Polarized luminescence spectrum of an impure liquid crystal: degeneracy lifted and restored by relaxation

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A general molecular-statistics approach is taken to analyze the polarized luminescence spectrum for impurity molecules of arbitrary symmetry in a matrix of a nematic liquid crystal. The particular case of uniaxial molecules is used to study how the electronic structure of the molecules, their orientational statistics, the molecular dynamics, and the anisotropic intermolecular interaction influence the positions $\nu_{ij}(t)$ of the peaks of the polarized impurity fluorescence bands $J_{ij}(\nu,t)$. It is shown, for the first time, that all these factors strongly influence the degree of degeneracy of the $\nu_{ij}(t)$ spectrum. At $t\neq 0$ the relaxation of the subsystem of excited impurity molecules toward an equilibrium orientational distribution lifts the partial degeneracy of the ν_{ij} spectrum which prevailed at $t=0$. It then restores a partial or complete degeneracy of the ν_{ij} spectrum in the limit $t=\infty$. If there is no degeneracy of the ν_{ij} spectrum at $t=0$, the relaxation may impose a partial degeneracy at $t\neq 0$, depending on the particular electronic structure of the molecules. The results of this study explain existing experimental data on the number of independent components ν_{ij}, the relations among them, the dependence of ν_{ij} on the order of the matrix and of the impurity subsystem, and the relationships between the positions of the polarized components of the impurity band in the absorption and fluorescence spectra.

1. INTRODUCTION

Recent years have seen increasing interest in the general physical consequences of, and new experimental manifestations of, such features of liquid crystals as the statistical nature of the molecular order and the anisotropy of the rotational diffusion of molecules, accompanied by a relaxation of the temporal correlation functions.[1] The latter effect can be seen in the intensity of the polarized luminescence bands of liquid crystals, among other places.[2–5] There has accordingly been a substantial increase in research on impure nematic liquid crystals by time-resolved fluorescence spectroscopy.[6–12] This research has provided new information on the anisotropy of the rotational-diffusion times and of the diffusion tensor of molecules, on the orientational statistics of impure nematic liquid crystals, and on their local order at the scale of molecular dimensions.

It has also been shown[13–15] that static splitting of polarized bands of electronic absorption and of Raman scattering is a general consequence of the nonuniformity of the orientational distribution of impurity molecules in a liquid crystal. By combining data on the intensity (dichroism) with data on the splitting of absorption bands, one can obtain information on the order parameters[15] $\langle P_{2,4}\rangle$ which is attainable (with the help of the band intensities) only by the methods of Raman scattering and polarized luminescence.

In the impurity luminescence, in contrast with the absorption of a liquid crystal the spectral positions of the polarized bands are determined by both the statistical properties of the orientational order and the anisotropy of the rotational diffusion of molecules. In this case we can thus expect an interesting joint manifestation of these properties of liquid crystals. It has been found that the positions ν_{ij} of the peaks of the impurity fluorescence $J_{ij}(\nu)$ in numerous liquid-crystal matrices[16–19] depend on the polarizations of the absorbed light (i) and of the emitted light (j) with respect to the director **n**. This circumstance, along with the giant spectral response of the liquid crystals to the application of fields in the course of Fréedericksz transitions,[20] opens up the possibility of new applications of liquid crystals in devices with controllable spectral properties.[21]

On the theoretical side, several questions concerning the interpretation of experimental data and the dependence of $\nu_{ij}(t)$ on the electronic structure of the molecules, the orientational statistics, and the molecular dynamics of liquid crystals remain open. These questions are the subject of the present study. The components $\nu_{xx}(0)$ and $\nu_{zz}(0)$ were found in Ref. 22 on the basis of a model for a particular type of intermolecular interactions, under a large number of special assumptions. In the present paper we instead take a general approach, which is not restricted by a model. We focus in particular on the role played by relaxation processes in shaping all the independent components $J_{ij}(\nu,t)$ and $\nu_{ij}(t)$ of the fluorescence spectrum.

In Sec. 2 of this paper we derive general expressions for $\nu_{ij}(t)$ and for the intensity components $J_{ij}(\nu,t)$ in the case of uniaxial molecules. We allow for a difference between the energies of the interaction of a molecule with its surroundings when the molecule is in its ground and excited states. We derive an expression for the anisotropy $r(t)$ of the polarized fluorescence, taking account of the difference between the equilibrium order parameters $\langle P_{2,4}(t)\rangle$ in the ground state ($t=0$) and in the excited state ($t=\infty$). In

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Sec. 3 we study the behavior of $\nu_{ij}(t)$ as a function of the particular features of the electronic structure, the order, and the orientational statistics of the molecules at $t \geqslant 0$ and ∞. We offer an explanation for the results of Refs. 16–19, and we identify features of the $\nu_{ij}(t)$ spectrum which stem from a relaxation of temporal orientational correlation functions.

2. INTENSITY OF THE POLARIZED FLUORESCENCE OF IMPURITY MOLECULES IN A NEMATIC LIQUID CRYSTAL

In order to avoid having to deal with effects which stem from the exchange of excitation in the impurity-matrix system and from the migration of excitation energy in the impurity subsystem, we consider a nematic liquid crystal with a low concentration of fluorescent molecules which absorb and emit light in the transmission region of the matrix. We also assume that the electronic excitation of the molecules is not accompanied by a change in their conformation. It was assumed in some previous studies,[2–5] which serve as the basis for an interpretation of experiments on the intensity of impurity fluorescence bands, that the properties of the fluorescing molecules do not depend on their electronic state. That purely geometric approach is inadequate for analyzing the shape of the bands $J_{ij}(\nu,t)$, and it is inconsistent with some recent experimental data.

Let us take a brief look at the physical picture. In the electronic ground state $E_g^{(\text{eq})}$, the subsystem of impurity molecules is characterized by an equilibrium orientational distribution function $f_g^{(\text{eq})}$ and by the equilibrium moments $\langle D_{0k}^L(\Omega)\rangle_g^{(\text{eq})}$ of this function. These moments are the orientational order parameters. During pulsed excitation of impurity molecules at the time $t=0$, the transition of these molecules into an excited electronic state leads to changes in several anisotropic molecular properties (the dipole moment and the polarizability tensor, among others[23,24]) and in the anisotropic impurity-matrix interactions. These changes can be seen directly in the static shift and splitting of the peaks of the polarized bands of impurity electronic absorption in the phase transition from an isotropic liquid to a liquid crystal.[13–15,25] The intramolecular relaxation from an absorbing level to an emitting level, accompanied by an additional change in the properties of the fluorescent molecule, occurs over a time significantly shorter than the time scales of the changes in the spatial coordinates of the molecules. The transition of an impurity molecule from the equilibrium ground state to the nonequilibrium emitting state $E_e^{(n)}(t)$ thus does not alter the orientational distributions of the impurity and matrix molecules. At $t=0$, the nonequilibrium distribution function $f_e^{(n)}(\Omega_t)$, of the excited molecules, and its nonequilibrium moments $\langle D_{0k}^L(\Omega_t)\rangle_e^{(n)}$ are the same as $f_g^{(\text{eq})}(\Omega)$ and $\langle D_{0k}^L(\Omega)\rangle_g^{(\text{eq})}$. The equilibrium order parameter of the impurity subsystem, $S_g \equiv \langle D_{00}^2(\Omega)\rangle_g^{(\text{eq})}$, can thus be determined from the dichroism of the electronic absorption bands.

If the lifetime of a molecule in the excited state is $t>0$, the rotational diffusion of impurity molecules occurs in a fashion which is matched with the spatial (orientational and translational) relaxation of the surrounding matrix molecules to the new equilibrium state $E_e^{(\text{eq})}(\infty)$. This new state corresponds to the maximum of the energy of the interaction of the excited impurity with the matrix. In this state the equilibrium distribution function $f_e^{(\text{eq})}(\Omega)$ of the excited molecules at $t=\infty$, and the equilibrium moments of this distribution, $\langle D_{0k}^L(\Omega)\rangle_e^{(\text{eq})}$, differ from $f_g^{(\text{eq})}(\Omega)$ and $\langle D_{0k}^L(\Omega)\rangle_g^{(\text{eq})}$. Experiments show that S_g can be either greater than[7,8] or less than[23,24,26] S_e, depending on the particular system. The difference can reach 30–70%. The approximation $f_g^{(\text{eq})}(\Omega) = f_e^{(\text{eq})}(\Omega)$, which is widely used in interpreting the intensities of polarized fluorescence spectra in the case of steady-state excitation, would thus introduce some uncontrollable errors in the values found for the order parameters $\langle P_{2,4}\rangle$.

If light is emitted at the time t, the impurity molecules go into a nonequilibrium ground state $E_g^{(n)}(t+\tau)$ with a nonequilibrium distribution function $f_g^{(n)}(\Omega_\tau)$ and with nonequilibrium order parameters $\langle D_{0k}^L(\Omega_\tau)\rangle_g^{(n)}$. For $\tau=0$, this distribution function and these order parameters are the same as the nonequilibrium values $f_e^{(n)}(\Omega_t)$ and $\langle D_{0k}^L(\Omega_t)\rangle_e^{(n)}$. With increasing τ, the relaxation of the state of the impurity subsystem to its original equilibrium state $E_g^{(n)}(\infty) = E_g^{(\text{eq})}(t=0)$ is accompanied by a relaxation of the distribution function to its original equilibrium version, as the result of a self-consistent orientational diffusion of impurity molecules and relaxation of the surroundings of these molecules. Under the assumptions adopted above, the presence of a nonequilibrium state $E_g^{(n)}(\tau)$ is not manifested in the intensity of the impurity fluorescence bands, but it does strongly influence the positions of these bands.

We consider a uniformly oriented nematic liquid crystal with a director $\mathbf{n}\parallel z$ in the laboratory system x, y, z. The electric vectors of the exciting light ($\mathbf{e}_i$) and of the light being analyzed ($\mathbf{e}_j$) coincide with axes of this coordinate system. The directions of the dipole moments of the molecular transitions associated with absorption and emission are specified by the unit vectors $\boldsymbol{\mu}$ and $\bar{\boldsymbol{\mu}}$, respectively. The intensity of the impurity fluorescence excited by a δ-function pulse at the time $t=0$ and measured after a time interval t is given by

$$\begin{aligned} J_{ij}(\nu,t) &= F(t)K_{ij}\langle I_{ij}(\Omega_0,\Omega_t)\rho(\nu,\Omega_t,t)\rangle, \\ I_{ij}(\Omega_0,\Omega_t) &= [\mathbf{e}_i\boldsymbol{\mu}(\Omega_0)]^2[\mathbf{e}_j\bar{\boldsymbol{\mu}}(\Omega_t)]^2. \end{aligned} \tag{1}$$

The function $F(t)=\exp(-t/\tau_F)/\tau_F$ characterizes the attenuation of the fluorescence of the impurity molecule in the sample, and τ_F is the effective lifetime of the molecules in the excited state. According to the experimental data of Refs. 6–12, this $F(t)$ dependence and the parameter τ_F remain the same in the course of the phase transition from an isotropic liquid to a nematic liquid crystal. The change in τ_F in the mesophase is negligible. The possible weak $F(\Omega)$ dependence for the impurity molecules in the liquid crystal can thus be ignored. The anisotropic coefficients K_{ij} depend on the optical anisotropy of the liquid-crystal matrix, on the anistropy of the local field of the light wave which is acting on a molecule, and on the experimental geometry.[27,28] We are omitting all the constant isotropic coefficients in (1).

The shape of the fluorescence band $\rho(\nu)$ of an individual impurity molecule is governed by intramolecular relaxation processes. To lowest order it is independent of the phase state of the matrix and of the orientation Ω_t of the molecule with respect to the director $\mathbf{n}$. However, the peak position ν_f of the $\rho(\nu)$ band is determined by the difference between the energies of the anisotropic interaction of the impurity with the matrix in the $E_e^{(n)}(t)$ and $E_g^{(n)}(t+0)$ states. Accordingly, ν_f depends on the orientation Ω_t of the impurity molecule in the field of its neighbors. In addition, even for a fixed orientation of the impurity with respect to the director, the relaxation of the surroundings in the $E_e^{(n)}(t)$ state and the corresponding change in the energy of the anisotropic impurity-matrix interaction over time, for both states $E_e^{(n)}(t)$ and $E_g^{(n)}(t+0)$, would lead to an explicit $\nu_f(t)$ dependence. The simultaneous, coordinated rotational diffusion of the impurity molecules and relaxation of their surroundings give rise to a $\nu_f(\Omega_t,t)$ dependence, which is reflected by the notation $\rho(\nu,\Omega_t,t)$ in Eq. (1). The angle brackets in (1) mean a statistical average over the impurity subsystem for all motions of the impurity molecules in the interval $0-t$.

In the isotropic phase of the liquid crystal, at a temperature sufficiently far from the temperature T_c at which the isotropic–nematic transition occurs, there is no local orientational order.[6,8,29] In this case the time evolution of the peak $\nu_0(t)$ of the $J_{ij}(\nu,t)$ bands is similar to that for the impurity fluorescence spectra in isotropic solutions.[30] In a nematic phase, the most common form of the $\nu_f(\Omega_t,t)$ dependence for an individual impurity molecule corresponds to an expansion in Wigner D functions:

$$\nu_f(\Omega_t,t)=\nu_0(t)-\sum_{Lmn}\varepsilon_{Lmn}(t)D_{mn}^{L}(\Omega_t), \tag{2}$$

where the coefficients are

$$\varepsilon_{Lmn}(t)=-\frac{2L+1}{8\pi^2}\int\nu_f(\Omega_t,t)D_{mn}^{L*}(\Omega_t)d\Omega_t. \tag{3}$$

The summation in (2) is over integer values $L>0$; the term with $L=0$ is incorporated in $\nu_0(t)$. The minus sign in (2) means that the energy of the anisotropic interaction of the excited impurity with its surroundings in the $E_e^{(n)}(t)$ state is larger than the energy of the unexcited impurity molecule with surroundings in the $E_g^{(n)}(t+0)$ state. Various types of intermolecular interactions contribute to the coefficients ε_{Lmn} of a certain rank L. In general, therefore, some of the coefficients ε_{Lmn} may be negative (cf. Ref 14). The time dependence $\varepsilon_{Lmn}(t)$ stems from relaxation of the surroundings of the excited molecule. The function $\nu_f(\Omega_t,t)$ must be invariant under the symmetry operations of the point symmetry groups of the liquid crystal and the impurity molecules. In a nematic, the uniaxial symmetry and the presence of a symmetry center restrict the summation in (2) to even values of L and to $m=0$. Limitations are imposed on the index n by the group symmetry operations of the impurity molecule.

The position of the peak $\nu_{ij}(t)$ of the component $J_{ij}(\nu,t)$ is given by the equation $dJ_{ij}(\nu,t)/d\nu=0$ or

$$\langle I_{ij}(\Omega_0,\Omega_t)\rho'(\nu,\Omega_t,t)\rangle=0. \tag{4}$$

A solution of this equation can be found, within a specified error, by expanding the derivative $\rho'(\nu,\Omega_t,t)$ in a series in $[\nu-\nu_f(\Omega_t,t)]$ near $\nu=\nu_f(\Omega_t,t)$ and by retaining only a finite number of terms. Since the difference $\nu_{ij}-\nu_0$ is usually considerably smaller than the half-width of the $J_{ij}(\nu)$ bands,[16-19] it is sufficient to use the linear approximation. As a result we find

$$\nu_{ij}(t)=\nu_0(t)-\left\langle I_{ij}(\Omega_0,\Omega_t)\sum\varepsilon_{Lmn}(t)D_{mn}^{L}(\Omega_t)\right\rangle\Big/ \langle I_{ij}(\Omega_0,\Omega_t)\rangle. \tag{5}$$

The position $\nu_{ij}(t)$ does not depend explicitly on the optical anisotropy of the matrix or the anisotropy of the local field. These factors do play a definite role in the derivation of the quantities $\nu_{xx}(0)$ and $\nu_{zz}(0)$ for a particular type of intermolecular interaction,[22] but they are not necessary for determining the features of the $\nu_{ij}(t)$ spectrum.

The correction to the intensity $J_{ij}(\nu_{ij},t)$ at the peak for the difference between the values of $\nu_{ij}(t)$ can be found by expanding the function $\rho(\nu)$ in (1) in a series of $[\nu-\nu_f(\Omega_t,t)]$ and retaining terms up to quadratic, and also by replacing ν by $\nu_{ij}(t)$ from (5). As a result we find

$$J_{ij}(\nu_{ij},t)=F(t)\rho(\nu_f)K_{ij}\left\langle I_{ij}(\Omega_0,\Omega_t)\left\{1-\frac{\alpha}{2}[\nu_{ij}(t)-\nu_f(\Omega_t,t)]^2\right\}\right\rangle, \tag{6}$$

where $\alpha=|\rho''(\nu_f)|/\rho(\nu_f)$ and where we have, in order of magnitude, $\alpha/2\simeq I/\Gamma^2$, where Γ is the half-width of the $\rho(\nu)$ band. For known systems,[16-19] the second term in curly brackets (braces) is therefore small in comparison with unity, and with good accuracy we can set

$$\begin{aligned}J_{ij}(\nu_{ij},t)&=F(t)\rho(\nu_f)K_{ij}\langle I_{ij}(\Omega_0,\Omega_t)\rangle\\&\equiv F(t)\rho(\nu_f)K_{ij}I_{ij}(t).\end{aligned} \tag{7}$$

As in the case of absorption,[13] the intensity of the polarized impurity fluorescence bands is only slightly sensitive to the anisotropic impurity-matrix interactions, provided that these interactions are not accompanied by the formation of complexes or by other perturbations of the electronic structure of the impurity molecules which would lead to significant changes in the shape of the $\rho(\nu)$ bands. However, the shape of the $J_{ij}(\nu,t)$ band in (1) and its half-width $\Gamma_{ij}(t)$ are not the same as $\rho(\nu)$ and Γ.

Below we discuss fluorescent molecules with an effective cylindrical symmetry. Expressing μ_i^2 and $\bar{\mu}_j^2$ in terms of the irreducible components of the tensor $\mathbf{A}=\boldsymbol{\mu}\otimes\boldsymbol{\mu}$ and $\bar{\mathbf{A}}=\bar{\boldsymbol{\mu}}\otimes\bar{\boldsymbol{\mu}}$ (Ref. 22), we switch to parameters which characterize the orientation of the transition moments in the molecular coordinate system and the orientation of this system with respect to the laboratory system. As a result we find the following expressions for the independent component $I_{ij}(t)$ in (7):

$$I_{zz}(t)=\tfrac{1}{9}+\tfrac{2}{9}S_{\beta a}\langle P_2(0)\rangle+\tfrac{2}{9}S_{\beta e}\langle P_2(t)\rangle$$
$$+\tfrac{4}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,\Phi^{22}_{0n}(t), \qquad (8)$$

$$I_{zx}(t)=\tfrac{1}{9}+\tfrac{2}{9}S_{\beta a}\langle P_2(0)\rangle-\tfrac{1}{9}S_{\beta e}\langle P_2(t)\rangle$$
$$-\tfrac{2}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,\Phi^{22}_{0n}(t), \qquad (9)$$

$$I_{xz}(t)=\tfrac{1}{9}-\tfrac{1}{9}S_{\beta a}\langle P_2(0)\rangle+\tfrac{2}{9}S_{\beta e}\langle P_2(t)\rangle$$
$$-\tfrac{2}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,\Phi^{22}_{0n}(t), \qquad (10)$$

$$I_{xy}(t)=\tfrac{1}{9}-\tfrac{1}{9}S_{\beta a}\langle P_2(0)\rangle-\tfrac{1}{9}S_{\beta e}\langle P_2(t)\rangle$$
$$+\tfrac{1}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,[\Phi^{22}_{0n}(t)$$
$$-3\Phi^{22}_{2n}(t)], \qquad (11)$$

$$I_{xx}(t)=\tfrac{1}{9}-\tfrac{1}{9}S_{\beta a}\langle P_2(0)\rangle-\tfrac{1}{9}S_{\beta e}\langle P_2(t)\rangle$$
$$+\tfrac{1}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,[\Phi^{22}_{0n}(t)$$
$$+3\Phi^{22}_{2n}(t)]. \qquad (12)$$

The angles β_a and α_e, β_e specify the orientation of the vectors $\boldsymbol{\mu}(\sin\beta_a,0,\cos\beta_a)$ and $\bar{\boldsymbol{\mu}}(\sin\beta_e\cos\alpha_e, \sin\beta_e\sin\alpha_e,\cos\beta_e)$ in the molecular coordinate system: $S_{\beta a}=P_2(\cos\beta_a)$, $S_{\beta e}=P_2(\cos\beta_e)$, $\langle P_2(\cos\theta_0)\rangle=\langle P_2(0)\rangle$, $\langle P_2(t)\rangle=\langle P_2(\cos\theta_t)\rangle$. Here θ is the angle between the long axis of the molecule and $\mathbf{n}$. The correlation functions

$$\Phi^{MN}_{mn}(t)=\langle D^M_{mn}(\Omega_0)\,D^{N*}_{mn}(\Omega_t)\rangle \qquad (13)$$

satisfy the symmetry conditions

$$\Phi^{MN}_{mn}(t)=\Phi^{NM}_{mn}(t)=\Phi^{MN}_{-m-n}(t)=(-1)^{M+N}\Phi^{MN}_{-mn}(t). \qquad (14)$$

The nonequilibrium order parameter $\langle P_2(t)\rangle$ of the excited impurity molecules in Eqs. (8)–(12) differs from $\langle P_2(0)\rangle=S_g$; in the limit $t\to\infty$ it relaxes to the value S_e. At $t\neq0$ we would thus have $I_{zx}\neq I_{xz}$ even if $\boldsymbol{\mu}$ and $\bar{\boldsymbol{\mu}}$ are in the same direction; this is what is actually observed.[10,31] The identification $\langle P_2(0)\rangle=\langle P_2(t)\rangle$ reduces (8)–(12) to known equations.[2–5]

The anisotropy of the fluorescence polarization,

$$r(t)=\frac{I_{zz}(t)-I_{zx}(t)}{I_{zz}(t)+2I_{zx}(t)}, \qquad (15)$$

is given by

$$r(t)=\frac{S_{\beta e}\langle P_2(t)\rangle+2\Sigma_n D^{2*}_{n0}(0,\beta_a,0)\,D^2_{n0}(\alpha_e,\beta_e,0)\,\Phi^{22}_{0n}(t)}{1+2S_{\beta a}\langle P_2(0)\rangle}. \qquad (16)$$

We see that the identification[6] $r(t)=\langle P_2(t)\rangle$ is valid for all t only if the conditions $S_{\beta e}=1$ and $S_{\beta a}=0$ hold simultaneously. For $\beta_a=\beta_e=0$, the exponential relaxation[6–8] of $r(t)$ reflects the combined relaxation of the functions $\langle P_2(t)\rangle$ and $\Phi^{22}_{00}(t)$; here

$$r(0)=\frac{14+55S_g+36\langle P_4(0)\rangle}{35(1+2S_g)}, \quad r(\infty)=\langle P_2(\infty)\rangle\equiv S_e. \qquad (17)$$

From the experimental values of $r(0)$ and S_g we can determine the parameter $\langle P_4(0)\rangle$ (cf. Refs. 7 and 8). In contrast with $\langle P_2(t)\rangle$, the nonequilibrium order parameter $\langle P_4(t)\rangle=[35\langle\cos^4\theta_t\rangle-30\langle\cos^2\theta_t\rangle+3]/8$ does not appear in the expressions for $I_{ij}(t)$ at $t\neq0$, and it cannot be found experimentally (cf. Ref. 6).

3. POLARIZED FLUORESCENCE SPECTRUM OF AN IMPURE NEMATIC

For uniaxial impurity molecules, the functions $D^L_{mn}(\Omega_t)$ in (5) are replaced by even Legendre polynomials, and expression (5) is conveniently put in the form

$$\nu_{ij}(t)=\nu_0(t)-\sum\varepsilon_L(t)\langle P_L(t)\rangle-\frac{1}{I_{ij}(t)}\sum\varepsilon_L(t)$$
$$\times[\langle I_{ij}(\Omega_0,\Omega_t)P_L(t)\rangle-I_{ij}(t)\langle P_L(t)\rangle]. \qquad (18)$$

The first two terms on the right side of this equation characterize either the position $\nu_{\rm cg}(t)$ of the center of gravity of the multiplet $\nu_{ij}(t)$ in the spectrum of a uniformly oriented sample or the position of the fluorescence band in the spectrum of an unoriented sample. The position $\nu_{\rm cg}(t)$ does not depend explicitly on the angles β_a and β_e, being determined exclusively by the parameters $\varepsilon_L(t)$ of the anisotropic impurity-matrix interaction and by the order parameters $\langle P_L(t)\rangle$ of the impurity subsystem. The parameters ε_L are functions of the orientational order of the matrix.[13–15] In a first approximation we can write $\varepsilon_L(t)=S_mA_L(t)$, where $S_m=\langle P_2(\cos\theta_m)\rangle$ is the orientational-order parameter of the matrix molecules. At fixed t (or in the case of steady-state excitation) we would expect the inequality $\nu_0>\nu_{\rm cg}$ to become stronger as the temperature of the mesophase decreases and S_m increases; this expectation agrees with experimental data.[18,19] At a fixed temperature of the liquid crystal, the values of $\varepsilon_L(t)$ increase with increasing t, and we would expect $\nu_0(t)>\nu_{\rm cg}(t)$ at all t. This expectation agrees with the results of time-resolved measurements.[32]

To pursue the analysis of (18) we introduce the correlation functions $I^L_{ij}(t)=\langle I_{ij}(\Omega_0,\Omega_t)P_L(t)\rangle$ for uniaxial molecules in a nematic liquid crystal:

$$I^L_{zz}(t)=\tfrac{1}{9}\langle P_L(t)\rangle+\tfrac{2}{9}S_{\beta a}\langle P_2(0)P_L(t)\rangle$$
$$+\tfrac{2}{9}S_{\beta e}\langle P_2(t)P_L(t)\rangle+\tfrac{4}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)$$
$$\times D^2_{n0}(\alpha_e,\beta_e,0)\langle D^2_{0n}(0)\,D^{2*}_{0n}(t)\,D^L_{00}(t)\rangle, \qquad (8')$$

$$I^{L}_{zx}(t)=\tfrac{1}{9}\langle P_L(t)\rangle+\tfrac{2}{9}S_{\beta a}\langle P_2(0)P_L(t)\rangle$$

$$-\tfrac{1}{9}S_{\beta e}\langle P_2(t)P_L(t)\rangle-\tfrac{2}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)$$

$$\times D^{2}_{n0}(\alpha_e,\beta_e,0)\langle D^{2}_{0n}(0)\,D^{2*}_{0n}(t)\,D^{L}_{00}(t)\rangle, \qquad (9')$$

$$I^{L}_{xz}(t)=\tfrac{1}{9}\langle P_L(t)\rangle-\tfrac{1}{9}S_{\beta a}\langle P_2(0)P_L(t)\rangle$$

$$+\tfrac{2}{9}S_{\beta e}\langle P_2(t)P_L(t)\rangle-\tfrac{2}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)$$

$$\times D^{2}_{n0}(\alpha_e,\beta_e,0)\langle D^{2}_{0n}(0)\,D^{2*}_{0n}(t)\,D^{L}_{00}(t)\rangle, \qquad (10')$$

$$I^{L}_{xy}(t)=\tfrac{1}{9}\langle P_L(t)\rangle-\tfrac{1}{9}S_{\beta a}\langle P_2(0)P_L(t)\rangle$$

$$-\tfrac{1}{9}S_{\beta e}\langle P_2(t)P_L(t)\rangle+\tfrac{1}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)$$

$$\times D^{2}_{n0}(\alpha_e,\beta_e,0)[\langle D^{2}_{0n}(0)\,D^{2*}_{0n}(t)\,D^{L}_{00}(t)\rangle$$

$$-3\langle D^{2}_{2n}(0)\,D^{2*}_{2n}(t)\,D^{L}_{00}(t)\rangle], \qquad (11')$$

$$I^{L}_{xx}(t)=\tfrac{1}{9}\langle P_L(t)\rangle-\tfrac{1}{9}S_{\beta a}\langle P_2(0)P_L(t)\rangle$$

$$-\tfrac{1}{9}S_{\beta e}\langle P_2(t)P_L(t)\rangle+\tfrac{1}{9}\sum_n D^{2*}_{n0}(0,\beta_a,0)$$

$$\times D^{2}_{n0}(\alpha_e,\beta_e,0)[\langle D^{2}_{0n}(0)\,D^{2*}_{0n}(t)\,D^{L}_{00}(t)\rangle$$

$$+3\langle D^{2}_{2n}(0)\,D^{2*}_{2n}(t)\,D^{L}_{00}(t)\rangle]. \qquad (12')$$

We consider the cases $\beta_e=0$ and $\beta_a=0$, in which we have $n=0$ in (8)–(12) and (8′)–(12′). In the first of these cases, the components $\nu_{ij}(t)$ are

$$\nu_{zz}(t)=\nu_{\rm cg}(t)$$

$$-2\frac{\Sigma\varepsilon_L(t)[S_{\beta a}\Delta^{0,t}_{2,L}+\Delta_{2L}(t)+2S_{\beta a}\Delta^{0t,t}_{22,L}]}{1+2S_{\beta a}\langle P_2(0)\rangle+2\langle P_2(t)\rangle+4S_{\beta a}\Phi^{22}_{00}(t)}, \qquad (19)$$

$$\nu_{zx}(t)=\nu_{\rm cg}(t)$$

$$-\frac{\Sigma\varepsilon_L(t)[2S_{\beta a}\Delta^{0,t}_{2,L}-\Delta_{2L}(t)-2S_{\beta a}\Delta^{0t,t}_{22,L}]}{1+2S_{\beta a}\langle P_2(0)\rangle-\langle P_2(t)\rangle-2S_{\beta a}\Phi^{22}_{00}(t)}, \qquad (20)$$

$$\nu_{xz}(t)=\nu_{\rm cg}(t)$$

$$-\frac{\Sigma\varepsilon_L(t)[2\Delta_{2L}(t)-S_{\beta a}\Delta^{0,t}_{2,L}-2S_{\beta a}\Delta^{0t,t}_{22,L}]}{1-S_{\beta a}\langle P_2(0)\rangle+2\langle P_2(t)\rangle-2S_{\beta a}\Phi^{22}_{00}(t)}, \qquad (21)$$

$$\nu_{xy}(t)=\nu_{\rm cg}(t)+\frac{\Sigma\varepsilon_L(t)[S_{\beta a}\Delta^{0,t}_{2,L}+\Delta_{2L}(t)-S_{\beta a}\Delta^{0t,t}_{22,L}+3S_{\beta a}\Delta^{0t,t}_{22,L}(22,0)]}{1-S_{\beta a}\langle P_2(0)\rangle-\langle P_2(t)\rangle+S_{\beta a}[\Phi^{22}_{00}(t)-3\Phi^{22}_{00}(t)]}, \qquad (22)$$

$$\nu_{xx}(t)=\nu_{\rm cg}(t)+\frac{\Sigma\varepsilon_L(t)[S_{\beta a}\Delta^{0,t}_{2,L}+\Delta_{2L}(t)-S_{\beta a}\Delta^{0t,t}_{22,L}-3S_{\beta a}\Delta^{0t,t}_{22,L}(22,0)]}{1-S_{\beta a}\langle P_2(0)\rangle-\langle P_2(t)\rangle+S_{\beta a}[\Phi^{22}_{00}(t)+3\Phi^{22}_{20}(t)]}. \qquad (23)$$

In the case $\beta_a=0$, the components $\nu_{ij}(t)$ are given by

$$\nu_{zz}(t)=\nu_{\rm cg}(t)$$

$$-2\frac{\Sigma\varepsilon_L(t)[\Delta^{0,t}_{2,L}+S_{\beta e}\Delta_{2L}(t)+2S_{\beta e}\Delta^{0t,t}_{22,L}]}{1+2\langle P_2(0)\rangle+2S_{\beta e}\langle P_2(t)\rangle+4S_{\beta e}\Phi^{22}_{00}(t)}, \qquad (19')$$

$$\nu_{zx}(t)=\nu_{\rm cg}(t)$$

$$-\frac{\Sigma\varepsilon_L(t)[2\Delta^{0,t}_{2,L}-S_{\beta e}\Delta_{2L}(t)-2S_{\beta e}\Delta^{0t,t}_{22,L}]}{1+2\langle P_2(0)\rangle-S_{\beta e}\langle P_2(t)\rangle-2S_{\beta e}\Phi^{22}_{00}(t)}, \qquad (20')$$

$$\nu_{xz}(t)=\nu_{\rm cg}(t)$$

$$-\frac{\Sigma\varepsilon_L(t)[2S_{\beta e}\Delta_{2L}(t)-\Delta^{0,t}_{2,L}-2S_{\beta}\Delta^{0t,t}_{22,L}]}{1-\langle P_2(0)\rangle+2S_{\beta e}\langle P_2(t)\rangle-2S_{\beta e}\Phi^{22}_{00}(t)}, \qquad (21')$$

$$\nu_{xy}(t)=\nu_{\rm cg}(t)+\frac{\Sigma\varepsilon_L(t)[\Delta^{0,t}_{2,L}+S_{\beta e}\Delta_{2L}(t)-S_{\beta e}\Delta^{0t,t}_{22,L}+3S_{\beta e}\Delta^{0t,t}_{22,L}(22,0)]}{1-\langle P_2(0)\rangle-S_{\beta e}\langle P_2(t)\rangle+S_{\beta e}[\Phi^{22}_{00}(t)-3\Phi^{22}_{20}(t)]}, \qquad (22')$$

$$\nu_{xx}(t)=\nu_{\rm cg}(t)+\frac{\Sigma\varepsilon_L(t)[\Delta^{0,t}_{2,L}+S_{\beta e}\Delta_{2L}(t)-S_{\beta e}\Delta^{0t,t}_{22,L}-3S_{\beta e}\Delta^{0t,t}_{22,L}(22,0)]}{1-\langle P_2(0)\rangle-S_{\beta e}\langle P_2(t)\rangle+S_{\beta e}[\Phi^{22}_{00}(t)+3\Phi^{22}_{20}(t)]}. \qquad (23')$$

Here we have used the expressions

$$\Delta_{ML}(t)=\langle P_M(t)P_L(t)\rangle-\langle P_M(t)\rangle\langle P_L(t)\rangle \tag{24}$$

for the measures of dispersion and the expressions

$$\Delta_{2,L}^{0,t}=\langle P_2(0)P_L(t)\rangle-\langle P_2(0)\rangle\langle P_L(t)\rangle, \tag{25}$$

$$\Delta_{22,L}^{0t,t}=\langle P_2(0)P_2(t)P_L(t)\rangle-\langle P_2(0)P_2(t)\rangle\langle P_L(t)\rangle, \tag{26}$$

$$\Delta_{22,L}^{0t,t}(22,0)=\langle D_{20}^2(0)D_{20}^{2*}(t)D_{00}^L(t)\rangle -\langle D_{20}^2(0)D_{20}^{2*}(t)\rangle\langle P_L(t)\rangle \tag{27}$$

for the correlation functions. These functions can be expressed in terms of the order parameters $\langle P_2(0)\rangle$ and $\langle P_K(t)\rangle$ and the correlation functions in (13), by making use of the formulas

$$P_M(t)P_L(t)=\sum_{K=|M-L|}^{M+L}[C_{M0L0}^{K0}]^2P_K(t), \tag{28}$$

$$\langle D_{20}^2(0)D_{20}^{2*}(t)D_{00}^L(t)\rangle=\sum_{K=L-2}^{L+2}C_{2-2L0}^{K-2}C_{20L0}^{K0}\Phi_{20}^{2K}(t), \tag{29}$$

where C_{mpnq}^{Kl} are the Clebsch–Gordan coefficients.[33] Considering only the values $L=2$ and 4, which are sufficient for interpreting experimental results (more on this below), we find

$$\Delta_{22,2}^{0t,t}=\tfrac{1}{5}\langle P_2(0)\rangle+[\tfrac{2}{7}-\langle P_2(t)\rangle]\Phi_{00}^{22}(t)+\tfrac{18}{35}\Phi_{00}^{24}(t), \tag{30}$$

$$\Delta_{22,4}^{0t,t}=[\tfrac{2}{7}-\langle P_4(t)\rangle]\Phi_{00}^{22}(t)+\tfrac{20}{77}\Phi_{00}^{24}(t)+\tfrac{5}{11}\Phi_{00}^{26}(t), \tag{31}$$

$$\Delta_{22,2}^{0t,t}(22,0)=-[\tfrac{2}{7}+\langle P_2(t)\rangle]\Phi_{20}^{22}(t)+\frac{3\sqrt{15}}{35}\Phi_{20}^{24}(t), \tag{32}$$

$$\Delta_{22,4}^{0t,t}(22,0)=[\tfrac{1}{21}-\langle P_4(t)\rangle]\Phi_{20}^{22}(t)-\frac{6\sqrt{15}}{77}\Phi_{20}^{24}(t) +\frac{\sqrt{70}}{33}\Phi_{20}^{26}(t). \tag{33}$$

It can be seen from these expressions that the positions of the components $\nu_{ij}(t)$, in contrast with the position of the center of gravity, $\nu_{cg}(t)$, depend strongly on the electronic structure of the impurity molecules, the orientational statistics of these molecules, and their dynamics. The kinetics of the $\nu_{ij}(t)$ spectrum is associated with relaxation of the correlation functions $\Phi_{n0}^{2K}(t)$ whose rank is higher than that of the correlation functions which determine the $I_{ij}(t)$ kinetics. To analyze the $\nu_{ij}(t)$ spectrum, we begin by looking at the limiting cases $t=0$ and ∞.

3.1. $t=0$

In this limit the correlation functions $\Phi_{20}^{2k}(0)$ can be written in the form

$$\Phi_{20}^{2k}(0)=\sum_{J=k-2}^{k+2}C_{22k-2}^{J0}C_{20k0}^{J0}\langle P_J(0)\rangle, \tag{34}$$

and the quantities $I_{ij}(\Omega_0)$ in (1) can be written in the compact form

$$I_{ij}(\Omega_0)=E_{ij}+F_{ij}P_2(\cos\theta_0)+H_{ij}P_4(\cos\theta_0),$$

where the numerical factors $(E,F,H)_{ij}$ are functions of the angles β_a and β_e. Expressions (19)–(23) and (19′)–(23′) thus assume a form which is valid for all L:

$$\nu_{ij}(0)=\nu_0(0)-\Sigma\varepsilon_L(0)\langle P_L(0)\rangle -\frac{\Sigma\varepsilon_L(0)[F_{ij}\Delta_{2L}+H_{ij}\Delta_{4L}]}{E_{ij}+F_{ij}\langle P_2(0)\rangle+H_{ij}\langle P_4(0)\rangle}. \tag{35}$$

Complete degeneracy of the $\nu_{ij}(0)$ spectrum corresponds to uniform orientation of the impurity molecules with $\Delta_{LM}=0$. Partial degeneracy of the $\nu_{ij}(0)$ components may stem from the particular electronic structure of the molecules or the particular intermolecular interaction (a relation between the values of ε_L for different ranks L). In the case $\beta_e=0$ we have

$$E_{zz}=\tfrac{1}{9}(1+\tfrac{4}{5}S_{\beta a}),\quad F_{zz}=\tfrac{2}{9}(1+\tfrac{11}{7}S_{\beta a}),\quad H_{zz}=\tfrac{8}{35}S_{\beta a}, \tag{36}$$

$$E_{zx}=\tfrac{1}{9}(1-\tfrac{2}{5}S_{\beta a}),\quad F_{zx}=\tfrac{1}{9}(\tfrac{10}{7}S_{\beta a}-1),\quad H_{zx}=-\tfrac{1}{2}H_{zz}, \tag{37}$$

$$E_{xz}=E_{zx},\quad F_{xz}=\tfrac{1}{9}(2-\tfrac{11}{7}S_{\beta a}),\quad H_{xz}=H_{zx}, \tag{38}$$

$$E_{xy}=E_{zx},\quad E_{xy}=\tfrac{1}{9}(\tfrac{1}{7}S_{\beta a}-1),\quad H_{xy}=\tfrac{1}{8}H_{zz}, \tag{39}$$

$$E_{xx}=E_{zz},\quad F_{xx}=-\tfrac{1}{2}F_{zz},\quad H_{xx}=\tfrac{3}{8}H_{zz}. \tag{40}$$

The angle β_a specifies the orientation of the transition moment $\boldsymbol{\mu}$ at the excitation frequency. When fluorescence is excited at various frequencies with various angles β_a, the values of ν_{ij} in (35) will evidently be different, although the emission comes from the same level. When fluorescence is excited at different frequencies with identical values of β_a, on the other hand, the quantities ν_{ij} should remain constant. This is what has been observed[17] for the components ν_{zz} and ν_{xx} for the dyes R823 and R829 in a 6CB matrix.

In the case $\beta_a=\beta_e=0$ we find from (37)–(40) the results $I_{zx}=I_{xz}$ and $I_{xx}=3I_{xy}$. These results correspond to partial degeneracy, $\nu_{zx}=\nu_{xz}$ and $\nu_{xx}=\nu_{xy}$, in (35). In this case we have $\nu_{xx}>\nu_{xz}>\nu_{zz}$. At the "magic" angle $\beta_a=\beta_m=54.7°$ and with the value $S_{\beta a}=0$, the relations $I_{xx}=I_{xy}=I_{zx}$ and $I_{xz}=I_{zz}$ hold. These results correspond to the degeneracy $\nu_{xx}=\nu_{xy}=\nu_{zx}\equiv\nu_\perp(0)$ and $\nu_{xz}=\nu_{zz}\equiv\nu_\parallel(0)$, where

$$\nu_\perp(0)=\nu_0(0)-\sum\varepsilon_L(0)\langle P_L(0)\rangle+\frac{\Sigma\varepsilon_L(0)\Delta_{2L}(0)}{1-\langle P_2(0)\rangle},$$

$$\nu_\parallel(0)=\nu_0(0)-\sum\varepsilon_L(0)\langle P_L(0)\rangle-2\frac{\Sigma\varepsilon_L(0)\Delta_{2L}(0)}{1+2\langle P_2(0)\rangle}. \tag{41}$$

The parameters $\nu_\perp(0)>\nu_\parallel(0)$ also give us the positions of the polarized components of the impurity absorption band associated with the direct transition from the $E_g^{(\mathrm{eq})}(0)$ ground state to the $E_e^{(n)}(0)$ excited emitting state.

This band is shifted in the low-frequency direction by an amount equal to the Stokes shift of the spectrum of the isotropic phase.

From (36)–(40) we find $I_{zz}(\beta_a=90°)=I_{xz}(\beta_a=0)$ and $I_{zx}(\beta_a=90°)=2I_{xx}(\beta_a=0)/3$; these results correspond to $\nu_{zz}(90°)=\nu_{xz}(0)$ and $\nu_{zx}(90°)=\nu_{xx}(0)$. Since the inequality $F_{xz}\geqslant F_{zx}$ holds for $\beta_a\geqslant 0$ in (37) and (38), we can set $\nu_{zx}\geqslant\nu_{xz}$ in (35). This inequality becomes stronger as β_a increases. This result agrees with the data of Ref. 1. It follows from (36)–(40) that in the case $\beta_a\neq 0$, β_m the degeneracy $\nu_{xx}=\nu_{xy}$ is lifted.

In the case $\beta_a=0$ in (36), (39), and (40) we should replace $S_{\beta a}$ by $S_{\beta e}$; Eqs. (37) and (38) then become

$$E_{zx}=\tfrac{1}{9}\,(1-\tfrac{2}{5}\,S_{\beta e}),\quad F_{zx}=\tfrac{1}{9}\,(2-\tfrac{11}{7}\,S_{\beta e}),\quad H_{zx}=-\tfrac{4}{35}\,S_{\beta e}, \tag{37'}$$

$$E_{xz}=E_{zx},\quad F_{xz}=\tfrac{1}{9}\,(\tfrac{10}{7}\,S_{\beta e}-1),\quad H_{xz}=H_{zx}. \tag{38'}$$

In the case $\beta_e\geqslant 0$ we thus have $\nu_{xz}\geqslant\nu_{zx}$. In the case $\beta_e=\beta_m$, the $\nu_{ij}(0)$ spectrum is partially degenerate with $\nu_{xx}=\nu_{xy}=\nu_{xz}=\nu_\perp\ (0)$ and $\nu_{zx}=\nu_{zz}=\nu_\parallel\ (0)$, where the frequencies $\nu_{\perp\ ,\parallel}\ (0)$ are given by the same expressions [expressions (41)], which in this case are unrelated to the positions of the polarized components of the absorption band for the direct transition from the $E_g^{(\mathrm{eq})}(0)$ ground state to the $E_e^{(n)}(0)$ excited state. Since we have $S_{\beta e}=0$, there is no splitting of these absorption components.[13] We now have $\nu_{zz}(\beta_e=90°)=\nu_{zx}(0)$ and $\nu_{xz}(\beta_e=90°)=\nu_{xx}(0)$.

To determine how the components ε_L affect the positions ν_{ij}, and also to determine how ν_{ij} depend on the orientational order of the molecules, we assume that the distribution function of the impurity subsystem, $f_g^{(\mathrm{eq})}(\theta)$, is of the Mayer–Saupe form:

$$f_g^{(\mathrm{eq})}(\theta)=\frac{1}{Z}\exp[aP_2(\cos\theta)]. \tag{42}$$

This distribution function corresponds well to experimental data[14,15,19] on $\langle P_{2,4}(0)\rangle$. The parameter $a=a(S)$ here is found for each value of S from the self-consistency condition for S; then it is used to calculate the values of $\langle P_k(0)\rangle$ for the given S.

Figure 1 shows the measures of dispersion $\Delta_{ML}(0)$ as a function of $S=\langle P_2(0)\rangle$ according to calculations from (42). For values $S<0.7$, which are typical of the nematic phase, the values of Δ_{2L} fall off with increasing $L>2$, while the values of Δ_{4L} fall off with increasing $L>4$. For nematic matrices we can thus restrict (35) to the values $L=2$ and 4, although in smectics with $S\simeq 0.7$–0.8 the role of measures of dispersion with $L>4$ may be significant. Support for the use of this restriction comes from the circumstance that in interpreting the polarized impurity absorption spectra it is usually sufficient to consider simply one parameter ε_L (specifically, ε_2; Refs. 13–15) or two such parameters ($\varepsilon_{2,4}$; Refs. 19 and 34). Switching to normalized peak shifts

$$\Delta\nu_{ij}=[\nu_{ij}(0)-\nu_0(0)]/A_2S_m,$$

which depend only on the properties of the impurity subsystem, in (35), we find

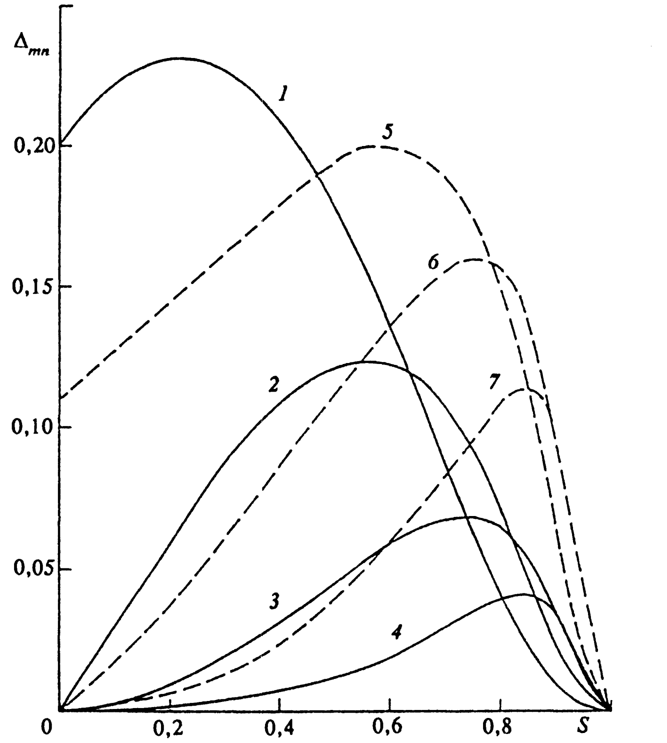

FIG. 1. The measures of dispersion Δ_{22} (*1*), Δ_{24} (*2*), Δ_{26} (*3*), Δ_{28} (*4*), Δ_{44} (*5*), Δ_{46} (*6*), and Δ_{48} (*7*) versus the order parameter *S*, calculated with distribution function (42).

$$\Delta\nu_{ij}=-\langle P_2\rangle-\alpha\langle P_4\rangle-\frac{F_{ij}(\Delta_{22}+\alpha\Delta_{24})+H_{ij}(\Delta_{24}+\alpha\Delta_{44})}{E_{ij}+F_{ij}\langle P_2\rangle+H_{ij}\langle P_4\rangle}, \tag{35'}$$

where $\alpha=\varepsilon_4/\varepsilon_2$. Figures 2a and 3a show the dependence $\Delta\nu_{ij}(S)$ for the two limiting cases $a=0$ and $a=10$, which correspond to known experimental situations with $\alpha\ll 1$ (Refs. 13–15) and $\alpha\gg 1$ (Refs. 19 and 34). Also shown here is the dependence $\Delta\nu_{\perp\ ,\parallel}\ (S)$ for normalized shifts $\Delta\nu_{\perp\ ,\parallel}\ =[\nu_{\perp\ ,\parallel}\ (0)-\nu_0(0)]/A_2S_m$ in the form

$$\begin{aligned}\Delta\nu_\perp\ &=-S-\alpha\langle P_4\rangle+(\Delta_{22}+\alpha\Delta_{24})(1-S)^{-1},\\ \Delta\nu_\parallel\ &=-S-\alpha\langle P_4\rangle-2(\Delta_{22}+\alpha\Delta_{24})(1+2S)^{-1}.\end{aligned} \tag{41'}$$

We see from Fig. 2a that the maximum splitting $\Delta\nu_f=\nu_{xx}-\nu_{zz}$ of the fluorescence components is greater than the splitting $\Delta\nu_a=\nu_\perp\ -\nu_\parallel$ of the absorption components for the direct transition to the radiating level. For the typical change $S=0.3$–0.7 we find $\Delta\nu_f/\Delta\nu_a=1.34$–$1.78$, in agreement with existing data.[18,19] An increase in α strongly influences the $\nu_{xx}(S)$ and $\nu_\perp\ (S)$ behavior, which becomes nonmonotonic at $\alpha\gg 1$. At sufficiently large values of α, an additional degeneracy, $\nu_{xx}=\nu_{xz}$, arises at $S=S_1(\alpha)$, so we have $\nu_{xx}\gtrless\nu_{xz}$ at $S\gtrless S_1$. It can be seen from Fig. 3b that the distribution function in (42) and the value $\alpha=10$ correspond to $S_1\simeq 0.37$. With increasing α, the ratio $\Delta\nu_f/\Delta\nu_a$ decreases slightly, and at $\alpha=10$ it lies in the interval 1.18–1.45 for the change $S=0.37$–0.7.

To analyze the $\Delta\nu_{ij}(\beta_e)$ dependence, we adopt $S=0.5$, which is an average value for nematics. For this value the

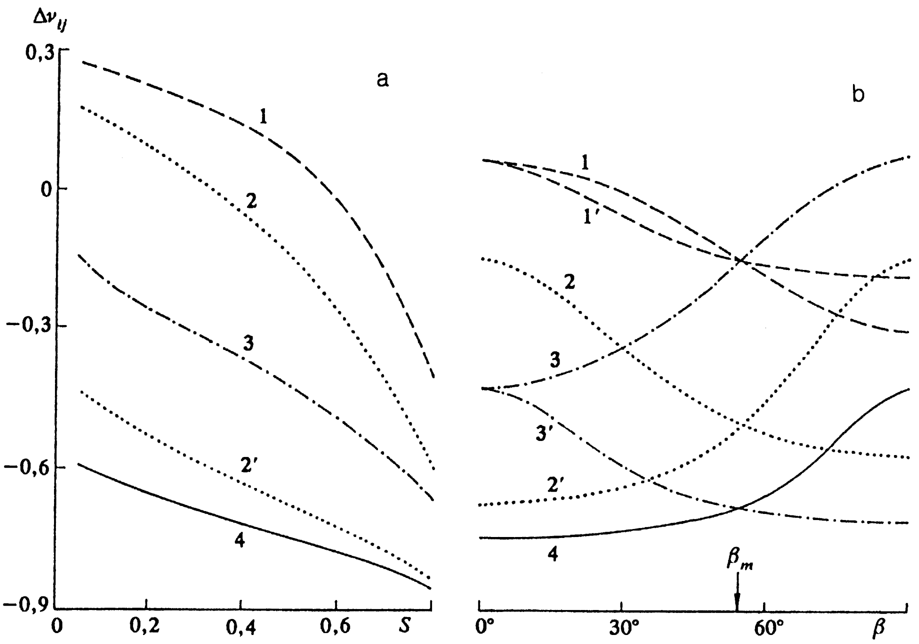

FIG. 2. a: Plot of $\Delta\nu_{ij}$ in (35′) for $ij=xx$ and xy (1), xz and zx (3), and zz (4), along with plots of $\Delta\nu_i$ in (41′) for $i=\perp$ (2) and $\parallel$ (2′) versus the order parameter S with $\alpha=\beta_e=\beta_a=0$. b: Plots of $\Delta\nu_{ij}$ in (35′) for $ij=xx$ (1), xy (1′), xz (3), zx (3′), and zz (4), along with plots of $\Delta\nu_i$ in (43) for $i=\perp$ (2) and $\parallel$ (2′) versus the angle $\beta=\beta_e$ with $\alpha=\beta_a=0$ and $S=0.5$.

measures of dispersion Δ_{24} and Δ_{44} are close to their maximum values, and we have $\Delta_{22}\simeq\Delta_{44}$. Figures 2b and 3b show $\Delta\nu_{ij}(\beta_e)$ along with the quantities

$$\Delta\nu_\perp\ (\beta_e,0)=-S-\alpha\langle P_4\rangle+S_{\beta e}(\Delta_{22}+\alpha\Delta_{24})(1-S_{\beta e}S)^{-1},$$
$$\Delta\nu_\parallel\ (\beta_e,0)=-S-\alpha\langle P_4\rangle-2S_{\beta e}(\Delta_{22}+\alpha\Delta_{24})\times(1+2S_{\beta e}S)^{-1}, \tag{43}$$

which characterize the position of the polarized absorption components for the direct transition from the $E_g^{(\mathrm{eq})}(0)$ ground state to the $E_e^{(n)}(0)$ excited radiating state. It can be seen from these figures that at $\beta_e\lessgtr\beta_m$ the relations $\nu_{xx}\gtrless\nu_{xy}$ hold. The switch from $\beta_e<\beta_m$ to $\beta_e>\beta_m$ changes the relations among the components ν_{ij}, from $\nu_{xx}>\nu_{xy}>\nu_{xz}>\nu_{zx}>\nu_{zz}$ to $\nu_{xz}>\nu_{xy}>\nu_{xx}>\nu_{zz}>\nu_{zx}$. At $\beta=90°$, the maximum (minimum) difference is observed between ν_{xz} and ν_{zx} (ν_{xx} and ν_{zz}). These quantities are equal (maximally different) in the case $\beta_a=\beta_e=0$. With $\beta_e=0$ and $\beta_a\neq0$, we should interchange ν_{xz} and ν_{zx} in these inequalities. In this case, with $\beta_a<\beta_m$, the expected relation among components, $\nu_{xx}>\nu_{xy}>\nu_{zx}>\nu_{xz}>\nu_{zz}$, was observed in Ref. 19. A change in α does not have any qualitative effect on the values of $\nu_{ij}(\beta_e)$ or the relations among them.

From (43) and the figures we see that in the cases $\beta_e\lessgtr\beta_m$ we have $\Delta\nu_\perp\gtrless\Delta\nu_\parallel$, and with $\beta_e=\beta_m$ we have $\Delta\nu_a=0$ in the absorption to the radiating level. With increasing $\beta_e<\beta_m$, the ratio $\Delta\nu_a/\Delta\nu_f$ decreases rapidly. This decrease explains the results of Ref. 17 for the dyes RM64 and E18 with $\beta_e>0$ and significant values of $\Delta\nu_f$, but undetectable values of $\Delta\nu_a$. Using the results of this analysis, along with the data in Figs. 2a and 3a, we can easily

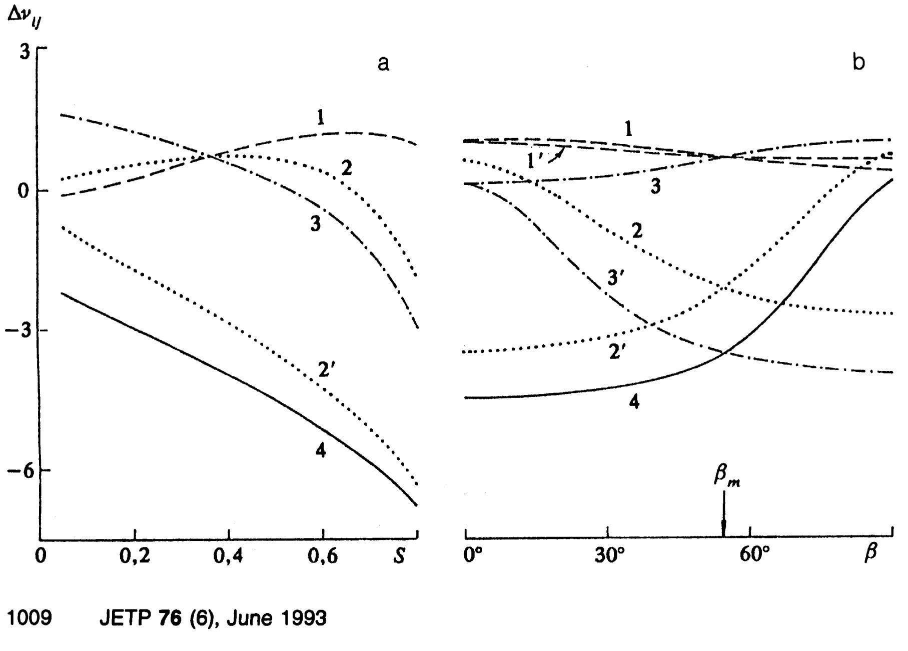

FIG. 3. The same as in Fig. 2, a and b, for $\alpha=10$.

reconstruct the $\nu_{ij}(\beta_e)$ dependence for other values of S. In general, at $t=0$, for all $S\neq S_1$, the number N_ν of independent quantities ν_{ij} is the same as the number N_J of independent intensity components $J_{ij}(\nu)$.

3.2. $t=\infty$

In this limit we have, for a uniaxial liquid crystal,

$$\Phi_{00}^{2k}(\infty)=\langle P_2(0)\rangle\langle P_k(\infty)\rangle, \quad \Phi_{2n}^{2k}(\infty)=\Delta_{2,L}^{0,\infty}=0, \tag{44}$$

$$\Delta_{22,L}^{0\infty,\infty}=\langle P_2(0)\rangle\Delta_{2L}(\infty), \quad \Delta_{22,L}^{0\infty,\infty}(22,0)=0.$$

As a result the relation $I_{xx}=I_{xy}$ holds for all β_a, β_e, α_e in Eqs. (11) and (12). When we incorporate (44) in (19)–(23′), we draw the following conclusions. With $\beta_e=0$ and $\beta_a\neq\beta_m$ there are four independent components, I_{xx}, I_{xz}, I_{zx}, I_{zz}, and only two independent values $\nu_{xx}=\nu_{xy}=\nu_{zx}\equiv\nu_\perp(\infty)$ and $\nu_{xz}=\nu_{zz}\equiv\nu_\parallel(\infty)$. They are given by

$$\nu_\perp(\infty)=\nu_0(\infty)-\sum\varepsilon_L(\infty)\langle P_L(\infty)\rangle +\frac{\Sigma\varepsilon_L(\infty)\Delta_{2L}(\infty)}{1-\langle P_2(\infty)\rangle}, \tag{45}$$

$$\nu_\parallel(\infty)=\nu_0(\infty)-\sum\varepsilon_L(\infty)\langle P_L(\infty)\rangle -2\frac{\Sigma\varepsilon_L(\infty)\Delta_{2L}(\infty)}{1+2\langle P_2(\infty)\rangle}.$$

With $\beta_a=\beta_e=0$, the orientational relaxation of impurity molecules lifts the degeneracy $\nu_{xz}=\nu_{zx}$ (which prevailed at $t=0$) in the long-time limit but does not affect the degeneracy $\nu_{xx}=\nu_{xy}$. With $\beta_e=0$ and $\beta_a=\beta_m$, the relations $I_{xx}=I_{xy}=I_{zx}$ and $I_{xz}=I_{zz}$ hold. This situation corresponds to a degeneracy $\nu_{xx}=\nu_{xy}=\nu_{zx}=\nu_\perp(\infty)$ and $\nu_{xz}=\nu_{zz}=\nu_\parallel(\infty)$. Accordingly, with $\beta_e=0$, in the limit $t=\infty$ (in contrast with $t=0$) the positions of the frequencies ν_{ij} do not depend on the angle β_a, which determines only the number of independent components I_{ij}. In the long-time limit the impurity system "forgets" the excitation conditions at $t=0$.

With $\beta_a=0$ and $\beta_e\neq0$, β_m, with four independent components I_{xx}, I_{xz}, I_{zx}, and I_{zz} there are only two independent values $\nu_{xx}=\nu_{xy}=\nu_{zx}\equiv\nu_\perp(\beta_e,\infty)$ and $\nu_{xz}=\nu_{zz}\equiv\nu_\parallel(\beta_e,\infty)$. They are given by

$$\nu_\perp(\beta_e,\infty)=\nu_0(\infty)-\sum\varepsilon_L(\infty)\langle P_L(\infty)\rangle -S_{\beta e}\frac{\Sigma\varepsilon_L(\infty)\Delta_{2L}(\infty)}{1-S_{\beta e}\langle P_2(\infty)\rangle}, \tag{46}$$

$$\nu_\parallel(\beta_e,\infty)=\nu_0(\infty)-\sum\varepsilon_L(\infty)\langle P_L(\infty)\rangle +2S_{\beta e}\frac{\Sigma\varepsilon_L(\infty)\Delta_{2L}(\infty)}{1+2S_{\beta e}\langle P_2(\infty)\rangle}.$$

This $\nu_{\perp,\parallel}(\beta_e,\infty)$ behavior at a fixed $\langle P_2(\infty)\rangle$ is analogous to the $\nu_{\perp,\parallel}(\beta_e,0)$ behavior shown in Figs. 2b and 3b at a fixed $\langle P_2(0)\rangle$. At $\beta_e=\beta_m$, there is a complete degeneracy of the spectrum, $\nu_{ij}(\infty)=\nu_{\rm cg}(\infty)$, with two independent components $I_{xx}=I_{xy}=I_{xz}$ and $I_{zx}=I_{zz}$. Overall, at $t=\infty$ and for all $\beta_a\neq\beta_m$ ($\beta_e=0$) or β_e ($\beta_a=0$) we have $N_\nu=N_J/2$.

Equations (45) and (46) are completely analogous to those which give the positions of the polarized impurity absorption bands at $t=0$ (Ref. 13). We can thus use a combination of the data on the intensity $J_{ij}(\infty)$ and the position of the fluorescence bands $\nu_{ij}(\infty)$ to determine the parameters $\langle P_2(\infty)\rangle$, $\varepsilon_2(\infty)$, and $\Delta_{22}(\infty)$ (or $\langle P_4(\infty)\rangle$) simultaneously, as has been done[15] in the case of absorption spectra, to find $\langle P_{2,4}\rangle$ and $\varepsilon_2(0)$. This appears to be the only possibility presently available to determine $\langle P_4(\infty)\rangle$ and to accurately reconstruct the distribution function $f_e^{(\mathrm{eq})}(\Omega)$. On the other hand, the combination of data on the polarized absorption to the radiating level and on the parameters $J_{ij}(\infty)$ and $\nu_{ij}(\infty)$ can be used to clarify the effect of the relaxation of the surroundings on $\varepsilon_2(t)$. The limiting values $\nu_{ij}(\infty)$ may have been measured in experiments which have already been performed.[32]

3.3. $0<t<\infty$

In this intermediate case, the relaxation of correlation functions (25)–(27) substantially affects the number of independent components $\nu_{ij}(t)$ and the relations among them. In contrast with the $t=0$ case, with $\beta_a=\beta_e=0$ we now have five independent components $I_{ij}(t)$ [see (8)–(12)] and five corresponding different values $\nu_{ij}(t)$. In other words, the degeneracy of the components $\nu_{zx}=\nu_{xz}$ and $\nu_{xx}=\nu_{xy}$ has been lifted by relaxation. With $\beta_e=0$ and $\beta_a=\beta_m$, by analogy with the $t=0$ case, the $\nu_{ij}(t)$ spectrum is partially degenerate and is characterized by two components, $\nu_{xx}=\nu_{xy}=\nu_{zx}\equiv\nu_\perp(t)$ and $\nu_{xz}=\nu_{zz}\equiv\nu_\parallel(t)$, given by

$$\nu_\perp(t)=\nu_0(t)-\sum\varepsilon_L(t)\langle P_L(t)\rangle+\frac{\Sigma\varepsilon_L(t)\Delta_{2L}(t)}{1-\langle P_2(t)\rangle}, \tag{47}$$

$$\nu_\parallel(t)=\nu_0(t)-\sum\varepsilon_L(t)\langle P_L(t)\rangle-2\frac{\Sigma\varepsilon_L(t)\Delta_{2L}(t)}{1+2\langle P_2(t)\rangle}.$$

At $t=0$ and ∞, these expressions become (41) and (45), respectively.

With $\beta_a=0$ and $\beta_e=\beta_m$, the $\nu_{ij}(t)$ spectrum is again characterized by two components, $\nu_{xx}=\nu_{xy}=\nu_{xz}\equiv\nu_\perp(0,t)$ and $\nu_{zx}=\nu_{zz}=\nu_\parallel(0,t)$, which are given by

$$\nu_\perp(0,t)=\nu_0(t)-\sum\varepsilon_L(t)\langle P_L(t)\rangle+\frac{\Sigma\varepsilon_L(t)\Delta_{2,L}^{0,t}}{1-\langle P_2(0)\rangle}, \tag{48}$$

$$\nu_\parallel(0,t)=\nu_0(t)-\sum\varepsilon_L(t)\langle P_L(t)\rangle-2\frac{\Sigma\varepsilon_L(t)\Delta_{2,L}^{0,t}}{1+2\langle P_2(0)\rangle}.$$

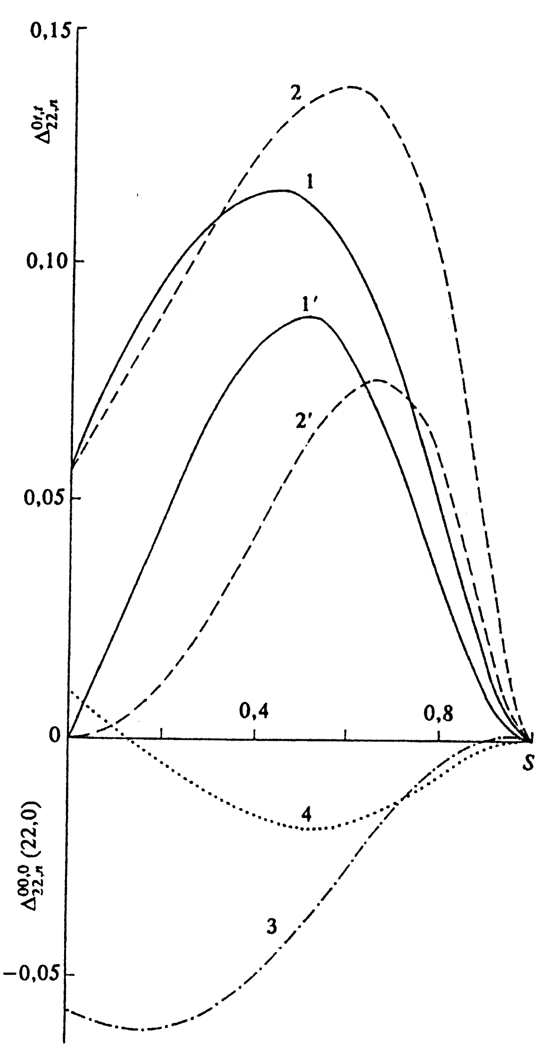

FIG. 4. The correlation functions $\Delta^{0t,t}_{22,2}$ (1,1′), $\Delta^{0t,t}_{22,4}$ (2,2′), $\Delta^{0t,t}_{22,2}(22,0)$ (3), and $\Delta^{0t,t}_{22,4}(22,0)$ (4) versus the order parameter $S=\langle P_2(0)\rangle$ for $t=0$ (1–4) and versus $S=\langle P_2(\infty)\rangle$ at $t=\infty$ (1′,2′).

At $t=0$, these expressions become (41), and as $t\rightarrow\infty$ the relaxation of the correlation functions $\Delta^{0,t}_{2,L}$ restores the complete degeneracy of the ν_{ij} spectrum with $\nu_{\perp,\parallel}(0,t)=\nu_{cg}(t)$, by virtue of (44).

The magnitudes and signs of the functions in (25)–(27) at $t\neq0$ can be estimated by comparing their limiting values at $t=0$ and $t=\infty$. For $t=0$, we find from (30)–(34) the expressions

$$\Delta^{00,0}_{22,2}=\tfrac{2}{7}\Delta_{22}+\tfrac{18}{35}\Delta_{24},\quad \Delta^{00,0}_{22,4}=\tfrac{2}{7}\Delta_{24}+\tfrac{18}{35}\Delta_{44},\tag{49}$$

$$\Delta^{00,0}_{22,2}(22,0)=-\tfrac{2}{7}\Delta_{22}+\tfrac{3}{35}\Delta_{24},\quad \Delta^{00,0}_{22,4}(22,0)=-\tfrac{2}{7}\Delta_{24}+\tfrac{3}{35}\Delta_{44}.\tag{50}$$

Figure 4 shows plots of these quantities versus S, calculated with the help of the $\Delta_{LM}(S)$ dependence in Fig. 1. Also shown here are plots of functions (30) and (31) versus $S=\langle P_2(\infty)\rangle$ at $t=\infty$; here we have used (44) under the assumption $\langle P_2(0)\rangle=\langle P_2(\infty)\rangle$ and under the assumption that (42) remains of the same form at $t=\infty$.

It can be seen from Fig. 4 and Eqs. (44) that for $L=2$ and 4 the inequalities $\Delta^{0t,t}_{22,L}>0$ and $\Delta^{0t,t}_{22,L}(22,0)<0$ hold for the entire range of S typical of nematics. For $\beta_e=\beta_a=0$, analysis of expressions (20) and (21) thus shows that at $t\neq0$ we have $\nu_{zx}>\nu_{xz}$. For $\beta_e=0$ and $\beta_a\neq0$, an increase in β_a and a relaxation of the functions (25)–(27) strengthen the inequality $\nu_{zx}>\nu_{xz}$ and cause the values of ν_{xz} and $\nu_{zz}(t)$ to move closer together. This result explains the observation[19] of a relation $\nu_{xz}\gtrsim\nu_{zz}$ for an impurity system which satisfies the requirements on β_e and β_a specified here. In the other case $\beta_a=0$ and $\beta_e\neq0$, an increase in β_e and a relaxation of functions (25)–(27) have the opposite effect on the relation between ν_{zx} and ν_{xz}. Analysis of (20′) and (21′) shows that for certain values of $0<\beta_e<\beta_m$ and $t\neq0$ the direction of the inequality $\nu_{zx}>\nu_{xz}$ may reverse at a fixed t with increasing β_e, and the direction of the inequality $\nu_{zx}<\nu_{xz}$ may also reverse at a fixed β_e with increasing t. For $\beta_e>\beta_m$ the relation $\nu_{zx}<\nu_{xz}$ holds for all t.

Analysis of expressions (22) and (23) along with the data in Fig. 4 shows that the inequalities $\nu_{xx}\gtrless\nu_{xy}$ may hold at $\beta_e=\beta_a=0$, depending on the particular features of the relaxation of the functions (25)–(27). In this case the relaxation lifts the degeneracy $\nu_{xx}=\nu_{xy}$ at $t=0$ and restores it at $t=\infty$. For $\beta_e=0$ and $\beta_a\lessgtr\beta_m$ at $t\neq0$, the relaxation may either strengthen or weaken the inequalities $\nu_{xx}(0)\gtrless\nu_{xy}(0)$, but as $t\rightarrow\infty$ the degeneracy $\nu_{xx}=\nu_{xy}$ is restored. The experimental observation[19] of a significant difference $\nu_{xx}-\nu_{xy}$, comparable to the difference $\nu_{zx}-\nu_{xz}$ for a dye with $\beta_e=0$ and $\beta_a<\beta_m$, is evidence of a strengthening of the inequality $\nu_{xx}>\nu_{xy}$ due to relaxation for the given system.

CONCLUSION

The analysis above shows that the positions of the $\nu_{ij}(t)$ peaks of the polarized fluorescence bands $J_{ij}(\nu,t)$ for impurity molecules in a nematic liquid crystal depend substantially on the electronic structure, the orientational order, and the dynamics of the impurity molecules. In general, the number (N_ν) of independent components ν_{ij} at $t\geqslant0$ is equal to the number (N_J) of independent intensity components $J_{ij}(\nu,t)$. At $t=0$, the degree of degeneracy of the $\nu_{ij}(0)$ spectrum is determined by the orientation of the transition dipole moments for transitions involving the absorption and emission of light, with respect to the longitudinal molecular axis. The number N_ν can vary from 5 to 2. For $t\neq0$ the relaxation of the orientational correlation functions of the impurity subsystem in the course of a rotational diffusion of molecules lifts this degeneracy, except for $\beta_a=\beta_m$, $\beta_e=0$ and $\beta_a=0$, $\beta_e=\beta_m$. However, a change in the angles $\beta_{a,e}$ and a relaxation may either strengthen or weaken each other as they jointly affect the differences between individual components $\nu_{ij}(t)$. It is thus possible that the degeneracy of certain components $\nu_{ij}(t)$ which were different at $t=0$ will be restored at $t\neq0$.

In the long-time limit, $t=\infty$, the relation $N_\nu=N_J/2$ holds for all values of $\beta_{a,e}$, except $\beta_e=0$, $\beta_a=\beta_m$, with $N_\nu=N_J$. In this case the relaxation may restore the partial or complete degeneracy of the ν_{ij} spectrum, which did not hold at $t\neq0$. The number N_ν may change from 2 to 1. By combining data on $J_{ij}(\infty)$ and $\nu_{ij}(\infty)$ one can in principle determine the values of $\langle P_{2,4}(\infty)\rangle$ and reconstruct the distribution function $f_e^{(\mathrm{eq})}(\Omega)$.

The results of this analysis agree qualitatively with all known experimental data on the number of independent components ν_{ij}, the relations among them, the relation between the maximum splitting $\Delta\nu_f$ of the components ν_{ij} in the fluorescence spectrum and the splitting $\Delta\nu_a$ of the components $\nu_{\perp,\parallel}$ in the absorption spectrum, the dependence of ν_{ij} on the order of the liquid-crystal matrix, and the $\nu_{\mathrm{cg}}(t)$ kinetics. The general approach developed here can be put in a concrete form to interpret the fluorescence spectra of impurity molecules of more complex form in uniaxial molecular media of various types (liquid crystals, Langmuir–Blodgett films, anisotropic polymer films, cell membranes, etc.).

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