

THE INFLUENCE OF THE ENVIRONMENT ON THE LUMINESCENCE OF DISSOLVED DYE MOLECULES

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The Stepanov—Neporent—Ketskemény relation which correlates absorption, fluorescence and solution characteristics was applied for solutions with ordered (micellar) structure and for solutions exposed to high electric field of laser light. The results show that the relation is fulfilled in both cases, although, there are exceptions for inordered solutions excited by intensive laser light. It can be concluded that the relation can give information on the interaction between excited molecules and their environment.

The absorption and fluorescence properties of luminescing molecules are significantly affected by the interaction of the environmental molecules. Important results were obtained by several authors from the investigations of the fluorescence characteristics for these interactions [1]. An appropriate way for studying the effect of the molecular environment is to test the validity of the Stepanov—Neporent—Ketskemény relation [2] which correlates absorption $k(\nu)$, fluorescence $f_q(\nu)$, quantum yield $\eta(\nu)$ spectra, and the mean lifetime of the excited system τ , since the environmental effects may lead to the violation of this relationship. By means of this method the dissipation of the excess excitation energy to the solvent, the „local temperature“ of the excited fluorescing centrum, were studied [3].

The results given below refer to systems in which the fluorescing molecules are significantly influenced by their environment, namely:

- a) they are embedded into ordered structures (micelles) [4],
- b) they are exposed to intense electric field (of the laser light).

In these cases the eigenstates of the molecules become significantly perturbed or/and the fluorescence is influenced by nonlinear processes. For studying these less known interactions the Stepanov—Neporent—Ketskemény relation

$$\frac{f_q(\nu)}{k(\nu)} = \frac{8\pi n_r^2}{c^2} \frac{\tau}{n_m^2} \frac{\eta(\nu)}{n} \nu^2 \exp[-h(\nu - \nu_0)/kT] \quad (1)$$

was applied. The notation used: n_r — the refractive index of the solution, c — velocity of light, η_m — maximum quantum yield of the fluorescence, n — the concentration of the fluorescing molecules, ν_0 — frequency of pure electron transition, ν —

frequency of light, h and k the Planck and the Boltzmann constants, T — the absolute temperature.

a) The experiments were carried out with $5 \cdot 10^{-6}$ M solutions of Rhodamin 6G dissolved in micellar systems. The solvent was a mixture of water and sodium-lauryl-sulphate (SLS) detergent, in which the detergent ions form micelles of lamellar structure [4]. In this system the Rhodamin 6G molecules are adsorbed onto/into the micelles and as a consequence the energy levels of the molecules are changed. This is demonstrated by the change of the absorption and the fluorescence spectra of the system. The dye molecules bound to the same micelles interact and energy migration takes place. The quantum yield and the mean lifetime of the fluorescence are changed by these interactions, too. It was demonstrated by our earlier experiments that changes in the detergent concentration have significant influence on the mean lifetime of the fluorescence [5]. Changing detergent concentration brings about the deformation of the spectra of the solutions, too. The Stepanov relation, however, is fulfilled in all cases and the effective temperature of the excited molecules calculated from Eq. (1) decreases with increasing lifetime. This leads to the conclusion that quenching processes should occur in the system; they depend on the detergent concentration and lead to the decrease of the mean lifetime and to the increase of the effective temperature of the molecules, similarly to the processes found in mole-

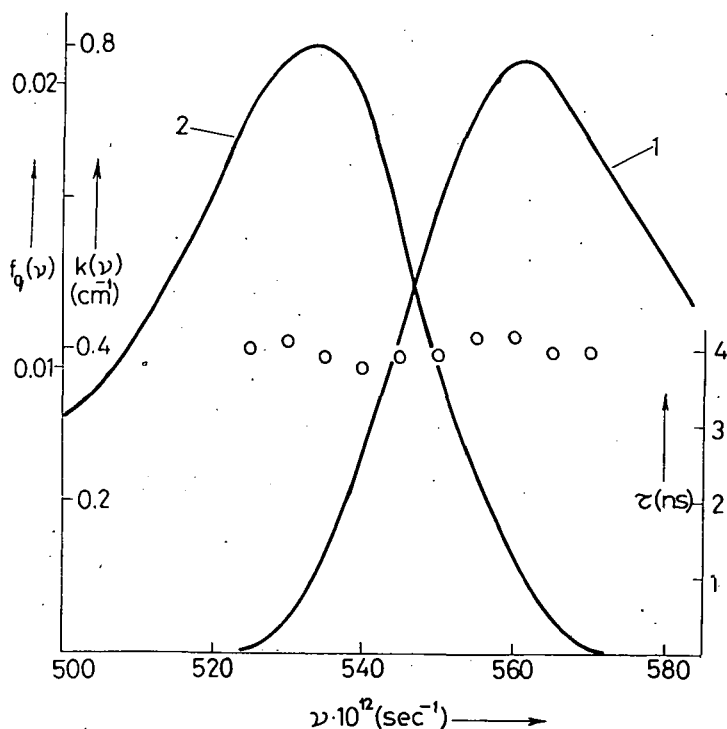


Fig. 1. Absorption (1) and fluorescence (2) spectra of $5 \cdot 10^{-6}$ M Rhodamin 6G solution and calculated values of τ v.s. frequency

cular solutions in the case of foreign quenching [6]. It seems plausible that the observed deformations of the spectra are caused by aggregates formed in the solution. In this case the τ mean lifetime, calculated by using Eq. (1), should depend strongly on the frequency.

The mean lifetime was calculated from fluorescence spectroscopical data of $5 \cdot 10^{-6}$ M Rhodamin 6G solutions containing SLS — detergent in different amounts according to Eq. (1), for frequencies corresponding to the overlapping region of the absorption and fluorescence spectra. The results are summarized in Table I. For demonstration the spectra used for the calculation and the calculated mean lifetime values of a particular solution are plotted in Fig. 1. It can be seen from the data and Fig. 1. that Eq. (1) is fulfilled for the luminescence characteristics of the dye molecules bound onto/into micelles similarly as for fluorescing molecules in solutions.

Table I

$\tau^{(v)}_{calc}$ and τ_{meas} values (in ns) of Rhodamin 6G solutions with concentration of $5 \cdot 10^{-6}$ M vs. detergent (SLS) concentration

$C_{SLS} 10^3$ (M)	0	2.5	3	3.5	4	6
$\nu \cdot 10^{-12}$ (S ⁻¹)	$\tau^{(v)}_{calc}$					
530	—	1.80	2.35	4.10	4.98	4.88
535	—	1.65	2.43	3.91	5.05	4.90
540	3.80	1.62	2.31	3.75	4.80	4.95
545	3.80	1.76	2.30	3.91	4.90	5.07
550	3.70	1.72	2.42	3.91	1.93	5.00
555	3.80	1.70	2.35	4.02	5.06	4.92
560	3.68	1.60	2.62	4.02	5.07	5.02
565	3.80	1.60	2.58	3.95	5.08	5.15
570	3.82	—	2.64	3.95	4.72	4.91
τ_{meas}	3.70	1.70	2.50	3.90	4.90	5.00

These results indicate that the eigenstates of dye molecules bound onto/into ordered structures are significantly perturbed due to the interaction with environment. This perturbation influences only the energy levels and the fluorescent and nonfluorescent transitions of molecules shown by the changes in $k(\nu)$, η_h and τ depending on the detergent concentration. Simultaneously the position of the spectra was shifted. The applied model for describing the fundamental properties of the fluorescing centrum and the processes within it is similar to that used for fluorescent molecules in molecular solutions. This is shown by the validity of Eq. (1), which

proves that the aggregates cannot play an important role in the applied concentration region.

b) Investigations were carried out for molecular dye solutions excited by high intensity (laser) light. For this case the Stepanov relation has the form [7]:

$$\frac{f_q(\nu)}{k(\nu)} = \frac{8\pi h\nu^3 n_2^2}{c^2} \cdot \frac{1}{\frac{n_1}{n_2} \exp\left[\frac{h(\nu - \nu_0)}{kT} - 1\right]} \quad (2)$$

where n_1 and n_2 is the concentration of the molecules in the ground state and in the excited states, respectively, ($n_1 + n_2 = n$) is the total concentration. Note that in the case of population inversion which is necessary to the functioning of dye lasers the absorption coefficient has to be negative in the laser emission frequency region. The practical importance of Eq. (2) is, that knowing the fluorescence spectra and the number of the excited particles the amplification curve can be easily determined from Eq. (2).

To study this case calculations were carried out for fluorescing solutions applied in dye lasers. The calculated values were compared with theoretical curves calculated for quasistationary dye lasers [8]:

$$k_a(\nu) = \frac{c^2}{8\pi\tau_0\nu^2} \cdot n_2 f_q(\nu) - n_1 k(\nu) \eta(\nu), \quad (3)$$

where $k_a(\nu) = -k(\nu)$ — the amplification coefficient, τ_0 — the natural lifetime of the fluorescence.

We found that the absorption spectra calculated from Eq. (2) become negative in all cases in the laser emission frequency region. The position of the maxima of the negative absorption band depends on the population of the excited state, con-

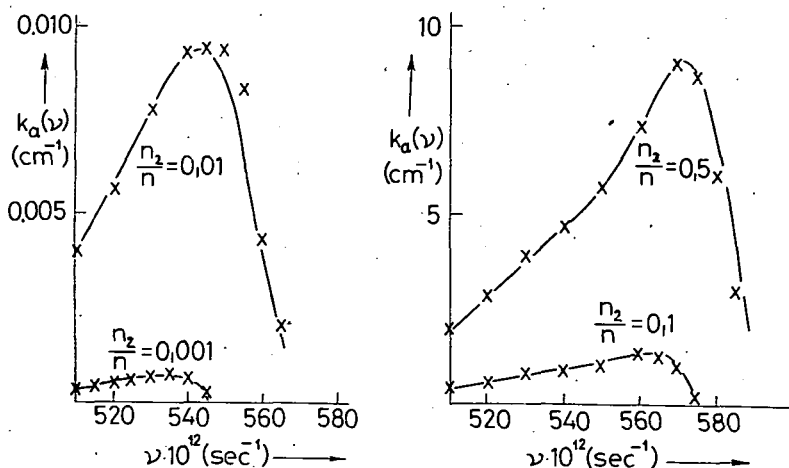


Fig. 2. Calculated values of $k_a(\nu)$ by using Eq. (3) [—] or Eq. (2) [× × ×] for different n_2/n ratios

sequently it describes well the dependence of the lasing wavelength on the output of the pumping. It has to be noted, however, that the shape of the curves calculated from Eq. (2) coincides with that of the curves calculated from Eq. (3) only in certain cases. In Fig. 2 an example is shown for $1 \cdot 10^{-4}$ M fluorescein solution.

From these results we concluded that the intense laser light with extremely high energy density does not exert deforming influence on the dye molecules as demonstrated by the rigorous fulfilment of the Stepanov relation. Any departure from this rigorous fulfilment could be observed only in special cases.

The applied method for studying the influence of the molecular environment of the excited molecules makes possible that, with further development of this method, the molecular processes of photosynthetic systems using conventional and laser light sources can be studied.

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ВЛИЯНИЕ ОКРУЖЕНИЯ НА ЛЮМИНЕСЦЕНЦИЮ РАСТВОРЕННЫХ КРАСИТЕЛЕЙ

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Универсальное соотношение Степанова-Непорента-Кечкемети, выражающее связь спектров поглощения, флуоресценции и характеристик растворов, применено для растворов с неоднородной структурой (мицеллы) при обычном возбуждении и нормальных растворов, находящихся в сильном электромагнитном поле. Полученные результаты показывают, что соотношение выполняется в обоих случаях, однако при возбуждении нормальных растворов интенсивным излучением наблюдаются некоторые особенности. Сделано заключение, что универсальное соотношение может дать информацию о взаимодействии между молекулами растворенного вещества и растворителя.