

Orientation of the excited molecules of a solution during configurational relaxation

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The analytic model developed by us to describe the kinetics of the anisotropy of a nonuniform ensemble of dipole molecules shows that the excited molecules of a luminescent material become oriented during configurational relaxation to an equilibrium state.

An analytic model describing the kinetics of depolarization of luminescence of spherical dipole molecules of a luminescent material in polar liquid solutions was proposed by Tomin and Shneerson.¹ The kinetics of the molecules of the luminescent material can be attributed, according to Tomin and Shneerson,¹ to two factors: 1) the rotational Brownian diffusion (with time scales τ_B) and 2) stimulated force moment \vec{M} which acts on the electric dipole $\vec{\mu}_e$ of the excited molecule due to the reactive field \vec{R} of the nonequilibrium (according to Franck–Condon) solvation sheath (the typical time it takes for this moment to vanish is equal to the time τ_R it takes the solvate to reach equilibrium state). The relative effect of these two mechanisms on the relaxation processes is determined, in particular, by the parameter $\beta = \tau_B/\tau_R$. The distribution function for the orientations of the dipoles of spherically symmetric molecules $f(\theta, t)$ can be written as a series in Legendre polynomials

$$f(\theta, t) = \sum_{n=0}^{\infty} A_n(t) P_n(\cos \theta). \quad (1)$$

The second harmonic $A_2(t)$ of expansion (1) completely determines the time evolution of the anisotropy of polarization of the radiation $r(t)$. The exact analytic expressions for the function $r(t)$ were determined in Ref. 1 by solving the kinetic equation for $f(\theta, t)$, which includes the two relaxation mechanisms mentioned above.

In the present letter we report the observation of a new effect which follows from the solutions obtained in Ref. 1: We observed that the excited dipole molecules of the luminescent material become oriented during the configurational relaxation. This effect occurs when the solvation sheath relaxes at a relatively slow rate ($\beta < 1$).

Figures 1 and 2 show plots of the analytic solutions of $r(\tau)$ in the relaxation-time function $\tau = t/\tau_B$ for various cases in which the excitation is caused by a linearly polarized light. As can be seen from these figures, the function $r(\tau)$ has three clearly defined regions in all cases, with a different behavior of the kinetics in each case (labeled τ_1, τ_2, τ_3 in Fig. 1). Immediately after the completion of the excitation pulse, the function $r(\tau)$ decays to a minimum value, and then begins to increase for a time τ_1 until it reaches a maximum value τ_{\max} . The fluctuation of the anisotropy is then seen to decay rapidly over a time interval τ_2 . During this time, the values of $r(\tau)$ are much

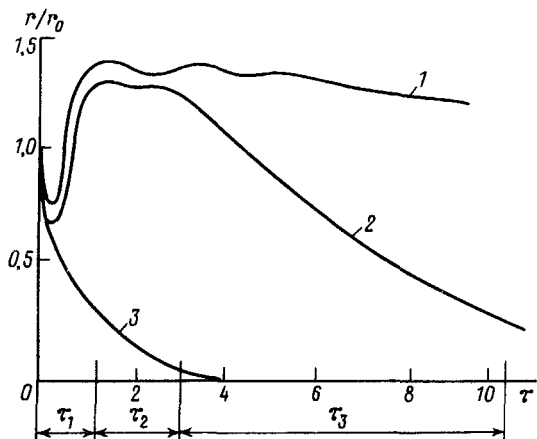


FIG. 1. Time evolution of the anisotropy of radiation for various ratios of the Brownian relaxation time and the configurational relaxation time. 1— $\beta = 0.1$; 2— $\beta = 0.5$; 3— $\beta = 5$. In all cases, $\lambda = 25$. Typical time intervals τ_1 , τ_2 , and τ_3 , corresponding to those in Fig. 2, are given.

higher than the limiting values $r_{\text{lim}} = r(0)$ which were derived from the Levshin-Perrin theory. The orientation of the excited molecules is disrupted in the region τ_3 .

The region τ_2 in Figs. 1 and 2 can thus be interpreted as the onset of the ordered orientational state of excited molecules during the configurational relaxation which begins in the solvate immediately after the excitation.

The plots in Figs. 1 and 2 show that orientation is observed at small values of the parameter β , $\beta \lesssim 1$. The orientation increases with the value $\lambda = \mu_e R / kT$; for $\lambda < 13$ we have $r_{\text{max}} = r_{\text{lim}}$. The strongest orientation occurs at large values of λ (at 25 and 50, for example).

The orientation can be explained qualitatively as follows. At small values of β the reactive field varies only slightly on the diffusion time scale, $\tau \sim 1$. Upon completion of the Brownian depolarization ($\tau \lesssim 1$), the stimulated moment, $\vec{M} = |\mu_e \vec{R}|$, whose val-

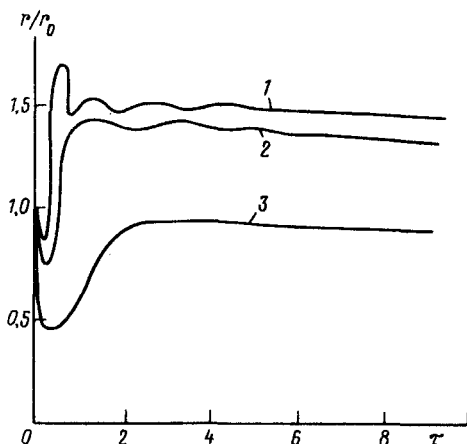


FIG. 2. Time evolution of the anisotropy of radiation for various values of the constants λ of the interaction of the dipole moment of a molecule with the reactive field of its solvation sheath. 1— $\lambda = 50$; 2— $\lambda = 25$; 3— $\lambda = 13$. In all cases $\beta = 0.1$.

ue remains the same, takes over the control of the kinetics. This moment changes in the direction of orientation of the diffusion-disoriented dipoles μ_e principally in the direction of the local field, so that the resulting orientation is ultimately attributable to the van der Waals interaction of the solvate molecules. We can thus legitimately say that excited molecules are oriented by the field of the van der Waals forces.

It should be noted that this effect is observed when a solution is excited by all the light frequencies contained in the absorption band of the molecules of an inhomogeneous ensemble which produces a nonequilibrium configuration of the molecules in the solvate.²

Experimental verification of the optical orientation would be useful, in our view, since only a destruction of the light-induced polarization has been observed until now during the relaxation of the excited state.

The plots that we obtained make it possible to clearly identify, on the basis of experimental data, the characteristic features of the different types of motion of the molecules in the solvate and of the solvate itself as a supermolecular structure in the liquid state.

Orientation of excited molecules can be utilized to construct devices with a dynamic polarization memory.

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¹V. I. Tomin and V. L. Shneerson, *Zh. Eksp. Teor. Fiz.* **98**(4), 1204 (1990) [*Sov. Phys. JETP* **71**(4), 674 (1990)].

²N. A. Nemkovich, V. I. Matseiko, L. N. Rubinov, and V. I. Tomin, *Pis'ma Zh. Eksp. Teor. Fiz.* **29**, 780 (1979) [*JETP Lett.* **29**, 717 (1979)].

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