

CONCENTRATION SHIFT OF FLUORESCENCE SPECTRA OF COMPOUND MOLECULES IN POLYMERIC MATRICES

V.V. Gruzinskii, M.A. Senyuk, and A.I. Golovaty

Belorussian State University, Minsk

Received January 6, 1993

Concentration shifts of the fluorescence spectra of compound molecules in stretched and free films of polyvinil alcohol are studied. It is shown that stretching of polymeric films leads to an increase of the efficiency of excitation energy migration between the activator molecules in the case of tryptaflavin and 2-(stilbenyl-4)-5-phenyloxazol, while in the case of rhodamine-6G and eosine the dependence is inverse. Investigation of polarization spectra of fluorescence and spectral behavior of dichroism allowed us to explain the observed facts by different orientation of absorbing and fluorescent oscillators of these substances relative to the film stretching axis.

It is well known that solutions of organic substances are most often used as active media of dye lasers.^{1,2} However, recently the number of papers devoted to investigations of the lasing properties of organic substances introduced into the polymeric films has been increased.³⁻⁵ In Ref. 3 the fluorescence and lasing characteristics of substances introduced into polymeric matrix are shown to have some peculiarities caused by the interaction between the doped molecules and a polymer. One of the reasons can be heterogeneity of the polymer structure because of different types of imperfection.^{6,7} The change in concentration of doped molecules ought to modify their arrangement in the polymer and, consequently, to change energies of intermolecular interactions between fluorescent molecules and their close surroundings. Knowledge of basic regularities of the influence of microenvironment of molecules on the spectral-luminescence and lasing properties of the organic substances is urgently needed when composing new active laser media of polymers doped with molecules of organic compounds at concentrations providing for optimal parameters of laser emission.

In this paper we present some results of our investigations of the influence of number densities of molecules of organic compounds on their luminescence spectral properties in stretched and free films of polyvinil alcohol (PVA).

To measure absorption spectra we used a KSVU-23 spectral-luminescence instrument. We recorded the fluorescence spectra using an SDL-2 spectrometer. Preparation of samples and their one-axis stretching were carried out using the technique described in Ref. 8.

Figure 1 shows fluorescence spectra of tryptaflavin in a free PVA film. As can be seen from Fig. 1 an increase of the concentration of activator molecules in a polymer matrix leads to a bathochromic shift of the fluorescence spectra. The long-wave shift of tryptaflavin emission band with increasing concentration (from 10^{-5} to $10^{-2.5}$ mole/liter) reaches 17 nm for a free PVA and 19 nm for a film stretched along one axis.

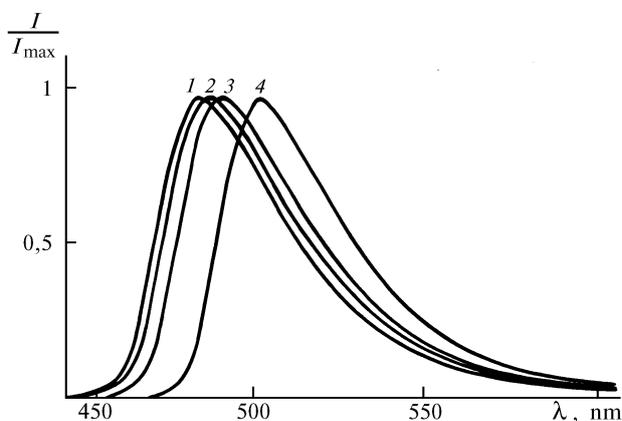


FIG. 1. Tryptaflavin fluorescence spectra in isotropic PVA films with concentrations: $C = 10^{-6} - 10^{-5}$ (1), $10^{-4.5}$ (2), $10^{-3.5}$ (3), and $10^{-2.5}$ mole/liter (4). $\lambda_{\text{excit}} = 360$ nm.

It should be noted that the bathochromic shift of the fluorescence spectrum of tryptaflavin molecules introduced into the PVA matrix becomes noticeable at $C = 10^{-5}$ mole/liter and reaches considerable values at $C = 10^{-4.5}$ mole/liter - 10^{-4} mole/liter. These results show that an efficient radiationless transfer of the excitation energy in the PVA films occurs at much lower concentration than in the viscous solutions of these same compounds.

As was mentioned above some stable structure imperfections of different types are always observed in polymers. As shown in Ref. 9 and 10 the activator molecules at low concentrations are primarily deposited into the stable defects of the polymer structure. As a consequence, local concentrations of the activator molecules here is higher than the concentration averaged over the whole volume of a polymer. This results in a radiationless exchange by the excitation energy among the activator molecules introduced into a polymer matrix at much smaller average concentrations than in isotropic solutions.

Let us now consider the dependence of the bathochromic shift of the tryptaflavin fluorescence spectral maximum on the concentration of the activator molecules in free and stretched PVA films.

First note that stretching of a polymer film along one axis results in a small hypsochromic shift of the tryptaflavin fluorescence spectrum measured at $C = 10^{-5}$ mole/liter compared to that observed for this same substance and at this same concentration but in a free film. Since there are practically no radiationless energy transfer at such a small concentration. Full coincidence of tryptaflavin spectra measured at concentration of 10^{-5} and 10^{-6} mole/liter confirms this. Then the hypsochromic shift of the emission band shows the appearance of fluorescent centers in the stretched film, and that purely electron transitions in these centers occur at higher frequencies. The origin of such centers most probably is due to tensile stress in a

mechanically stretched film, because such stresses change local electric fields that, in turn, changes energy of interaction between the fluorescent molecules and the molecules of the closest surrounding.

As follows from Fig. 2 *a* the dependence of bathochromic shift $\Delta\nu_{\max}$ of the fluorescence spectral maximum on the tryptaflavin concentration in the free PVA film is stronger than that in a stretched film in the region of low concentrations ($C = 10^{-5}$ – $10^{-3.5}$ mole/liter). In other words the fluorescence spectra of tryptaflavin in a free PVA film undergo bathochromic shift at lower tryptaflavin concentration than the spectra of this compound measured in stretched films. This effect can evidently be explained by a change of volumes of stable defects due to stretching the polymer matrices along only one axis and, as a consequence, because of rearrangement of molecules in a defect.

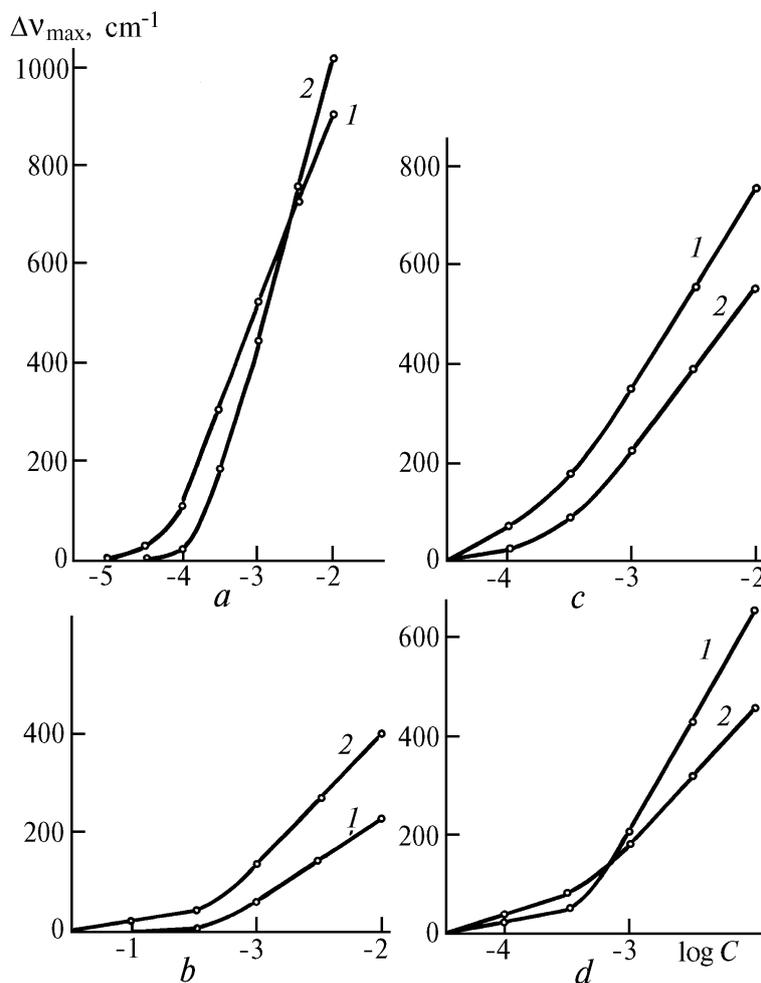


FIG. 2. Dependence of the shift of the fluorescence spectrum maximum in isotropic (1) and anisotropic (2) PVA films on the concentration of tryptaflavin (a), 2-(stylybenyl-4)-5-phenyloxazol (b), rhodamine 6G (c), and eosine (d) molecules.

In the region of high tryptaflavin concentrations ($C = 10^{-3.5}$ – $10^{-2.5}$ mole/liter) the dependence of bathochromic shift of the fluorescence spectra on concentration $\Delta\nu_{\max} = f(C)$ in the free film is, on the contrary, more slow than that in the stretched PVA film. A stronger dependence of this shift on concentration is indicative of higher probability of radiationless transfer of the excitation energy among the tryptaflavin molecules in the stretched film compared to the

probability of energy redistribution among the activator molecules in the free film.

The change of the probability of radiationless energy transfer can be caused by both the change of distances between the molecules and the change of their mutual orientation. A simulation of this process have been carried out to estimate the influence of one-axis stretching on the efficiency of radiationless energy transfer.

Let us write down the balance equation for the population of excited states

$$\frac{dn_i}{dt} = -\frac{n_i}{\tau} + (1 - n_i) Bu - n_i \sum_j W_{ij}, \quad (1)$$

where n_i is the fraction of molecules that are in the excited state, τ is the molecule lifetime in the excited state, B is the Einstein coefficient for the absorption and stimulated emission, u is the spectral density of the excitation energy, and W_{ij} is the probability of the radiationless energy transfer between the i th donor molecule and the j th acceptor molecule defined as¹¹

$$W_{ij} = \frac{1}{\tau} \left(\frac{R_0}{R_{ij}} \right)^6, \quad (2)$$

where R_0 is the critical transfer radius. Under stationary excitation we have $\frac{dn_i}{dt} = 0$. After the transformations we obtain

$$n_i = \frac{Bu\tau}{1 + Bu\tau + R_0^6 \sum_j \frac{1}{R_{ij}^6}}. \quad (3)$$

Assuming that $Bu\tau = 1$, that means that the relative fraction of excited molecules equals to unity, and choosing the coordinate system so that the critical radius of transfer makes a distance unit in it we have

$$n_i = \frac{1}{2 + \sum_j \frac{1}{R_{ij}^6}}. \quad (4)$$

Let us now introduce the quantity m_i value that, in fact, is the rate of the excited state depletion due to radiationless transfer of the excitation energy

$$m_i = \frac{1}{1 + \frac{1}{2} \sum_j \frac{1}{R_{ij}^6}}. \quad (5)$$

To simulate the process of the electron excitation energy transfer a donor molecule was placed at the origin of the coordinate system. A hundred of molecules, as possible acceptors, were randomly scattered around it. The stretching of a polymer film was simulated by transformation of the molecular coordinates. Since measurements showed that the volume of a polymer matrix keeps constant under the stretching of a PVA film. The coordinates were transformed according to the following formulas:

$$z' = kz, \quad x' = \frac{x}{\sqrt{\kappa}}, \quad y' = \frac{y}{\sqrt{\kappa}}, \quad (6)$$

where k is the degree of one-axis stretching of the film. The calculation carried out for a wide range of concentrations demonstrated that the change in fraction of radiating molecules occurring due to radiationless transfer is the same in both cases of free and stretched films. As a consequence, a change of distances between individual molecules of the activator due to stretching of the polymer matrix cannot cause the change of the excitation energy transfer.

However, the results of calculations carried out taking into account mutual orientation of the doped molecules demonstrated that the efficiency of the radiationless energy transfer is higher in stretched films than in the free ones within the whole range of concentrations available in the experiment. This result well explains stronger dependence of Δv_{\max} on the concentration ($\Delta v_{\max} = f(C)$) in stretched PVA films for tryptaflavin (Fig. 2 *a*) and 2-(stylybenyl-4)-5-phenyloxazol (Fig. 2 *b*) by easier energy exchange between partially oriented molecules compared to that between the isotropically oriented molecules.

At the same time an investigation of the concentration shifts of the fluorescence spectra of rhodamine 6G and eosine in PVA showed that for these substances we have stronger concentration dependences $\Delta v_{\max} = f(C)$ in isotropic matrices (Figs. 2 *c* and *d*). To explain the observed effect one can put forward the following suppositions: (1) The axes of dipoles of absorption and emission of the molecules under study are perpendicular. (2) The molecules of rhodamine 6G and eosine can form associates in the range of concentrations used in this study. (3) The dipole moments of the electron transitions of eosine and rhodamine 6G molecules are oriented at some angles with respect to the axis of stretching of the polymer film.

Investigation of the polarization spectrum of eosine fluorescence in a free film of PVA ($C = 10^{-5}$ mole/liter) shows that the degree of fluorescence polarization is a high positive value ($P = 42\%$) within the whole emission band. Close values of the fluorescence polarization degree ($P = 36\%$ in the region of maximum of the emission band) are characteristic of the rhodamine 6G as well. These results unambiguously show that orientations of dipole moments of electron transitions responsible for long-wave absorption and emission bands are parallel.

The presence in the polymer of associates of eosine or rhodamine 6G molecules fluorescing at longer wavelengths can result in the radiationless transfer of electron excitation energy from molecules of a monomeric form to the associates. We have studied the influence of concentration of doped molecules on the shapes of the absorption and emission bands to check up the presence of associates. Some small broadening of the absorption bands with increasing concentration has been observed for the eosine and rhodamine-6G spectra. It can be explained by inhomogeneous distribution of the doped molecules over the PVA matrix with increase of their number in a polymer.

The calculation of the efficiency of radiationless energy transfer for the molecules with the dipole moments of electron transitions oriented at different angles ϕ with respect to the stretching axis has been carried out to elucidate the influence of the third factor, i.e., of nonparallel orientations of dipole moments of the transitions and the stretching axis. The calculations showed that the probability of excitation energy migration for the molecules with the dipole moment of transitions oriented at 45° with respect to the axis of anisotropy occurring due to stretching is higher in a free film than in a stretched one. In this case many of molecules have mutually perpendicular dipole moments of transitions. The mean value of the orientation factor must be equal to $\langle \Phi^2 \rangle = 0.406$ according to Refs. 12 and 13, as opposed to $\langle \Phi^2 \rangle = 0.476$ for the isotropically oriented molecules. Consequently, the probability of concentration transfer for such a kind of molecules decreases as a result of stretching.

To determine the orientation of dipole moments of the electron transitions responsible for absorption of light by eosine and rhodamine 6G we have studied spectral behavior of dichroism within the long-wave absorption bands of

these compounds. It was found from these investigations that dichroism of the absorption of these compounds are not very high (7% for rhodamine 6G and 4% for eosine). This allows us to arrive at a conclusion that the dipole moments of the electron transitions of these compounds are oriented at some angle with respect to the stretching axis of a film. High positive values of dichroism ($d = 81\%$) for the films activated by tryptaflavin show, on the contrary, that the absorption oscillator is oriented along the stretching axis of a polymer film. In this case the mean orientation factor equals to $\langle \Phi^2 \rangle = 0.593$ and, correspondingly, the probability of excitation energy transfer is higher in stretched films activated by tryptaflavin molecules than in free films.

It follows from the above results that tryptaflavin molecules can be modeled as a prolate top with orientation of the dipole moment of electron transition along the long axis of the molecule. At the same time, the eosine and rhodamine 6G molecules are needed to be modeled as oblate tops according to Ref. 14.

Summarizing the above discussion we should like to note that the absolute orientation of transition dipoles with respect to the stretching axis can be determined from measured values of the change of the concentration shift in anisotropic samples in comparison with that in the isotropic ones.

REFERENCES

1. E.S. Voropai, V.V. Gruzinskii, and A.A. Kirsanov, *Characteristics of New Active Media for Lasers on Complex Organic Compounds*, Preprint, Part. I, Physics Institute AS BSSR : 595, Minsk (1990).
2. E.S. Voropai, V.V. Gruzinskii, and A.A. Kirsanov, *ibid.*, Part. II.
3. M.V. Bondar, O.V. Przhonskaya, E.A. Tikhonov, and N.M. Fedotkina, *Zh. Prikl. Spektrosk.* **52**, No. 4, 554–560 (1990).
4. G.A. Scripko, V.R. Sender, L.E. Zolotareva, et al., *Zh. Prikl. Spektrosk.* **42**, No. 5, 723–727 (1985).
5. D.A. Gromov, K.M. Dyumaev, A.A. Manenkov, et al., *Izv. Akad. Nauk SSSR, Ser. Fizika* **48**, No. 7, 1364–1369 (1984).
6. Yu.A. Shlyapnikov, *Dokl. Akad. Nauk SSSR* **202**, No. 6, 1377–1378 (1972).
7. G.E. Krichevskii, *Photochemical Transformations of Dyes and Photostabilization of Dyed Materials* (Moscow, 1986).
8. K.R. Popov, *Opt. Spektrosk.* **39**, No. 3, 509–513 (1975).
9. V.A. Gaisenok, V.V. Gruzinskii, G.H. Sitsko, and L.Sh. Afanasiadi, *Zh. Prikl. Spektrosk.* **46**, No. 5, 750–754 (1987).
10. V.V. Ivanov and O.M. Anisimova, *Dokl. Akad. Nauk SSSR* **253**, No. 6, 1401–1405 (1980).
11. V.L. Ermolaev, E.N. Bodunov, E.B. Sveshnikova, and T.A. Shakhverdov, *Radiationless Transfer of the Electron Excitation Energy* (Leningrad, 1977).
12. I.M. Rozman, *Opt. Spektrosk.* **4**, No. 4, 536–538 (1958).
13. M.Z. Maximov and I.M. Rozman, *Opt. Spektrosk.* **12**, No. 5, 606–609 (1962).
14. V.A. Gaisenok and A.M. Sarzhevskii, *Anisotropy of Absorption and Luminescence of Polyatomic Molecules* (Minsk, 1986).