (\tau_R + \tau_F). \quad (13)
\end{aligned}$$

The quantity ν_0 gives the position of the center of gravity of the band

$$\rho(\nu) = \int dt F(t) \rho(\nu, t) = \frac{1}{3} [J_{VV}(\nu) + 2J_{VH}(\nu)], \quad (14)$$

obtained at the magic angle $\theta_M = 54.7^\circ$ between the electric vectors of the exciting and analyzed radiation. Approximating the function $\nu_0(t)$ by the familiar expression^{2,17-19}

$$\nu_0(t) = \nu_0(\infty) + \Delta \nu \exp(-t/\tau_0), \quad (15)$$

where $\Delta \nu = \nu_0(0) - \nu_0(\infty)$, we obtain from Eq. (13)

$$\delta_{\nu R} = \frac{\Delta \nu \tau_0 \tau_R \tau_F^2}{(\tau_0 + \tau_F)(\tau_R + \tau_F)[(\tau_0 + \tau_F)(\tau_R + \tau_F) - \tau_F^2]}. \quad (16)$$

Since the function $\nu_0(t)$ is determined by the structural relaxation of the environment surrounding the fluorescent molecules while they are in the excited state,^{2,17-19} the parameter $\delta_{\nu R}$ characterizes the temporal correlation between two relaxational processes—rotational Brownian diffusion rearrangement of the coordination environment of the excited molecules.

In contrast to the previously studied²² influence of the correlation of these relaxational processes on the polarization characteristics of the spectra $J_{ij}(\nu, t)$, the difference of ν_{ij} discussed here refers only to the stationary spectrum $J_{ij}(\nu)$. There is no difference for the centers of gravity $\nu_{ij}(t) = \nu_0(t)$ of the bands $J_{ij}(\nu, t)$ in the isotropic phase.¹² The parameter $\delta_{\nu R}$ vanishes when at least one of the following conditions holds: $\tau_0 \gg \tau_F$ or $\tau_R \gg \tau_F$ or the inverse inequalities. The physical reason for the difference of ν_{VV} and ν_{VH} is that for $S_\beta \Delta \nu > 0$ the short-lived (long-lived) molecules with the spectrum $\rho(\nu, t)$ occupying higher (lower) frequencies make the greatest contribution to the component $J_{VV}(\nu)[J_{VH}(\nu)]$.

For $\tau_0 = \tau_R = \tau_F$, $\beta = 0$, and the typical value $\Delta \nu = 10^3 \text{ cm}^{-1}$, the splitting $\nu_{VV} - \nu_{VH} \approx 10^2 \text{ cm}^{-1}$ can be easily observed experimentally, and it is comparable to the difference $\nu_{xx} - \nu_{zz}$ in the stationary spectrum $J_{ij}(\nu)$ of the impurity fluorescence of nematic liquid crystals.⁶⁻¹⁰ The difference between the components ν_{VV} and ν_{VH} is larger for wide bands $\rho(\nu)$ (14) with a flat maximum. In the case of Stokes excitation of fluorescence we have $\Delta \nu > 0$,¹⁷⁻¹⁹ and the inequalities $\nu_{VV} \geq \nu_{VH}$ correspond to the inequalities $\beta \leq \beta_M = 54.7^\circ$. In the case of anti-Stokes excitation of fluorescence, in viscous solutions $\Delta \nu < 0$,¹⁸ and in the case $\beta \geq \beta_M$ we have $\nu_{VV} \leq \nu_{VH}$.

2.2. Nematic phase

For $\beta_e=0$ we obtain from Eqs. (5)–(9)

$$\nu_{ij} = \nu_0 - \rho$$

$$-\frac{g_{ij}(d - \delta_{\nu S}) + S_{\beta a}[f_{ij}a + h_{ij}(b - \delta_{\nu 0}) + q_{ij}(c - \delta_{\nu 2})]}{1 + g_{ij}S + S_{\beta a}[f_{ij}S_g + h_{ij}\Phi_{00} + q_{ij}\Phi_{20}]}. \quad (17)$$

The parameter ν_0 (13) can be represented here in terms of measured quantities in the form

$$\nu_0 = \frac{1}{3} (\nu_{VV} + 2\nu_{VH}) + \frac{2}{3} r (\nu_{VV} - \nu_{VH}), \quad (13')$$

where the fluorescence anisotropy

$$r = (J_{VV} - J_{VH}) / (J_{VV} + 2J_{VH}) \quad (18)$$

is expressed in terms of the spectrum-integrated intensities $J_{VV(VH)}$.

The stationary quantities S , Φ_{m0} , p , a , b , c , and d are the averages, calculated as in Eq. (6) by the $S(t)$ values, of the correlation functions $\Phi_{m0}(t)$ and the functions

$$p(t) = \sum \varepsilon_L(t) \langle P_L(t) \rangle, \quad (19)$$

$$a(t) = \sum \varepsilon_L(t) [\langle P_2(0)P_L(t) \rangle - S_g \langle P_L(t) \rangle], \quad (20)$$

$$d(t) = \sum \varepsilon_L(t) [\langle P_2(t)P_L(t) \rangle - S(t) \langle P_L(t) \rangle], \quad (21)$$

$$b(t) = \sum \varepsilon_L(t) [\langle P_2(0)P_2(t)P_L(t) \rangle - \Phi_{00}(t) \langle P_L(t) \rangle], \quad (22)$$

$$c(t) = \sum \varepsilon_L(t) [\langle D_{20}^2(\Omega_0)D_{20}^{2*}(\Omega_t)D_{00}^L(\Omega_t) \rangle - \Phi_{20}(t) \times \langle P_L(t) \rangle]. \quad (23)$$

The parameter p characterizes the shift of the center of gravity of the multiplet ν_{ij} at an isotropic liquid–liquid crystal phase transition. It does not depend explicitly on the angles $\beta_{a,e}$, and it is determined by both the magnitude and the relaxational characteristics of the parameters $\varepsilon_L(t)$ and $\langle P_L(t) \rangle$. To a first approximation,^{23,24} $\varepsilon_L(t) \sim S_M A_L(t)$, where S_M is the orientational order parameter of the matrix molecules. If the impurity–matrix anisotropic interaction energy in the state $E_e^{(n)}(t)$ is higher than in the state $E_g^{(n)}(t+0)$, then $A_L(t) > 0$. For the absorption spectra of dyes in liquid-crystal matrices, this has been confirmed in the case of the parameter $A_2(0)$ for a wide range of objects.^{9,10,23,24} As a result of the relaxation of the environment surrounding the excited fluorescent molecules in the state $E_e^{(n)}(t)$, the function $A_L(t)$ increases with time t . Together with the expected similar increase in the parameters $\langle P_L(t) \rangle$, which has been confirmed only for $\langle P_2(t) \rangle = S(t)$,^{13,16} this results in an increasing function $p(t)$ for fixed S_M . For a direct transition from the ground state into the excited emitting state of the fluorescent molecule, the value of $p(0)$ determines the displacement of the center of gravity of the doublet ν_{\perp} of the polarized components of the impurity absorption relative to

the position ν_i of the absorption band in the spectrum of the isotropic phase.²³ For this reason, for fixed parameter S_M in Eq. (17) $p > p(0)$, and at an isotropic liquid–liquid crystal transition, the long-wavelength shift in the center of gravity of the multiplet ν_{ij} is greater than the shift in the center of gravity of the doublet ν_{\perp} . This agrees with the experimental data.^{9,10} The inequality $p > p(0)$ should become stronger as τ_F increases.

The fraction in Eq. (17) is responsible for the difference of the quantities ν_{ij} , and it depends strongly on the angles $\beta_{a,e}$, the values and relaxational properties of the functions (19)–(23), and the values of τ_F . In limiting cases, when τ_F is much less or much greater than all characteristic relaxation times of the functions (19)–(23), the expression (17) reduces to the expression obtained previously¹² for $\nu_{ij}(t)$ at $t=0$ or $t=\infty$. We assume below that we are dealing with an intermediate situation. According to Eqs. (19)–(23), p , a , b , c , and d are proportional to S_M , and all other things being equal, the difference of the components ν_{ij} increases with S_M . This agrees with the data of Refs. 6, 9, and 10. The difference of the components ν_{ij} does not depend on the magnitude of the Stokes shift ν_0 with respect to ν_i in the isotropic phase. This is confirmed by the fact that the values of $\Delta\nu_f = \nu_{xx} - \nu_{zz}$ are close for different dyes, whose Stokes shifts ν_0 differ by an order of magnitude, in the same 5CB matrix.^{7,8,10}

When fluorescence is excited in different purely electronic or vibronic transitions with different angles $\beta_a(\nu_a)$, the values of ν_{ij} will be different, even though emission occurs from the same level. When, however, fluorescence is excited at different frequencies ν_a with the same values of β_a , the values of ν_{ij} should remain unchanged, as was observed in Ref. 8 in the components ν_{zz} and ν_{xx} for the dyes R823 and R829 in a 6CB matrix. By analogy to the case $\nu_{ij}(t=0)$,¹² Eqs. (10) and (17) imply that $I_{xz}(\beta_a=0) = I_{zz}(\beta_a=90^\circ)$ and $\nu_{xz}(\beta_a=0) = \nu_{zz}(\beta_a=90^\circ)$, but in contrast to $\nu_{ij}(t=0)$ the quantities $\nu_{xx}(\beta_a=0)$ and $\nu_{zx}(\beta_a=90^\circ)$ are now different, though they are close to one another. The degree of degeneracy of the spectrum ν_{ij} is specified by the quantity τ_F , the angles $\beta_{a,e}$, and the ratio of the parameters appearing in Eq. (17).

For $\beta_a = \beta_M$ we have $I_{xx} = I_{xy} = I_{zx}$ and $I_{xz} = I_{zz}$. This corresponds, for all possible values of τ_F , to partial degeneracy of the spectrum ν_{ij} with independent components $\nu_{xx} = \nu_{xy} = \nu_{zx} = \nu'_\perp$ and $\nu_{xz} = \nu_{zz} = \nu'_\parallel$, where

$$\nu'_\perp = \nu_0 - p + (d - \delta_{\nu S}) / (1 - S),$$

$$\nu'_\parallel = \nu_0 - p - 2(d - \delta_{\nu S}) / (1 + 2S). \quad (24)$$

At $t=0$ the quantity $a(0) = d(0)$ determines the splitting of the components ν_{\perp} in the absorption spectrum of the impurity for a direct transition from the equilibrium ground state $E_g^{(eq)}(0)$ into the excited emitting state $E_e^{(n)}(0)$,^{12,23} and for the dyes investigated thus far $a(0) > 0$,^{7–10,24} so that $a, d > 0$ and $\nu'_\perp > \nu'_\parallel$.

The parameters $\delta_{\nu S}$ and $\delta_{\nu m}$ in Eqs. (17) and (24) are given by

$$\delta_{\nu S} = \int dt F(t) S(t) [\nu_0(t) - p(t)] - S(\nu_0 - p), \quad (25)$$

$$\delta_{vm} = \int dt F(t) \Phi_{m0}(t) [v_0(t) - p(t)] - \Phi_{m0}(v_0 - p). \quad (26)$$

Since $v_0(t) \gg p(t)$ and $v_0 \gg p$, these parameters characterize primarily the temporal correlation in the relaxation of the local environment (which in the nematic phase is not much different from the isotropic phase) of the excited fluorescent molecules, and in the relaxation of the functions $S(t)$ and $\Phi_{m0}(t)$, which reflect the long-range orientational order and the rotational diffusion of these molecules in the nematic phase. The parameters δ_{vS} and δ_{vm} vanish in the limits $\tau_F \rightarrow 0$ and $\tau_F \rightarrow \infty$. If $\Delta v > 0$ in Eq. (15), then the difference $v_0(t) - p(t)$ decreases as t increases. Since $S(t)$ then increases^{13,16} and the functions $\Phi_{m0}(t)$ decrease, we have $\delta_{vS} < 0$ and $\delta_{vm} > 0$. For $\varepsilon_L(t) > 0$ we obtain, taking into account the results of Ref. 12, the inequalities $b(t) > 0$ and $c(t) < 0$, which also hold for the values of b and c averaged as in Eq. (6). The contributions of the parameters d and δ_{vS} (c and δ_{v2}) to ν_{ij} therefore reinforce one another, and the contributions of the parameters b and δ_{v0} to ν_{ij} suppress one another.

In the general case with $\beta_a \neq \beta_M$, the five independent components ν_{ij} correspond to five independent components I_{ij} . It follows directly from Eqs. (10) and (17) that $(\nu_{xx} \geq \nu_{xy}) > \nu_{zx} > \nu_{xz} > \nu_{zz}$ for $\beta_a = \beta_e = 0$. For $\nu_{xy} > \nu_{xx}$ and $\beta_a = 0$, there exists in the interval $0 < \beta_a < \beta_M$ an angle $\beta_a = \beta'_a$ for which $\nu_{xx} = \nu_{xy}$, and for $\beta_a > \beta'_a$, ν_{xx} and ν_{xy} vary with increasing β_a qualitatively as in the case $t = 0$.¹² For $\nu_{xx} > \nu_{xy}$ with $\beta_a = 0$, these parameters vary with increasing β_a as in the case $t = 0$,¹² and the inequalities $\beta_a \leq \beta_M$ correspond to the inequalities $\nu_{xy} \leq \nu_{xx}$. The inequality $\nu_{zx} > \nu_{xz}$ holds for all β_a , and becomes stronger as β_a increases. The expected ratios of the parameters ν_{ij} with $0 < \beta_a < \beta_M$ agree with the experimentally observed values.⁷⁻¹⁰

In Ref. 6, impurity fluorescence polarized along the z and x axes was excited by unpolarized radiation, i.e., the components $J_{iz}(\nu) = [J_{zz}(\nu) + J_{xz}(\nu)]/2$ and $J_{ix}(\nu) = [J_{zx}(\nu) + J_{xx}(\nu)]/2$ were recorded. The maxima ν_{iz} and ν_{ix} of these components satisfy $\nu_{zz} < \nu_{iz} < \nu_{zx}$ and $\nu_{zx} < \nu_{ix} < \nu_{xx}$. Accordingly, one would expect that $\nu_{ix} > \nu_{iz}$, which was in fact observed experimentally.⁶ For $\beta_a = 90^\circ$, $\nu_{zx} > \nu_{xy} > \nu_{xx} > \nu_{zz} > \nu_{xz}$.

Accidental degeneracy of the spectrum ν_{ij} could be due to the ratio of the parameters appearing in Eq. (17). For example, $\nu_{xz} = \nu_{zz}$ is possible if

$$2(d - \delta_{vS})(S_g + 2\Phi_{00}) = (a + 2b - 2\delta_{v0})(1 + 2S)$$

irrespective of the value of β_a . This situation was realized in Ref. 10 for a dye with $\beta_e = 0$ and $\beta_a = 15^\circ$.^{13,16}

For $\beta_a = 0$, the values of ν_{ij} are

$$\nu_{ij} = \nu_0 - p - \frac{f_{ij}a + S_{\beta e}[g_{ij}(d - \delta_{vS}) + h_{ij}(b - \delta_{v0}) + q_{ij}(c - \delta_{v2})]}{1 + f_{ij}S_g + S_{\beta e}[g_{ij}S + h_{ij}\Phi_{00} + q_{ij}\Phi_{20}]} \quad (27)$$

Comparison of Eqs. (10), (17), and (27) shows that β_e ($\beta_a = 0$) has the same effect on the ratio of ν_{xx} and ν_{xy} as

does β_a ($\beta_e = 0$) studied above, taking into account the unimportant replacement of $S_{\beta a}S_g$ by $S_{\beta e}S$. From Eqs. (10) and (27) it follows, by analogy with the case $\nu_{ij}(t=0)$,¹² that $I_{zx}(\beta_e = 90^\circ) = I_{zx}(\beta_e = 0)$, which corresponds to $\nu_{zz}(\beta_e = 90^\circ) = \nu_{zx}(\beta_e = 0)$. In contrast to $\nu_{ij}(t=0)$, however, the quantities $\nu_{xz}(\beta_e = 90^\circ)$ and $\nu_{xx}(\beta_e = 0)$ are now different, though close.

For $\beta_e = \beta_M$, partial degeneracy of the intensities $I_{xx} = I_{xy} = I_{xz}$ and $I_{zx} = I_{zz}$ corresponds to partial degeneracy of the spectrum ν_{ij} with components $\nu_{xx} = \nu_{xy} = \nu_{xz} = \nu'_\perp$ and $\nu_{zx} = \nu_{zz} = \nu''_\parallel$, which are given by

$$\begin{aligned} \nu'_\perp &= \nu_0 - p + a/(1 - S_g), \\ \nu''_\parallel &= \nu_0 - p - 2a/(1 + 2S_g). \end{aligned} \quad (28)$$

In contrast to $\nu'_{\perp,\parallel}$, the parameters $\nu''_{\perp,\parallel}$ do not depend on the values of δ_{vS} and δ_{vm} . Moreover, the difference $\nu'_\perp - \nu''_\parallel$ depends strongly on τ_F , and because $a \rightarrow 0$, it approaches zero as $\tau_F \rightarrow \infty$.¹²

In the case $\beta_e \geq \beta_M$, in the inequalities presented above for $\beta_a = 90^\circ$ ($\beta_e = 0$) the quantities ν_{zx} and ν_{xz} must also be interchanged for all $\nu_{xz} > \nu_{zx}$. For $0 < \beta_e < \beta_M$, however, the ratio of ν_{zx} and ν_{xz} depends on both parameters β_e and τ_F . For sufficiently large (small) τ_F and sufficiently small (large) β_e , the inequality $\nu_{xz} < \nu_{zx}$ ($\nu_{xz} > \nu_{zx}$) probably holds. The accidental degeneracy $\nu_{xz} \approx \nu_{zx}$ is therefore possible for intermediate values of τ_F and β_e .

In summary, in both cases $\beta_e = 0$ and $\beta_a = 0$ considered above, for values of τ_F comparable to the characteristic relaxation times of the system, except for cases of accidental degeneracy of the spectrum ν_{ij} , the number of independent components ν_{ij} corresponds to the number of independent components $J_{ij}(\nu)$ in the isotropic and nematic phases of the liquid crystal.

3. POLARIZED-FLUORESCENCE SPECTRUM AND THE RELAXATION OF THE ENVIRONMENT SURROUNDING IMPURITY MOLECULES

The relaxation of the environment surrounding excited impurity molecules in the nematic phase is of great interest for the theory of rotational Brownian diffusion of such molecules²⁵ and the interpretation of the observed anisotropy of the relaxation times τ_{m0} of the correlation functions $\Phi_{m0}(t)$.¹⁶ Relaxation of the environment changes $\varepsilon_L(t)$ and influences the values of each of the five unknown parameters appearing in Eqs. (17) and (27): p , a , $d' = d - \delta_{vS}$, $b' = b - \delta_{v0}$, and $c' = c - \delta_{v2}$. These parameters can be expressed, by means of Eqs. (10), (17), and (27), in terms of the measured quantities ν_{ij} and I_{ij} . For $\beta_e = 0$ we obtain

$$P = \nu_0 - \sum_j (\nu_{zj}I_{zj} + 2\nu_{xj}I_{xj}), \quad (29)$$

$$a = S_g(\nu_0 - p) - \frac{1}{S_{\beta a}} \sum_j (\nu_{zj}I_{zj} - \nu_{xj}I_{xj}), \quad (30)$$

$$d' = S(\nu_0 - p) - \sum_i (\nu_{iz}I_{iz} - \nu_{ix}I_{ix}), \quad (31)$$

$$b' = \frac{1}{2S_{\beta a}} [(\nu_0 - p)(1 + 2S_{\beta a}\Phi_{00}) - 3(\nu_{xx}I_{xx} + \nu_{xy}I_{xy} + \nu_{zz}I_{zz})], \quad (32)$$

$$c' = \Phi_{20}(\nu_0 - p) - \frac{3}{2S_{\beta a}} (\nu_{xx}I_{xx} - \nu_{xy}I_{xy}). \quad (33)$$

Here the summation extends over $i, j = x, y, z$ and the equivalence of the pairs zx and zy , xz and yz , and xy and yx is taken into account. The formula (29) does not depend on the orientation of the vectors μ_a and μ_e in the molecular coordinate system. For $\beta_a = 0$ and $\beta_e \neq 0$, we must set $S_{\beta a} = 1$ in Eq. (30); in Eq. (31) the sum must be divided by $S_{\beta e}$, and in Eqs. (32) and (33) $S_{\beta a}$ must be replaced by $S_{\beta e}$. The products $S_{\beta a}S_g$, $S_{\beta e}S$, and $S_{\beta}\Phi_{m0}$ in I_{ij} can be found from the three degrees of depolarization $R_j = J_{ij}/J_{ii}$ ($j = x, y, z$) of the fluorescence bands (1) and the dichroism of the absorption of the exciting radiation.^{13,16}

The most informative parameters are p and a and the parameter

$$\varphi = a + pS_g, \quad (34)$$

defined in terms of them. Comparison of quantities with the experimental values of $p(0)$, $a(0)$, and $\varphi(0)$ yields information about the relaxation of $\varepsilon_L(t)$. According to Ref. 23, in the case of uniaxial impurity molecules with the electronic transition moment polarized along the long axis of the molecule, the positions of the maxima ν_{\perp} of the polarized components $D_{\parallel,\perp}(\nu)$ of the optical density are

$$\begin{aligned} \nu_{\perp} &= \nu_i - p(0) + a(0)/(1 - S_g), \\ \nu_{\parallel} &= \nu_i - p(0) - 2a(0)/(1 + 2S_g), \end{aligned} \quad (35)$$

where ν_i is the position of the maximum of the impurity absorption band in the isotropic phase of the matrix. Hence we obtain

$$\begin{aligned} p(0) &= \nu_i - \frac{1}{3}(\nu_{\parallel} + 2\nu_{\perp}) + \frac{2}{3}S_g(\nu_{\perp} - \nu_{\parallel}), \\ a(0) &= \frac{1}{3}(1 - S_g)(1 + 2S_g)(\nu_{\perp} - \nu_{\parallel}). \end{aligned} \quad (36)$$

We now use the experimental data on $\nu_{\parallel,\perp,i}$, ν_0 , and ν_{ij}^0 and S_g , S , and Φ_{m0}^3 for a fluorescent dye with $\beta_a = 15^\circ$ and $\beta_e = 0$ in the nematic 5CB matrix, to determine the values of p , $p(0)$, a , and $a(0)$ for different values of $\Delta T = T_c - T$, where T_c is the temperature of the nematic-isotropic liquid phase transition. For $\Delta T = 1$ K, we obtain (in cm^{-1})

$$\begin{aligned} p(0) &= 5, \quad \varphi(0) = 14, \quad a(0) = 13, \\ p &= 24, \quad \varphi = 20, \quad a = 12. \end{aligned} \quad (37)$$

Using Eqs. (19), (20), and (34) and the difference between S_g and S ,¹³ it follows that the parameters $\varepsilon_L(t)$ increase with t , and their rate of change is greater than the rate of increase of $\langle P_L(t) \rangle$ or the rate of decrease of the correlation functions $\langle P_2(0)P_L(t) \rangle$, but comparable to the rate of decrease of the correlation functions¹²

$$\Delta_{2,L}^{0,t} = \langle P_2(0)P_L(t) \rangle - \langle P_2(0) \rangle \langle P_L(t) \rangle.$$

This agrees with the experimental data of Ref. 15 on the kinetics of $\nu_{cg}(t) = \nu_0(t) - p(t)$ for the maximum of the monomeric fluorescence band of the 5CB molecules themselves at temperatures $T \leq T_c$. After pulsed excitation at $t=0$, the quantity $\nu_{cg}(t)$ saturates at $t \approx 100$ ps,¹⁵ i.e., the effective relaxation time τ_e^t of the parameters $\varepsilon_L(t)$ is some tens of picoseconds for this liquid crystal and this temperature range, and is less than the relaxation time τ_{00} of the correlation function $\Phi_{00}(t) = \langle P_2(0)P_2(t) \rangle$ (which is of the order of nanoseconds). It should be noted that just as in the case of isotropic solutions, different types of anisotropic impurity-matrix interactions with a corresponding spectrum of relaxation times contribute to the parameters $\varepsilon_L(t)$ of each rank.^{17,19} It is therefore only to a first approximation that $\varepsilon_L(t)$ can be regarded as relaxing with only a single effective relaxation time τ_e^t . For $\Delta T = 13$ K, we obtain (in cm^{-1})

$$\begin{aligned} p(0) &= 26, \quad \varphi(0) = 30, \quad a(0) = 17, \\ p &= 32, \quad \varphi = 31, \quad a = 15. \end{aligned} \quad (38)$$

Comparison with Eq. (37) shows that far from T_c , in addition to ε_L increasing owing to an increase in the orientational ordering of the liquid crystal, the rate of change of $\varepsilon_L(t)$ decreases, as a result of which the ratios $p/p(0)$, $\varphi/\varphi(0)$, and $a/a(0)$ decrease compared to their values at $T \approx T_c$. This agrees with existing data on the relaxation of a solvent in the case of isotropic solutions,^{17,19} and it may be connected with both an increase in the local viscosity of the matrix with decreasing temperature T and a change in the orientational ordering of the liquid crystal. The large difference in $p(0)$ at $\Delta T = 1$ K and 13 K indicates that the contributions to $p(0)$ of terms with different values of L become redistributed as the orientational ordering of the impurity subsystem changes. Moreover, the ratios of the parameters $\varepsilon_L(t)$ of different rank can vary with time t .

4. CONCLUSIONS

The present approach to analyzing the stationary polarized fluorescence spectrum of an impurity in a nematic liquid crystal is not tied to any specific type of intermolecular interaction or model representation of the ordering and dynamics of the impurity molecules. The results of our analysis agree with all existing experimental data for uniaxial fluorescence molecules with respect to the number of independent components ν_{ij} , the ratio between these components for different orientations of the absorbing and emitting oscillators relative to the longitudinal molecular axis, and the dependence of the shift of the center of gravity ν_{cg} of the multiplet ν_{ij} and the differences of the components ν_{ij} on the orientational ordering of the matrix and the impurity subsystem. If there is no accidental degeneracy of the spectrum ν_{ij} , the number of independent components ν_{ij} equals the number of independent components of the intensity $J_{ij}(\nu)$ in the isotropic and nematic phases of the liquid crystal.

Quantitative information about the parameters characterizing the relaxation of the environment surrounding the excited impurity molecules in the nematic phase can be obtained by using data on the intensity, together with data on the position of the polarized bands in the impurity absorption

and stationary fluorescence spectra. The temporal correlation between the coupled Brownian rotational diffusion of excited molecules and the relaxation of their environment contributes to the difference of the components ν_{ij} in the nematic phase, and it is responsible for the difference of the centers of gravity of the two independent polarized components $J_{ij}(\nu)$ in the isotropic phase. The latter effect is a characteristic feature of the stationary spectrum $J_{ij}(\nu)$ and is absent from the kinetic spectrum $J_{ij}(\nu, t)$ of the same system.

The approach developed here can be tailored to the interpretation of the stationary fluorescence spectra of arbitrary impurity molecules in uniaxial molecular media of different nature.

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