

Model of induced configurational relaxation of molecular rotation in an inhomogeneous ensemble

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A theoretical model is proposed for considering the main characteristics of the luminescence emitted by phosphor molecules in polar liquid solutions allowing for thermal fluctuation inhomogeneities of reactive electric fields of the solvate sheaths of the molecules. The energy in these molecules in excess of the equilibrium value results in a torque which is additional to that obtained in the diffusion case. It is shown that the relevant kinetic equations can be solved analytically and that they give the time-dependent depolarization of the radiation. An analysis of the resultant solution is made and appropriate mathematical calculations are carried out for different values of the main parameters of the model. The results obtained are compared with the data yielded by high-temporal-resolution laser spectroscopy of liquid solutions of some organic phosphors.

1. INTRODUCTION

The structure and the motion of molecules in a liquid influence strongly the optical properties of a phosphor in a solution because of the van der Waals interactions. In particular, these factors determine the statistical causes of the broadening of the spectra of solutions, which is called inhomogeneous configurational broadening and is strongest in polar systems.^{1,2} It is responsible for the striking properties of these systems.

The inhomogeneous configurational broadening was discovered in 1970 for systems with broad diffuse spectra^{3,4} frozen by cooling to a temperature of $T = 77$ K, and later in 1972 it was observed^{5,6} in similar solutions frozen at lower (helium) temperatures. In the last two papers it was shown that at liquid helium temperatures one could observe, instead of the usual diffuse spectra, line fluorescence spectra of complex molecules with a resolved vibrational structure. The resolution was due to suppression of inhomogeneous broadening resulting from selective monochromatic excitation. This made it possible to achieve a much deeper understanding of the nature of the electronic spectra of complex molecules and led to the development of new and finer-scale methods for the investigation of these spectra.

Systematic studies of inhomogeneous configurational broadening have led to the development of new ideas on the nature of the spectra of complex molecules in solutions at various temperatures. General models of a solution allowing for the statistical causes of the broadening of the spectra were developed^{1,2} and allowed the spectroscopic properties due to such broadening to be described satisfactorily. Analysis of the models led to the discovery of new spectroscopic effects and relationships. The majority of them were confirmed subsequently by the work of many research teams.

For example, it was demonstrated experimentally^{7,8} that the inhomogeneous configurational broadening occurs not only in solid but also in liquid solutions. It is then of dynamic nature and as a rule can be detected only by kinetic spectroscopy techniques characterized by a high temporal resolution. This approach was found to be very fruitful and it revealed "upward" relaxation involving an increase in the

energy of a photon emitted by a fluorescing molecule in the course of configurational relaxation of its solvate sheath. Experiments revealed^{9,10} directional energy transfer between the components of an inhomogeneous ensemble of complex molecules in solid solutions. This made it possible to explain such well-known phenomena as the Weber effect¹¹ and the concentration-induced red shift of the fluorescence spectra in these systems, and to understand better the mechanism of energy transfer in photosynthetic apparatus of plants.

A result of fundamental importance was reported in Ref. 12, where "selective hole burning" was used to demonstrate that the homogeneous width of zero-phonon lines in an electronic-vibrational spectrum of complex molecules is very low at helium temperatures and corresponds to the radiation limit.

One of the most interesting effects associated with the inhomogeneous configurational broadening was discovered relatively recently¹³ in a study of the kinetics of the anisotropy of the polarization $r(t)$ of phosphor molecules in a polar solution. This is the light-induced rotation of phosphor molecules. It involves accelerated (compared with the classical Brownian) rotation of molecules during the first stages after excitation. It was established quite reliably that this light-induced rotation of phosphor molecules is related directly to the margin of the configurational intermolecular energy E_e of the solvate in an excited single state S_1 , which is governed by the degree of inhomogeneity of the ensemble of luminescing centers in the solution and by the frequency ν_{exc} of their excitation, transforming selectively to the luminescing state those solvates which have spectra in resonance with ν_{exc} . Therefore, such light-induced rotation of molecules is manifested by the dependence of the anisotropy kinetics $r(t)$ on ν_{exc} . If the energy margin E_e is zero, the rotation is purely Brownian in nature.

There are at least two mechanisms that can contribute to the light-induced rotation of phosphor molecules: 1) induced rotation of a phosphor dipole deflected, as a result of an excitation event, from its position in the ground state; 2) fast pulsed heating of the solvate, due to conversion of the configurational energy into the thermal energy in the course of relaxation.

The rotation of a dipole molecule was considered earlier¹⁴ using the Debye model of dielectric relaxation and allowing for the first of the mechanisms mentioned above. The second mechanism and the inhomogeneity of the solution were ignored in Ref. 14.

Here we propose a model which makes it possible to obtain an analytic form of the time dependence of the anisotropy of the polarization of the luminescence $r(t)$ of various members of an inhomogeneous molecular ensemble excited by a δ -like light pulse. This model provides a unified approach that can be used to explain both mechanisms contributing to the light-induced rotation of molecules, and also to account for the inhomogeneous nature of the members of the ensemble.

Section 2 describes our model and gives the derivation of the relevant kinetic equation. In Secs. 3–6 we find the solutions of this equation for the polarization anisotropy. We discuss the results and draw the conclusions in Secs. 7 and 8.

2. DESCRIPTION OF THE MODEL. KINETIC EQUATION

It is sufficient to use only an elementary theory of a polar solution^{1,2,15} in which the carrier of spectroscopic information about the solution is an elementary cell (solvate) which includes a fluorescing complex molecule and its immediate environment consisting of the solvent molecules. The dipole electric moment μ of the phosphor creates in each solvate the polarization of the immediate environment so that inside the cell a reactive electric field of intensity $R_I = \kappa\mu_g$ now appears; κ is the susceptibility of the solvent.

The inhomogeneous broadening factor is due to the thermal motion of molecules in a solution. For this reason the different solvates in the solution have somewhat different configurations of their own solvate sheaths and, consequently, different fluctuating (relative to the average value R_I) values of the reactive field R . Since the frequency of the 0–0 transition in the activator molecule depends on the reactive field intensity, an inhomogeneous ensemble of molecules, which are distributed in a certain manner in respect of the frequencies of the 0–0 transition, exists in the solution. This type of distribution is the main characteristic of the induced broadening.

In the model of a solution developed in Refs. 2 and 15 it is assumed that the state of the solvate is governed by the action of two forces: a polarizing force due to a permanent dipole moment of the activator molecule causing the appearance of a reactive field R inside the solvent, and a restoring force due to the action of the reactive field on the dipole molecule in the solvate sheath. The action of these two forces has the effect that the state of a solvate is characterized at any energy level by a parabolic dependence with a minimum corresponding to the equilibrium value of the reactive electric field. Thus, for example, in the case of the ground and first excited singlet electron states (g and e) of the dipole molecule, these energies become

$$E_g = \frac{(R - R_I)^2}{2\kappa}, \quad (1)$$

$$E_e = \frac{(R - R_{II})^2}{2\kappa} + \Delta E, \quad (2)$$

where

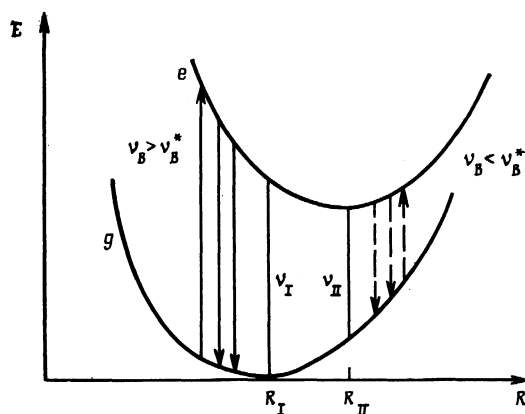


FIG. 1. Field diagram of the electron-configuration energy of the solvate.

$$\Delta E = h\nu_0 - \kappa\Delta\mu \frac{(\mu_g + \mu_e)}{2}. \quad (3)$$

The diagram shown in Fig. 1 is similar to the potential energy of a molecule, but instead of a molecule we are now considering the whole of the solvate and, consequently, instead of the vibrational energy, we are now dealing with the energy of the configurational interaction of molecules in the solvate. The generalized coordinate can naturally be the field intensity inside the solvate.

Such a diagram was introduced in Ref. 16 and is currently employed widely in an analysis of the spectral properties of solutions. It allows automatically for the inhomogeneous broadening and each inhomogeneously broadened state is represented by a point on the R axis. As in the case of molecules, we find that the Franck–Condon principle is obeyed (since the structure of the cell and, consequently, the field of R do not change during the time needed for an electronic transition), i.e., quantum transitions between both potential curves occur in this diagram along the vertical.

In the case of unexcited solvates we find that usually the equilibrium Boltzmann distribution of the configurational energy is satisfactory. The distribution function of excited solvates, expressed in terms of the configurational energy, depends on the ratio of the lifetime of an excited molecule τ_c and the configurational relaxation time of the solvate τ_k .

If

$$\tau_e > \tau_k, \quad (4)$$

then an equilibrium distribution of the configurational energies of excited solvates is established, whereas for the opposite inequality

$$\tau_e < \tau_k \quad (5)$$

the distribution is not in equilibrium and depends on the frequency of the excited light ν_{exc} .

In the case of liquid solutions we usually find that Eq. (4) is obeyed. Therefore, the steady-state fluorescence spectra show no dependence on ν_{exc} . In other words, in this situation the spectra behave as if homogeneously broadened. However, if we use the kinetic spectroscopy technique and determine numerous fluorescence spectra, then subject to the condition

$$\Delta t < \tau_k \quad (6)$$

(Δt is the time interval between the excitation and recording events) a liquid should exhibit, like a solid solution, a dependence of the position of the spectrum on ν_{exc} .

Brief exposure to monochromatic radiation results in selective excitation of solvates which begin to relax to the most probable configuration. The simplest form of the relaxation law can be described by the dependence

$$\nu_{\text{lum}}(t) = \nu_{\text{lum}}^{\text{II}} + (\nu_{\text{exc}} - \nu_{\text{exc}}^*) e^{-t/\tau_k}, \quad (7)$$

where $\nu_{\text{lum}}^{\text{II}}$ is the position of the middle frequency in the steady-state luminescence spectrum, whereas ν_{exc}^* is a special parameter of the solution which has the meaning of the frequency of the absorption maximum of solvates with a local field R_{II} .

Equation (7) explains well the evolution of the spectra of an inhomogeneous solution when it is excited by pulses of different frequencies. It follows from this equation that initially at $t = 0$ the position of the fluorescence maximum depends linearly on ν_{exc} , i.e., strong stimulated broadening of the spectra is observed. As time passes, the dependence of ν_{lum} on ν_{exc} becomes weaker, i.e., the stimulated broadening decreases and disappears completely when $t \rightarrow \infty$.

Therefore, in the case of a liquid solution the degree of inhomogeneous broadening decreases with time, i.e., the broadening is dynamic. If $t \rightarrow \infty$, the fluorescence maximum tends to its equilibrium value governed by the frequency $\nu_{\text{lum}}^{\text{II}}$.

The nature of relaxation of the fluorescence spectrum has a strong influence on the excitation frequencies ν_{exc} , i.e., on the nature of the solvate subjected to selective excitation. Exposure to radiation of frequencies $\nu_B > \nu_B^*$ (continuous arrows in Fig. 1) causes a long-wavelength shift to the fluorescence maximum during relaxation, whereas excitation in the frequency range $\nu_{\text{exc}} < \nu_{\text{exc}}^*$ (dashed arrows in Fig. 1) has the opposite effect: the band shifts toward shorter wavelengths with time. In all cases the fluorescence spectrum approaches the same equilibrium value $\nu_{\text{lum}}^{\text{II}}$. The characteristic frequency is ν_{exc}^* . The process of relaxation of excited solvates is related to this frequency.

As shown in Ref. 8, all these laws governing the dynamic inhomogeneous broadening have been observed experimentally.

We use these ideas about inhomogeneous solutions to develop a model describing rotation of the phosphor in the course of relaxation from an excited state.

When a molecule is excited electronically, its dipole moment changes abruptly, followed by the process of relaxation and modification of the solvate sheath with a characteristic time τ_h . The initial field \mathbf{R} , acting on the molecules in an ensemble, is excited selectively at the transition frequency ν_{exc} and begins to relax with time approaching firstly the equilibrium value R_{II} corresponding to the excited electronic term and, secondly, tending to become concurrent with the modified direction of the dipole axis. The mechanisms of relaxation of the field R and its transverse (relative to μ_e) component R_{\perp} are assumed to be identical:

$$R(t) = R_{\text{II}} + \Delta R e^{-t/\tau_k}, \quad R_{\perp}(t) = R_{\perp}(0) e^{-t/\tau_k}, \quad \Delta R = R(0) - R_{\text{II}}. \quad (8)$$

The dipole transition of a molecule to an excited state

corresponds to a polarization vector \mathbf{d} (linear absorption oscillator). Its strong binding to a molecule makes it possible (in the case of a spherical molecule) to determine uniquely the orientation, in the laboratory reference system, of the angle θ between the vector \mathbf{d} and the vector \mathbf{e}_a of the polarization of an excitation light pulse. The initial anisotropy of the function representing the density of the distribution of the dipoles $f(\theta, t)$ is characterized by the dependence $\cos^2 \theta$. Therefore, the initial condition is

$$f|_{t=0} = \text{const} + \text{const} P_2(\cos \theta), \quad (9)$$

where P_2 is a second-order Legendre polynomial.

The quantity $2\pi f(\theta, t) \sin \theta d\theta$ represents the density of absorption oscillators oriented in a belt ($\theta, \theta + d\theta$) of the phase surface. The rate of change $2\pi (\partial f / \partial t) \sin \theta d\theta$ of this density is governed by the difference between the rates $N(\theta + d\theta)$ and $N(\theta)$ of the fluxes through the upper and lower boundaries of this belt:

$$N(\theta + d\theta) - N(\theta) = \frac{\partial N}{\partial \theta} d\theta.$$

The quantity $N(\theta)$ is governed by two factors. First of all, there is the usual contribution of the isotropic Brownian rotational diffusion $D(\partial f / \partial \theta) 2\pi \sin \theta$. Moreover, there is a contribution due to the angular drift at the rate $M(t)/\xi$, where $M(t) = \mu_e R_{\perp}(t)$ is the relaxing torque due to the nonequilibrium nature of the solvate and ξ is the viscous friction coefficient of the solution. The contribution to the rate of change of the flux corresponding to this drift is $[M(t)/\xi] f(\theta, t) 2\pi \sin \theta$. Bearing all these points in mind, we obtain the following kinetic equation:

$$\frac{\partial f(\theta, t)}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left\{ \sin \theta \left[\frac{\partial f}{\partial \theta} + \frac{1}{\xi} M(t) f \right] \right\}, \quad (10)$$

where the torque is

$$M(t) = \mu_e R_{\perp}(0) e^{-t/\tau_k}. \quad (11)$$

Equation (10) is formally similar to the familiar Smoluchowski equation. However, there is a difference: the second term is governed by the interaction of a dipole molecule not with the external field but with the reactive field R fluctuating over an ensemble. The corresponding induced torque M appears as a result of a change in the dipole moment $\mu_g \rightarrow \mu_e$ in the course of absorption of light by a molecule. The subsequent relaxation terminates in a new equilibrium state of the solvate in which the reactive field R_{II} acting on an excited molecule differs from R_{\perp} if $\mu_g \neq \mu_e$.

In the case of selective excitation of molecules at a frequency corresponding to the field $R(0) = R_{\text{II}} + \Delta R$ the transverse component of the field is

$$R_{\perp}(0) = R_{\text{II}}(1 + \Gamma) \sin \delta,$$

where $\Gamma = \Delta R / R_{\text{II}}$ is the dimensionless parameter representing nonequilibrium of the system and δ is the angle between $\mathbf{R}(0)$ and μ_e . If $R(0) = R_{\text{II}}$, then $\mu_e \parallel \mathbf{R}(0)$ follows from minimalization of the equilibrium energy. Therefore, $\sin \delta$ vanishes simultaneously with the parameter Γ . In the case of a small deviation from equilibrium (low values of Γ) and, consequently, in the case of small angles δ the sines of these angles are of the same order of magnitude as Γ . Therefore, we shall assume subsequently that $R_{\perp}(0) = R_{\text{II}}(1 + \Gamma)\Gamma$ (Fig. 2).

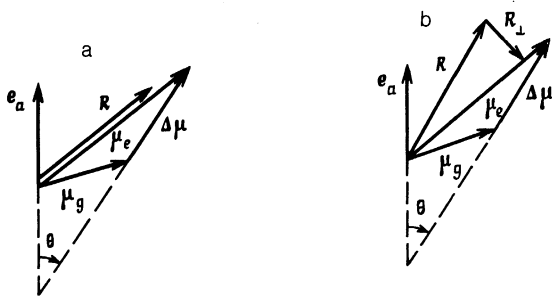


FIG. 2. Relative positions, in the plane of the diagram, of the reactive field \mathbf{R} , of the dipole moment of the ground (μ_g) and excited (μ_e) states of a molecule, and of moment of the transition $\Delta\mu$ on excitation with light polarized along the e_a direction. The angle θ defines uniquely the orientation of a spherical molecule in the laboratory system: a: $\nu_{exc} = \nu_{II}$ ($\Gamma = 0$). The reactive field $\mathbf{R} = \mathbf{R}_{II}$ does not create a torque rotating the molecule and relaxation to the equilibrium isotropic distribution occurs due to the Brownian motion; b: $\nu_{exc} \neq \nu_{II}$ ($\Gamma \neq 0$). The torque $\mathbf{M} = [\mathbf{u}_e \times \mathbf{R}]$ differs from zero and the rotation caused by it is superimposed on the Brownian diffusion.

The kinetic equation (10) can be written conveniently in terms of reduced (dimensionless) quantities. We shall express the time in units of Brownian diffusion time $\tau_D = 1/2D$:

$$\tau = t/\tau_D. \quad (12)$$

Then, instead of Eq. (10) we obtain

$$\frac{\partial f(\theta, \tau)}{\partial \tau} = \frac{1}{2} \Delta f(\theta, \tau) + \frac{1}{2} \lambda \Gamma (1+\Gamma) e^{-\beta \tau} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} [f(\theta, \tau) \sin \theta], \quad (13)$$

where the dimensionless interaction constant is

$$\lambda = \frac{\mu_e R_{II}}{kT} \quad (14)$$

(we have used here the Einstein relationship $D\xi = kT$), whereas the parameter

$$\beta = \tau_D/\tau_R \quad (15)$$

represents the ratio of the configurational and rotational-diffusion relaxation rates.

In view of the azimuthal symmetry of the distribution of spherical molecules, the solution of the kinetic equation (13) can be found in the form of a sum of Legendre polynomials:

$$f(\theta, \tau) = \sum_{l=0}^{\infty} A_l(\tau) P_l(\cos \theta). \quad (16)$$

Allowing for the normalization and for the condition (9), we find that the density of the initial distribution of the excited molecules is given by the function

$$f|_{\tau=0} = \frac{1}{4\pi} + A_2(0) P_2(\cos \theta). \quad (17)$$

As pointed out already, the light-induced rotation of molecules appears in the kinetics of the anisotropy of the polarization $r(\tau)$ of the luminescence emitted by solutions. It is therefore necessary to establish the relationship between

the kinetics of r and the kinetics of the nonequilibrium distribution (16) of the phosphor molecules discussed here.

3. REPRESENTATION OF THE POLARIZATION ANISOTROPY IN TERMS OF HARMONICS OF AN EXPANSION OF THE DISTRIBUTION FUNCTION $f(\theta, \tau)$

It follows from the Levshin-Perrin relationship that the maximum degree of anisotropy of the luminescence of the molecules modeled by linear absorption \mathbf{d}_a and emission \mathbf{d}_e oscillators, oriented in a molecular coordinate system at an angle α relative to one another, is

$$r = \frac{1}{5} (3 \cos^2 \alpha - 1) = \frac{2}{5} P_2(\cos \theta). \quad (18)$$

Rotation of molecules means that at a moment τ the polarization of the molecular luminescence $\mathbf{d}_e(\tau)$ makes an angle $\gamma(\tau) \neq \alpha$ relative to the direction of the absorption polarization $\mathbf{d}_a(0)$, as shown in Fig. 3. In view of the statistical scatter of the orientations of the molecules in our ensemble, it is necessary to carry out averaging of these orientations, so that

$$r(\tau) = \frac{2}{5} \langle P_2(\cos \gamma(\tau)) \rangle. \quad (19)$$

Rotations of a molecule can be followed by observing the rotating vector \mathbf{d}_e . Then, the statistical averaging in Eq. (19) is carried out using a distribution function $f(\xi, \tau)$ of the values of the angle ξ between the initial position of the vector $\mathbf{d}_e(0)$ and its current position $\mathbf{d}_e(\tau)$. Using the expansion (16), we obtain

$$r(\tau) = \frac{2}{5} \sum_{l=0}^{\infty} A_l(\tau) \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta P_2(\cos \gamma(\tau)) P_l(\cos \xi(\tau)). \quad (20)$$

Application of the addition theorem,¹⁷ transforms Eq. (20) to

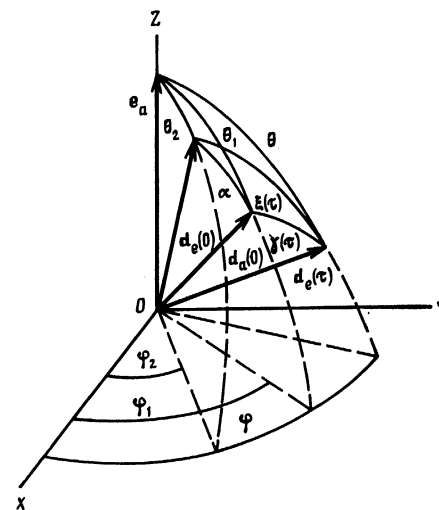


FIG. 3. Distribution of the axes of the absorption and emission (luminescence) dipoles (identified by the indices a and e , respectively) at the initial $\mathbf{d}(0)$ and subsequent arbitrary $\mathbf{d}(\tau)$ moments in time, plotted for a molecule rotating in a laboratory reference system characterized by the angular coordinates θ and φ .

$$\begin{aligned}
r(\tau) = & \frac{2}{5} \sum_{l=0}^{\infty} A_l(\tau) \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta \left\{ P_2(\cos \theta) P_2(\cos \theta_1) \right. \\
& + 2 \sum_{m=1}^2 \frac{(2-m)!}{(2+m)!} P_2^m(\cos \theta) P_2^m(\cos \theta_1) \cos[m(\varphi - \varphi_1)] \left. \right\} \\
& \times \left\{ P_l(\cos \theta) P_l(\cos \theta_2) \right. \\
& + 2 \sum_{k=1}^l \frac{(l-k)!}{(l+k)!} P_l^k(\cos \theta) P_l^k(\cos \theta_2) \cos[k(\varphi - \varphi_2)] \left. \right\}, \quad (21)
\end{aligned}$$

where (θ, φ) , (θ_1, φ_1) , (θ_2, φ_2) are the angular coordinates of the vectors $\mathbf{d}_e(\tau)$, $\mathbf{d}_e(0)$ and $\mathbf{d}_e(0)$ in the laboratory coordinate system (Fig. 3). In evaluating the integrals we allow for the fact that

$$\begin{aligned}
\int_0^{\pi} P_l(\cos \theta) P_2(\cos \theta) \sin \theta d\theta &= \frac{2}{5} \delta_{l,2}, \\
\int_0^{2\pi} \cos[m(\varphi - \varphi_1)] d\varphi &= 2\pi \delta_{m,0}
\end{aligned}$$

[and that it vanishes since $m \neq 0$ in Eq. (21)],

$$\begin{aligned}
\int_0^{2\pi} \cos[m(\varphi - \varphi_1)] \cos[k(\varphi - \varphi_2)] d\varphi &= \pi \delta_{m,k} \cos[m(\varphi_2 - \varphi_1)], \\
\int_0^{\pi} P_l^m(\cos \theta) P_2^m(\cos \theta) \sin \theta d\theta &= \frac{2}{5} \frac{(2+m)!}{(2-m)!} \delta_{l,2}.
\end{aligned}$$

The result is then

$$\begin{aligned}
r(\tau) = & \frac{8\pi}{25} A_2(\tau) \left\{ P_2(\cos \theta_1) P_2(\cos \theta_2) \right. \\
& + 2 \sum_{m=1}^2 \frac{(2-m)!}{(2+m)!} P_2^m(\cos \theta_1) P_2^m(\cos \theta_2) \cos[m(\varphi_1 - \varphi_2)] \left. \right\}. \quad (22)
\end{aligned}$$

Once again we apply the addition theorem, which yields

$$r(\tau) = r_0 A_2(\tau) \quad (23)$$

with a constant factor

$$r_0 = \frac{8\pi}{25} P_2(\cos \alpha). \quad (24)$$

Therefore, the kinetics of polarization of the instantaneous luminescence spectra is governed entirely by the time dependence of the second harmonic in the expansion (16), the initial condition for which is

$$A_2(0) = \frac{r(0)}{r_0} = \frac{50r(0)}{8\pi(3\cos^2\alpha - 1)}. \quad (25)$$

Specifying the values of $r(0)$ and of the angle α between the oscillators, we then use Eq. (25) to obtain the initial value $A_2(0)$ and to calculate the anisotropy of the polarization from the expression

$$r(\tau) = \frac{r(0)}{A_2(0)} A_2(\tau). \quad (26)$$

It follows from Eq. (26) that we can find r if we know $A_2(\tau)$; the latter can be obtained by solving the kinetic equation (13), which we now do.

4. CLOSED SYSTEM OF EQUATIONS FOR HARMONICS OF THE EXPANSION $A(\theta, \tau)$

We substitute the expansion of Eq. (16) into the kinetic equation (13) bearing in mind that the Legendre polynomials are eigenfunctions of the Laplace operator $[\Delta P_n = -n(n+1)P_n]$

$$\begin{aligned}
\sum_{n=0}^{\infty} \frac{dA_n}{d\tau} P_n(y) = & - \sum_{n=0}^{\infty} \frac{n(n+1)}{2} A_n(\tau) P_n(y) \\
- \frac{\lambda}{2} \Gamma(1+\Gamma) e^{-\beta\tau} \sum_{n=0}^{\infty} A_n(\tau) \frac{d}{dy} & [(1-y^2)^{1/2} P_n(y)], \quad (27)
\end{aligned}$$

where $y = \cos \theta$.

We now convolve both parts of equation with $P_l(y)$ (where the orthonormalization condition for the polynomials is $\int_{-1}^1 P_n(y) P_l(y) dy = 2/(2l+1) \delta_{ln}$):

$$\frac{dA_l}{d\tau} = -\frac{l(l+1)}{4} A_l + \frac{2l+1}{4} \lambda \Gamma(1+\Gamma) e^{-\beta\tau} \sum_{n=0}^{\infty} J_{ln} A_n. \quad (28)$$

The overlap integrals J_{ln} occurring in the system (28) are

$$J_{ln} = \int_{-1}^1 (1-y^2)^{1/2} P_n(y) \frac{dP_l}{dy} dy.$$

Our calculations show that these integrals decrease rapidly on increase in the difference $n-l$:

$$\begin{aligned}
J_{10} \approx 1,571; \quad J_{12} \approx -0,589; \quad J_{14} \approx -0,024; \\
J_{21} \approx 1,178; \quad J_{23} \approx -0,098; \quad J_{25} \approx -0,015.
\end{aligned}$$

It therefore follows that in the case of the first harmonics we can limit ourselves to the closed system obtained from Eq. (28) allowing for the smallness of the overlap with the other harmonics:

$$\begin{aligned}
\frac{dA_0}{d\tau} &= 0, \\
\frac{dA_1}{d\tau} &= -A_1 - \lambda \Gamma(1+\Gamma) e^{-\beta\tau} (\alpha_1 A_2 - \alpha_0 A_0), \\
\frac{dA_2}{d\tau} &= -3A_2 + \alpha_2 \lambda \Gamma(1+\Gamma) e^{-\beta\tau} A_1, \\
\alpha_0 &= 1,571, \quad \alpha_1 = 0,442, \quad \alpha_2 = 1,545
\end{aligned} \quad (29)$$

subject to the initial conditions

$$A_0(0) = \frac{1}{4\pi} (\equiv A_0(\tau)), \quad A_1(0) = 0, \quad A_2(0) \neq 0 \quad (30)$$

[$A_2(0)$ is given by Eq. (25)].

In the work referred to above¹⁴ the depolarization of the luminescence in a solution is divided into two stages: kinetic and stochastic, which occur independently of one another. During the first stage the rotation occurs only under the influence of the reactive field with a characteristic dielectric relaxation time τ_k . During the second stage, when the field has reached its equilibrium value, the governing factor is the diffusion mechanism with a characteristic time τ_D . There-

fore, the two-exponential nature of the kinetics of depolarization is assumed right from the beginning in Ref. 14.

In our model no such initial assumption is made. For example, in the second equation of the system (29) we cannot ignore the first diffusion term for small values of τ even in the range of strong fields $\lambda \gg 1$, since for these values of τ the second harmonic obeys $A_2 \gg |A_1|$. Therefore, the splitting of the process into two stages adopted in Ref. 14 should be regarded simply as the zeroth approximation.

The system of the first-order equations (29) can be reduced in the usual manner to one second-order equation for the function

$$F = \frac{r(\tau)}{r_D(\tau)} A_2(0), \quad (31)$$

which represents the ratio of the anisotropy to its time dependence in the pure Brownian diffusion case [$r_D(\tau) = r(0) e^{-3\tau}$]. The equivalent equation can be conveniently written in terms of a variable $x = e^{-\beta\tau}$:

$$xF''(x) + \frac{2}{\beta} F'(x) + \left(\frac{k}{\beta}\right)^2 xF(x) = \left(\frac{q}{\beta}\right)^2 x^{(\beta-3)/\beta} \quad (32)$$

subject to the initial conditions

$$F(1) = A_2(0), \quad F'(1) = 0. \quad (33)$$

The effective interaction constants are

$$k = (\alpha_1 \alpha_2)^{1/2} \lambda |\Gamma| (1 + \Gamma), \quad q = (\alpha_0 \alpha_2 / 4\pi)^{1/2} \lambda |\Gamma| (1 + \Gamma).$$

It is important to note that the coefficients in Eq. (32) are quadratic in terms of the parameter Γ and, consequently, the nature of the solution of this equation is independent of the sign of the transverse component of the field R_1 .

We shall now consider the procedure used in obtaining the solution of Eq. (32) in the general case, and also for the most typical and interesting case $\beta = 1$ because then the solution method is simplest. In both cases we shall show that an analytic solution can be obtained.

5. SIMPLEST CASE ($\beta = 1$)

In the case $\beta = 1$ ($\tau_D = \tau_k$), substitution for the required function of

$$\varphi(x) = xF(x) \quad (34)$$

modifies Eq. (32) to the equation for forced harmonic oscillations:

$$\varphi''(x) + k^2 \varphi(x) = \left(\frac{q}{x}\right)^2 \quad (35)$$

subject to the initial conditions

$$\varphi(1) = \varphi'(1) = A_1(0). \quad (36)$$

It is useful to consider directly the nature of the solution at the initial moments (when τ is small). Expanding $\varphi(x)$ as a Taylor series in the vicinity of the point $x = 1$, retaining only the quadratic terms, and defining $\varphi''(x)$ on the basis of Eq. (35), we find that

$$\varphi(x) \approx A_2(0) \left[x - \left(k^2 - \frac{q^2}{A_0(0)} \right) (1-x)^2 \right].$$

Therefore,

$$\frac{r(\tau)}{r(0)} \approx e^{-2\tau} \left[e^{-\tau} - \left(0,682 - \frac{0,145}{A_2(0)} \right) \lambda^2 \Gamma^2 (1 + \Gamma)^2 (1 - e^{-\tau})^2 \right].$$

We can see that during the initial stage the process of relaxation is known to be faster than the Brownian diffusion and, moreover, in the anti-Stokes range ($\Gamma > 0$) it is faster than in the Stokes case ($\Gamma < 0$).

We now consider the solution for arbitrary values of τ . The general solution of a homogeneous equation corresponding to Eq. (35) is

$$\varphi_0(x) = a_k \cos(kx) + b_k \sin(kx),$$

whereas the particular solution of the inhomogeneous equation (35) is

$$\varphi_1(x) = \frac{q^2}{k} \int_1^x \sin[k(x-t)] \frac{dt}{t^2}.$$

In evaluating the last integral we obtained the sine integral ($\text{Si}(x) = \int_0^x (\sin t/t) dt$) and the cosine integral ($\text{Ci}(x) = -\int_x^\infty (\cos t/t) dt$). We then have

$$\varphi_1(x) = -q^2 \left\{ \frac{\sin[k(1-x)]}{k} + [\text{Ci}(kx) - \text{Ci}(k)] \cos(kx) + [\text{Si}(kx) - \text{Si}(k)] \sin(kx) \right\}.$$

It follows from the initial conditions given by Eq. (36) that

$$a_k = A_2(0) \frac{(k \cos k - \sin k)}{k}, \quad b_k = A_2(0) \frac{(k \sin k + \cos k)}{k}.$$

We have therefore

$$\varphi_0(x) = A_2(0) \left\{ \cos[k(1-x)] - \frac{\sin[k(1-x)]}{k} \right\},$$

and the solution for the harmonic $A_2(\tau)$ is

$$A_2(\tau) = e^{-2\tau} [\varphi_0(x) + \varphi_1(x)].$$

Using next Eq. (26), we obtain

$$r(\tau) = r(0) e^{-2\tau} \left\{ \cos[k(1-x)] - \left(1 + \frac{q^2}{A_2(0)} \right) \frac{\sin[k(1-x)]}{k} - \frac{q^2}{A_2(0)} \{ [\text{Ci}(kx) - \text{Ci}(k)] \cos(kx) + [\text{Si}(kx) - \text{Si}(k)] \sin(kx) \} \right\}. \quad (37)$$

It is interesting that this exponential decay with time is "hidden" in the arguments of the oscillatory functions.

6. GENERAL CASE OF ARBITRARY VALUES OF β

We introduce the function $\varphi(x) = x^\nu F(x)$, for which Eq. (32) can be rewritten in the form

$$x^2 \varphi''(x) + \left(\frac{2}{\beta} - 2\nu \right) \varphi'(x) x + \left[\left(\frac{kx}{\beta} \right)^2 - \nu \left(\frac{2}{\beta} - \nu - 1 \right) \right] \varphi(x) = \left(\frac{q}{\beta} \right)^2 x^{\nu + (2\beta - 3)/\beta}. \quad (38)$$

We select the index ν so that the numerical coefficient of the first derivative $\varphi'(x)$ in Eq. (38) is unity:

$$\nu = \frac{2-\beta}{2\beta}. \quad (39)$$

As a result of this solution we obtain an inhomogeneous Bessel equation:

$$\xi^2 \varphi''(\xi) + \xi \varphi'(\xi) + (\xi^2 - \nu^2) \varphi(\xi) = \left(\frac{q}{\beta}\right)^2 \left(\frac{\beta \xi}{k}\right)^{(1-4\nu)/2} \quad (40)$$

with an exponent ν and with a variable

$$\xi = \frac{k}{\beta} e^{-\beta\tau} \quad (41)$$

subject to the initial conditions

$$\varphi\left(\frac{k}{\beta}\right) = A_2(0), \quad \varphi'\left(\frac{k}{\beta}\right) = \frac{\nu\beta}{k} A_2(0). \quad (42)$$

The general solution of the homogeneous Bessel equation is a superposition of the Bessel J_ν and Neumann N_ν functions. Variation of the arbitrary constants yields the solution of the inhomogeneous Bessel equation (40) in the form

$$\begin{aligned} \varphi(\xi) = & J_\nu(\xi) \left[C_1 - \left(\frac{q}{\beta}\right)^2 \left(\frac{\beta}{k}\right)^{(1-4\nu)/2} \frac{\pi}{2} \int_{k/2}^{\xi} J_\nu(t) t^{-(1+4\nu)/2} dt \right] \\ & + N_\nu(\xi) \left[C_2 + \left(\frac{q}{\beta}\right)^2 \left(\frac{\beta}{k}\right)^{(1-4\nu)/2} \frac{\pi}{2} \int_{k/2}^{\xi} N_\nu(t) t^{-(1+4\nu)/2} dt \right]. \end{aligned} \quad (43)$$

By definition, the expression

$$s_{\mu,\nu}(\xi) = \frac{\pi}{2} \left[N_\nu(\xi) \int_0^{\xi} J_\nu(t) t^\mu dt - J_\nu(\xi) \int_0^{\xi} N_\nu(t) t^\mu dt \right] \quad (44)$$

represents the Lommel functions.¹⁸ Using these functions and also the relationship that follows from Eqs. (31) and (34)

$$A_2(\tau) = e^{(\beta\nu-3)\tau} \varphi(\xi),$$

we find that

$$\begin{aligned} r(\tau) = & \frac{r(0)}{A_2(0)} e^{-(2+\beta/2)\tau} \left\{ C_1 J_\nu\left(\frac{k}{\beta} e^{-\beta\tau}\right) + C_2 N_\nu\left(\frac{k}{\beta} e^{-\beta\tau}\right) \right. \\ & \left. + \left(\frac{q}{\beta}\right)^2 \left(\frac{\beta}{k}\right)^{1+\mu} \left[s_{\mu,\nu}\left(\frac{k}{\beta} e^{-\beta\tau}\right) - s_{\mu,\nu}\left(\frac{k}{\beta}\right) \right] \right\}, \end{aligned} \quad (45)$$

where

$$\mu = -\frac{1+4\nu}{2}. \quad (46)$$

The constants C_1 and C_2 are found from the conditions (42) and are given by

$$\begin{aligned} C_1 = & \frac{\pi}{2} A_2(0) \frac{k}{\beta} \left[N_\nu'\left(\frac{k}{\beta}\right) - \frac{\beta\nu}{k} N_\nu\left(\frac{k}{\beta}\right) \right], \\ C_2 = & \frac{\pi}{2} A_2(0) \frac{k}{\beta} \left[\frac{\beta\nu}{k} J_\nu\left(\frac{k}{\beta}\right) - J_\nu'\left(\frac{k}{\beta}\right) \right]. \end{aligned} \quad (47)$$

It should be pointed out that if $\beta = 1$, then $\nu = 1/2$, $J_{1/2}(\xi) = (2/\pi\xi)^{1/2} \sin \xi$, $N_{1/2}(\xi) = -(2/\pi\xi)^{1/2} \cos \xi$ and we come back to the solution (37).

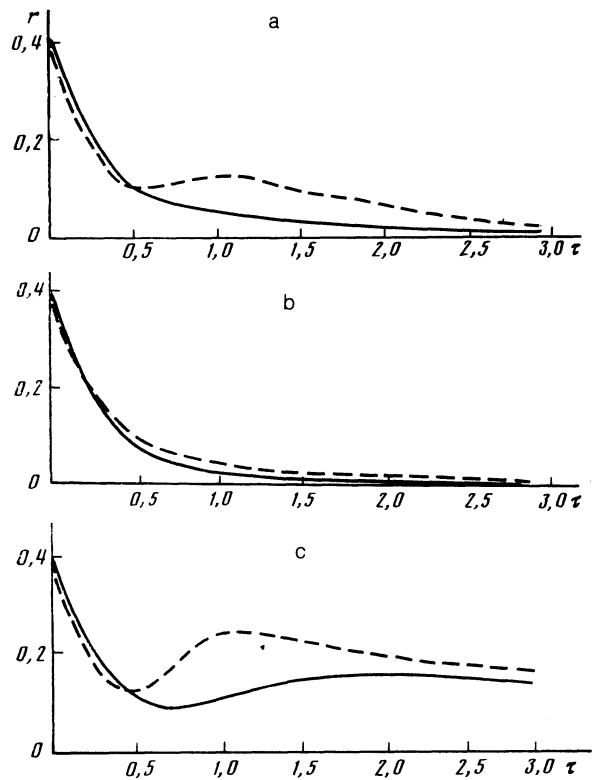


FIG. 4. Dependence of the anisotropy of the luminescence polarization r on the reduced time τ for $\alpha = 0$, $\lambda = 13$, $r(0) = 0.4$, and the following values of β : a) $\beta = 1$; b) $\beta = 2$; c) $\beta = 0.1$. The continuous curves represent excitation in the Stokes part of the spectrum ($\Gamma = -0.3$), whereas the dashed curves correspond to the anti-Stokes part ($\Gamma = +0.3$).

7. DISCUSSION OF RESULTS

Figure 4 shows graphically our analytic solutions given by Eqs. (37) and (45); they are plotted for different values of the parameters of the model on the assumption that the absorption and emission (luminescence) oscillators of a molecule are parallel ($\alpha = 0$) and that the initial anisotropy is typically $r(0) = 0.4$.

A common feature of all the cases plotted there is the absence of a simple monoexponential relaxation with time. It is quite clear that the solutions can be represented by two exponential functions, one of which represents rapid decay of the anisotropy at the initial moments and the other represents slowing down during the final stage of the relaxation process. For example, for $\beta = 1$ and $\Gamma = 0.3$ (Fig. 4a) and within the time interval $0 \leq \tau \leq 0.4$ the decay is exponential with the argument 3.2τ (it is faster than the case of pure Brownian diffusion), whereas after $\tau > 2$ the argument is 1.4τ (slower compared with the diffusion case).

For all values of β there is a characteristic difference between the relaxation processes on the Stokes ($\Gamma < 0$) and anti-Stokes ($\Gamma > 0$) sides of the spectrum. The latter corresponds to higher values of the reactive field ($R > R_{II}$) than the former ($R < R_{II}$). Therefore, we can estimate the role of the field intensity. We can see that during the initial stage the field imparts rotation to molecules which is additional to the Brownian motion and relaxation on the right-field side ($\Gamma > 0$) is faster, as pointed out already in Sec. 5. However, the situation then changes and in high fields the polarization

decays more slowly with time than in weak fields. This is due to the orienting effect of the field, which imparts an additional "rigidity" to the system. This "rigidity" is manifested most clearly for low values of the parameter β ($\tau_D \ll \tau_k$) when, on the scale of the diffusion time $\tau \sim 1$, the quantity R_1 remains practically constant.

The graphs in Fig. 4c show a characteristic plateau, which is due to the fact that if $\tau \lesssim 1/\beta$, the almost constant reactive field of the solvate orients (like a static external field) the dipole along its own direction and there is no significant depolarization of the luminescence in this range of values of τ . Naturally, in the anti-Stokes range of the stronger fields the orienting effect is manifested more clearly than in the Stokes range (higher plateau). If $\tau > 1/\beta$, the non-equilibrium orienting moment begins to decay and $r(\tau)$ tends to zero.

We can readily obtain the solution of Eq. (29) in the limiting hypothetical case $\beta = 0$, when the plateau extends to any time, no matter how long. We then have

$$\lim_{\tau \rightarrow \infty} r(\tau) = \frac{r(0)}{A_2(0)} \frac{q^2}{k^2 + 3}.$$

For the specified parameters [$\alpha = 0$, $r(0) = 0.4$] we find that $r(\infty) = 0.6$. It is interesting to note that in this case the relaxation processes enhance the anisotropy compared with its initial value.

The relationships illustrated in Fig. 4 discussed so far apply, as pointed out already, to the parallel orientation of the absorption and emission (luminescence) oscillators ($\alpha = 0$). However, $r(\tau)$ should depend fairly strongly on α , because $r(0)/A_2(0)$ in the solution given by Eq. (45) depends on α in accordance with Eq. (25). Figure 5 shows the

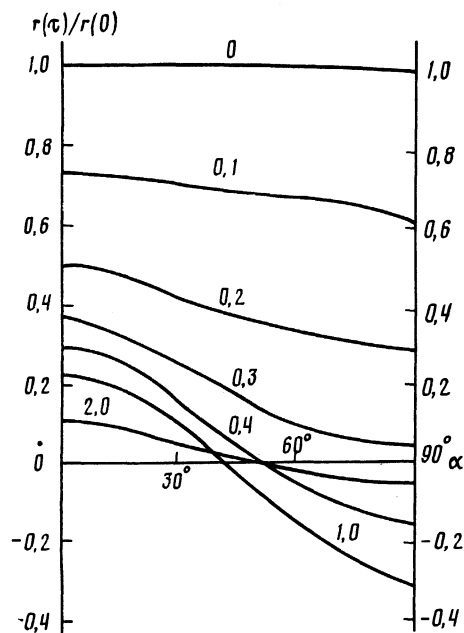


FIG. 5. Isochronous curves representing the anisotropy r for the case when $\beta = 1$ and $\Gamma = +0.3$. The numbers alongside the curves identify the corresponding moments in time τ . An increase in τ makes the dependence of r on the angle α between the absorption and luminescence oscillators stronger (this is true right up to $\tau \approx 1$) and then the slope of the curves decreases and the curves themselves approach the abscissa with increasing τ .

isochronous curves for different values of the angle α of the phosphor molecule (which is a characteristic analog of the polarization diagrams). In the range $\alpha \geq 40^\circ$ we observed behavior which is qualitatively new compared with the $\alpha = 0$ case: the polarization anisotropy becomes negative. Naturally, the change in the sign of r tends to increase the angle between the directions of polarization of light absorbed and emitted by a molecule.

Moreover, as α increases, the two-exponential nature of the time dependence $r(\tau)$ becomes even clearer. For example, in the case $\beta = 1$ and $\Gamma = 0.3$ under discussion, but on the assumption that $\alpha = 90^\circ$, we find that the initial stage corresponding to $\tau \lesssim 0.2$ is characterized by an exponential decay with an argument $\approx 10\tau$, whereas beginning from $\tau \sim 1$ the argument becomes $\approx 1.36\tau$.

The following comments should be made about the selected value of the interaction constant $\lambda = \mu_e R_{II}/kT$. We had in mind a polar solution of 3-amino-N-methyl-phthalimide (3ANMP) in glycerin, for which the two-exponential kinetics of the anisotropy was observed, among other solutions, in Ref. 19 by the method of selective laser spectroscopy with nanosecond resolution. In this case we have $\mu_e \approx 5$ D and $R_{II} = (3-5) \times 10^7$ V/cm. Then, at room temperature we obtain $\lambda \approx 13-18$.

8. CONCLUSIONS

This analytic solution for the anisotropy kinetics of molecules of the dipole solution reflects correctly the main physical relationships of the light-induced rotation of molecules of some of the investigated polar solutions. Naturally, all the observed features apply only to dipole molecules in polar solvents. In the case of nonpolar solvents the induced torque M in Eq. (10) is small and the constant is $\lambda \ll 1$. In this case the usual diffusive nature of the kinetics of depolarization of the luminescence is retained.

Our model works best in the following two situations: 1) molecules of a phosphor are nearly spherical, so that it is necessary to generalize these results to the more complicated case of nonspherical molecules, which should make it possible to carry out a more detailed quantitative comparison with experimental data; 2) heat evolution in the immediate molecular environment of a phosphor does not affect strongly the rotational diffusion coefficient D . In the case of real systems this condition may be satisfied quite well. Nevertheless, heat evolution in a solvate after excitation of an activation center with light can be allowed for also on the basis of the above model. It appears in particular in the time dependence of the temperature T and, consequently, in the time dependence of the interaction constants $\lambda(\tau) = \mu_e R_{II}/kT(\tau)$, which are given by the solution of the problem of a point pulsed heat source in the surrounding thermostat. In the final analysis this mechanism is also due to the induced torque $M(\tau)$.

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