

FURTHER INVESTIGATIONS ON THE VALIDITY OF STEPANOV'S RELATION IN VISCOUS LUMINESCENT SOLUTIONS

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STEPANOV'S relation appears to be fulfilled both for rhodamine B in aqueous-glycerol solutions quenched by KI, as well as of glycerol-ethanol solutions of tryptaflavine, rhodulin orange and eosine of different viscosity and excited at different wavelengths. As the temperature T^* , which should be interpreted as the temperature in the vicinity of the fluorescent particle, depends on the concentration of quencher, the wavelength of the exciting light and the viscosity of the solution, it can be concluded that, in the system of solutions investigated, part of the excess energy of excitation is not dissipated during the mean life time of the excited state and may cause a local heat which persists even during the emission process, in accordance with some earlier assumptions.

1. Introduction

In the last years it became increasingly important to know the further way of the energy which appears as excess energy in the case of optical excitation of complicated molecules excited with frequencies greater than those of the pure electron transition 0—0 and is degraded by radiationless processes.

JABŁOŃSKI suggested [1] that in fluorescent solutions the above-mentioned energy should appear as an excess of the vibrational energy according to the Franck-Condon principle. This energy should increase the probability of rotation of the excited particle and thus cause the dependence of the "depolarization by initial shock" of the emitted fluorescence; on the mean life time and the frequency of the exciting light. Such an effect has been demonstrated by LISICKI [2]; the degree of polarization in the different alcoholic and alcohol-glycerol solutions of tryptaflavine and acriflavine was found to increase considerably with excitation near to the 0—0 transition frequency. Later JABŁOŃSKI suggested [3] the possibility of the degradation of the excess-energy both by a quick and a slow mechanism. In case of the quick mechanism, the energy of the "initial shock" should be comparatively quickly dissipated (in $\sim 10^{-12}$ sec) from the vicinity of the excited particle in the form of elastic waves, while in case of the slow mechanism, thermal energy should persist in the environment of the excited particle causing local heat, which is dissipated comparatively slowly in a greater space presumably according to the laws of heat conduction.

The appearance of the excess of the electron exciting energy in solids as local heat was considered by NORMAN and PORTER [4] to cause the translational diffusion

of the products of photodissociation. ALBRECHT and SIMPSON [5] postulated the appearance of similar local heat as a cause of rotational diffusion in condensed systems. ALBRECHT [6] supposed the possibility of a similar mechanism in connection with the "photo-orientation" of molecules excited by polarized light in solutions. The excess exciting energy in form of local heat should increase the probability of the dissolved particles to get oriented in a mechanical sense. Since such an effect could not be demonstrated experimentally as yet, ALBRECHT [7] suggested the local heat to be dissipated very quickly.

The above problems are closely connected with the results obtained by the investigation of STEPANOV's relation concerning the connection of absorption and emission spectra. According to STEPANOV [8], the following relation between the absorption spectrum $\varepsilon(\nu)$ and the emission spectrum $f_e(\nu)$ should exist

$$f_e(\nu)/\varepsilon(\nu) = d\nu^3 \exp(-h\nu/kT), \quad (1)$$

where d is a constant independent of frequency (ν), T the temperature of the solution, h and k are PLANCK's and BOLTZMANN's constants, respectively. It has been shown by KETSKEMÉTY and co-workers [9] that the formula

$$f_e(\nu)/\varepsilon(\nu) = d\nu^3 \eta^*(\nu) n^2(\nu) \exp(-h\nu/kT) \quad (2)$$

is more generally valid. Here $\eta^*(\nu)$ and $n(\nu)$ are the relative yield and the refractive index of the solution, both depending on frequency (ν). The validity of equation (1) [respectively (2)] has been studied by several authors. In the papers of ALENCEV [10], ALENCEV and PAHOMITCHEVA [11], KRAVCOV and RUBINOV [12], HEVESI and KOZMA [13], RAZANOVA and coworkers [14], BORISSEVICH and GRUSINSKI [15], as well as KETSKEMÉTY and co-workers [9] STEPANOV's relation was found to be valid both in case of vapours, solutions and solids, but the slope of the straight found by plotting

$$F(\nu) \equiv 3 \ln \nu - \ln f_e(\nu) + \ln \varepsilon(\nu) = -h\nu/kT$$

versus ν gives, in the majority of cases, a temperature T^* higher than the temperature T of the solution. According to [10] this higher temperature appears because of the transformation of part of the absorbed energy into vibrational energy, which is not transmitted to the surroundings within the mean life of the excited state. In vapours this phenomenon may take place with a great probability and makes possible to determine the vibrational specific heat experimentally (see [15] and [16]).

It could be expected, however, that in liquid and solid systems the vibrational energy should be dissipated before the act of emission as a result of the very close interaction between the dissolved particles and those of the solvent, consequently a local heat should not appear. Therefore in [11] it is suggested that in the case of $T^* > T$ the solution should consist of more than two components slightly differing in optical characteristics and this causes a temperature $T^* > T$. According to their opinion, however, the distribution of the excited molecules among the vibrational levels always corresponds to the real temperature T . In other terms, the emission spectra should be independent of the exciting frequency. Yet, according to some recent publications (see *e. g.* KAWSKI [17]), though such a dependence may appear, it can not be reliably stated in most cases. Thus KAWSKI came to the conclusion that the process of energy transition between the fluorescent "centre" and its surroundings takes place very quickly both in solutions of high and low viscosity.

The aim of the present paper is to investigate how equation (1) is fulfilled as a function of quenching, viscosity of the solution and exciting frequency in solutions of some organic dyestuffs and to draw some conclusions concerning the local heat in solutions.

2. Experimental method and solutions investigated

According to our program, the dependence of temperature T^* on quenching and on the frequency of exciting light calculated with equation (1) was investigated in solutions of four dyestuffs. The most important data of the solutions and the conditions of the investigations are given in Table I. As it can be seen from Table I, the dependence of T^* on quenching with constant glycerol concentration was investigated in rhodamine B solutions, while in tryptaflavine, rhodulin orange and eosine solutions our aim was to investigate the dependence on glycerol concentration and wavelength of the exciting light. These dyestuffs had been chosen, because according to former results (see *e. g.* KOZMA [19]) T^* appeared to be relatively high compared with T ; thus it was to be expected that the possible dependence of T^* on viscosity and wavelength of exciting light could be more easily demonstrated.

An Optica Milano grating spectro-photometer (Type CF-4) was used to measure the absorption spectra. As it is very important to measure the absorption spectra very precisely, the layer thickness was varied from 0,05 to 5 cm, to keep the extinction between 0,2 and 0,8, in which region the error of measurements is minimal. The smallest values of extinction in the long-wave region could not be plotted, though they are very important for the calculations.

For the measurement of emission spectra a method given in [18] was used, taking great care to fulfil the condition $k(\lambda)_{\max} \cdot l < 0,1$ by appropriate choosing of the layer thickness l . In this case the emission spectrum obtained experimentally agrees with that corrected to secondary luminescence within 0,5 per cent. (The values of $k(\lambda)_{\max}$ are given in Tables III-V.). The emission spectra were obtained with a high-pressure Hg-lamp (Hg 500) and the corresponding interference filter, or a Xenon-lamp (XBO 500) using a double monochromator (denoted by DM). (In the latter case the exciting band width was of 5-10 m μ).

The dyestuffs were purified by repeated recrystallization, the criterion of purity was that the absorption spectrum should not change during two subsequent recrystallizations. The glycerol used for the varying of the viscosity was purified by repeated vacuum-distillation. Ethanol, water, glycerol and their mixtures in suitable proportions were used as solvents. In order to shift the proportion of the dyestuff ions in the solution to the corresponding luminescent ionic form, HCl or NaOH were given to the solution.

The investigations were carried out at a temperature of $T = 298 \pm 2$ °K. Values of T^* in the Tables were calculated with an accuracy of 0,1 degree, though this high accuracy should not be expected to be reliable.

3. Results and discussion

a) In a former paper [13] the dependence of the temperature difference $T^* - T = \Delta T$ on quenching and viscosity of the solution has been studied.

To investigate the dependence of ΔT on quenching further measurements were carried out on solutions in which the concentration of the quencher (KI) was varied between the limits given in Table I, the concentration of the dyestuff (rhodamine B), NaOH and glycerol being held constant. To illustrate the dependence, in Fig. 1 only the absorption and emission spectra belonging to quencher concentration zero (solid line) and 1 mol/l (dotted line) and the respective STEPANOV's straights are given. As it can be seen, the quencher concentration does not essentially influence the spectra and STEPANOV's relation is well fulfilled. The relative yield η/η_0 obtained by measurements, and determined with the method given in [20] and the values of T^* calculated from STEPANOV's straights are given in Table II. Absorption and

Table I

Dyestuff	Concentration mole/l	Composition of solvent	Additive agent	Layer thickness for emission spectra (cm)	Light source, filter, monochromator
Rhodamine B	$1 \cdot 10^{-4}$	H ₂ O glycerol (per cent) (60)	NaOH (3 per cent) KI (0-1 mole/l)	0,01	HBO 500 SIF 547
Trypaflavine	$2 \cdot 10^{-4}$	C ₂ H ₅ OH glycerol (per cent) (0, 40, 90)	CH ₃ COOH (2 per cent)	0,01	HBO 200 SIF 436 XBO 500 DM
Rhodulin-orange	$5 \cdot 10^{-5}$	C ₂ H ₅ OH glycerol (per cent) (0, 40, 90)	HCl ($5 \cdot 10^{-3}$ mole/l)	0,05	XBO 500 DM
Eosine	$5 \cdot 10^{-5}$	C ₂ H ₅ OH glycerol (per cent) (0, 40, 90)	NaOH ($5 \cdot 10^{-3}$ mole/l)	0,02 0,05	HBO 200 SIF 480 XBO 500 DM

emission maxima of the solutions were found at 555μ and 580μ respectively. The maximal value of the absorption coefficient was $k(\lambda)_{\max} = 23,13 \text{ cm}^{-1}$.

In Fig. 2 the measured values of relative yield η/η_0 (●) and of T^* calculated from STEPANOV's straights (○) are plotted versus the logarithm of quencher concentration. It is to see that T^* increases with the increase of quenching (*i. e.* decrease of the mean life time of excited state). This increase can be interpreted by supposing

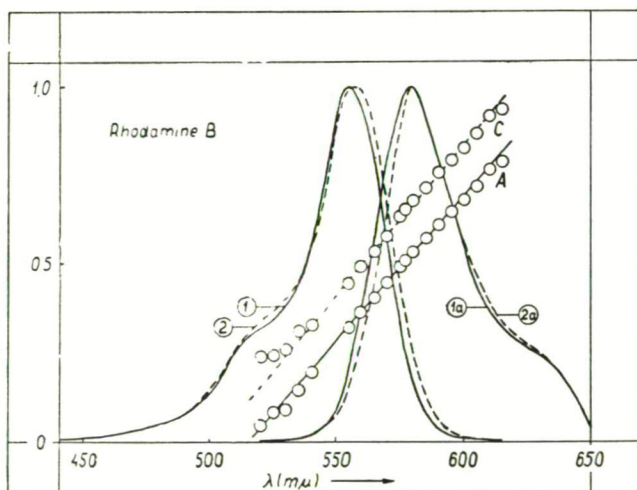


Fig. 1

that with decreasing decay time the possibility of the dissipation of the excess exciting energy decreases and therefore the local heat increases (for the case of quenched fluorescein solution see [13]).

b) As it had been referred to in [13] it could be inferred from the results given in [9] that the calculated values of T^* may depend on the wavelength of the exciting light. Such a dependence of T^* had been observed in several cases in vapours ([15], [16]).

The dependence of T^* on the wavelength of exciting light and the glycerol concentration was investigated in the solutions listed in Table I with the method mentioned above. The values of T^* , the wavelengths of the maxima of absorption and emission spectra ($\lambda_{a, \max}$ and $\lambda_{e, \max}$) and the maxima of the absorption coefficients ($k(\lambda)_{\max}$) for different glycerol concentrations are given in the Tables III–V. It can be seen that the values of T^* depend on the frequency of exciting light and on the glycerol concentration. The results show that the difference $T^* - T = \Delta T$ increases with the increase of the difference between the absorbed

Table II

c_{KI} (mole/l)	T^* (°K)	η/η_0
0	332,6	1,000
$5,62 \cdot 10^{-2}$	334,3	0,949
$1 \cdot 10^{-1}$	336,1	0,896
$1,78 \cdot 10^{-1}$	338,0	0,804
$3,16 \cdot 10^{-1}$	339,8	0,693
$5,62 \cdot 10^{-1}$	341,6	0,584
1	343,5	0,473

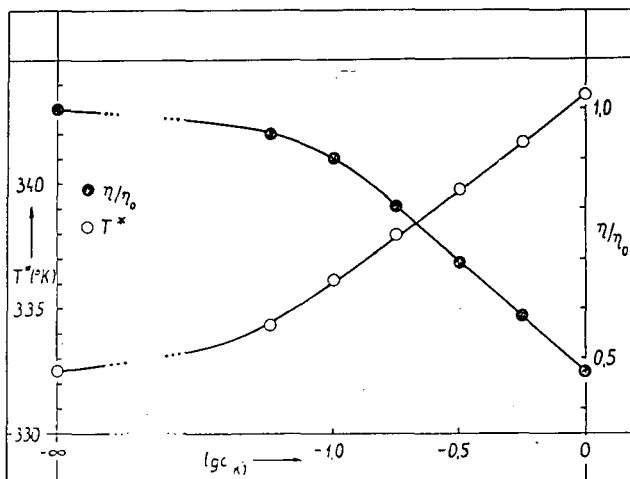


Fig. 2

and emitted energies ($h\nu_g - h\nu_e$). Similarly ΔT increases with increasing glycerol concentration in the cases investigated.

The absorption and emission spectra belonging to the values T^* listed in Tables III–V and the calculated straights are plotted in figures 3–5. Fig. 3–5 give these curves for the solutions of tryptaflavine, rhoduline orange and eosine, respectively. In these figures curve 1 and 2 represent the absorption spectrum of the dyestuff dissolved in pure ethanol, and in a 1:9 v/v mixture of ethanol and glycerol, while

1a and **2a** denote the respective emission spectra excited by the shortest wavelengths; curve **1b** is the emission spectrum for ethanol solution excited by the longest waves. *A*, *B*, *C* are STEPANOV'S straights calculated from emission spectra **1a**, **1b**, **2a** and the corresponding absorption spectra using equation (1).

Table III

<i>c</i> _{glyc.} (per cent)	<i>T</i> * (°K)			$\lambda_{a, \max}$ (m μ)	$\lambda_{e, \max}$ (m μ)	<i>k</i> (λ) _{max} (cm ⁻¹)
	wavelength of exciting light					
	436 (m μ)	455 (m μ)	475 (m μ)			
0	325,6	319,0	314,1	460	495	23,03
40	330,8	325,6	319,0	461	497	22,36
90	361,4	347,3	336,1	462	500	20,10

Table IV

<i>c</i> _{glyc.} (per cent)	<i>T</i> * (°K)			$\lambda_{a, \max}$ (m μ)	$\lambda_{e, \max}$ (m μ)	<i>k</i> (λ) _{max} (cm ⁻¹)
	wavelength of exciting light					
	460 (m μ)	480 (m μ)	510 (m μ)			
0	339,8	319,0	302,0	492	521	3,23
40	343,5	322,3	309,5	494	524	3,19
90	365,6	357,3	332,6	497	528	3,21

Table V

<i>c</i> _{glyc.} (per cent)	<i>T</i> * (°K)			$\lambda_{a, \max}$ (m μ)	$\lambda_{e, \max}$ (m μ)	<i>k</i> (λ) _{max} (cm ⁻¹)
	wavelength of exciting light					
	460 (m μ)	520 (m μ)	555 (m μ)			
0	339,8	325,6	314,2	522	540	11,36
40	345,4	330,8	322,3	522,5	543	11,36
90	363,5	347,3	334,3	523	545	10,35

The figures show that in each of these solutions there exists a slight dependence of the emission spectrum on the exciting wavelength appearing in Tables III–V, as a corresponding dependence of *T**. This connection, already pointed out in several papers (see *e. g.* [21]–[25] and [17]), is interpreted by some authors with the supposition of more than one kind of luminescent molecules with somewhat different optical characteristics. This supposition is not sufficiently supported by the present investigations because of the results of chromatographical analysis of the dyestuffs. Rhodamine B in a mixture of ethanol, butanol and water in presence of ammonium hydroxide on silicagel as adsorbent appeared to consist of a single component. Eosine behaved similarly in the same system. Yet the respective values of *T** were greater than those of *T*, especially in case of eosine. On the other hand trypaflavine in the same system was separated in the presence of ammonium hydroxide as well

as of acetic acid into two components acriflavine and proflavine (according to WALERYS [26]). The behaviour of acriflavine purified chromatographically [2] points decidedly to the existence of local heat though it represents a single kind of luminescent particle in the solution. Rhodulin orange also appears to consist of two components in the mentioned chromatographical system. In case of fluorescein earlier investigations ([9], [11] and [13]) showed to have $T^* \approx T$ in unquenched and not viscous fluorescein solutions, with two different exciting wavelengths, though the dyestuff

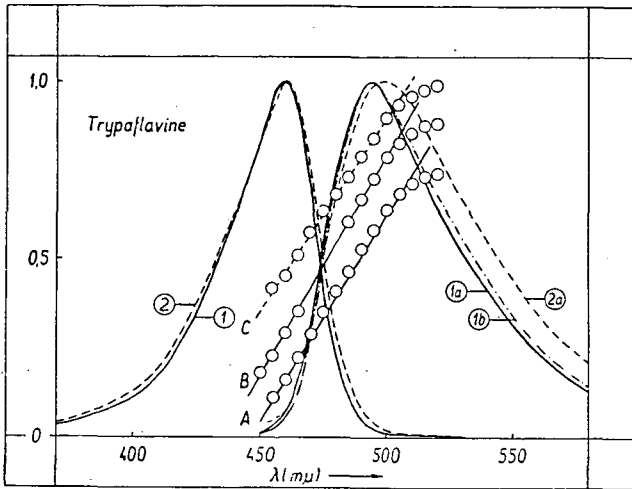


Fig. 3

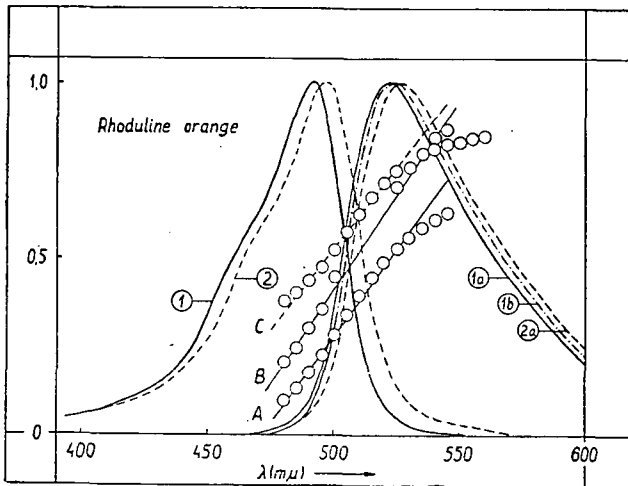


Fig. 4

used contained two kinds of impurities, however, in very little concentrations according to recent chromatographical analysis. Consequently the emission spectrum may be really independent of the exciting wavelength in some cases while it seems to depend on the exciting wavelength not only in solutions with more luminescent components, but also in case of a single luminescent component. In other terms the local temperature $T^* > T$ should be considered as physically existent in some

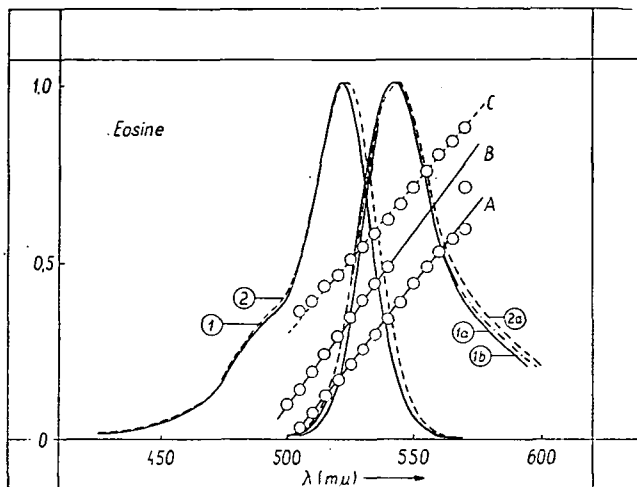


Fig. 5

solutions in agreement with JABLOŃSKI's supposition [3] and LISICKI's investigations [2]. This seems further supported by measurements of KOZMA [19] according to which T^* increases with the molecular weight in dyestuffs of a similar structure (the molecular weights of fluorescein, rhodamine B, eosine and rose bengale are 376; 479; 692; 949; and the corresponding values of T^* in the solutions 314; 328; 350; 395 °K respectively). This regularity may be understood if we consider that the energy carried away in form of elastic waves by the "initial shock" must decrease with increasing molecular weight.

It may be assumed that the dependence of T^* on viscosity is to be ascribed to two kinds of causes: α) the absorption and emission spectra may shift with the change of viscosity and thus the difference of absorbed and emitted energy may be altered (as supposed in [13]); β) with increasing viscosity the quick process ("initial shock") may carry away less and less energy from the surroundings of the excited particle (see [1]–[3]) and thus the local heat may increase. A similar role of the change of viscosity has been supposed earlier (see [4] and [6]) and this supposition was confirmed by experimental data obtained for solid solutions [14].

The above connections are also fulfilled in case of the spectra not plotted in the figures. It is to mention that, according to KETSKEMÉTY and co-workers [9] the change in the slope the STEPANOV's straights in the long wave region of the spectra is to be ascribed to the decrease of quantum yield in this region.

c) As an attempted thermodynamical interpretation of these phenomena let us consider the system of the excited molecules as a sub-system of temperature T^* to be in a thermal interaction with the sub-system of the solvent molecules of temperature $T \cong T^*$. Since the number of the excited molecules is negligible against the number of the solvent molecules, the solvent may be treated as an infinitely large heat reservoir of temperature $T = \text{constant}$. Applying de GROOT's considerations [27] to this system we have

$$\frac{d(T^* - T)}{dt} = -\frac{1}{\tau'} (T^* - T), \quad (3)$$

where τ' is the relaxation time of the interaction process. From Eq. (3)

$$T^* - T = (T^* - T)_0 \exp\left(-\frac{\tau}{\tau'}\right), \quad (4)$$

where $(T^* - T)_0$ and $(T^* - T)$ denote the temperature difference of the sub-systems in time $t=0$ (*i. e.* at the end of excitation) and in time $t=\tau$ (*i. e.* at the moment of emission), respectively.

According to Eq. (4) the temperature difference $T^* - T$ should increase if: α) the exciting frequency is increased (because of the respective increase of $(T^* - T)_0$); β) the mean life time of the excited state, τ , is decreased; γ) the viscosity is increased (because of the respective increase of τ' provided the interaction between the sub-systems is influenced by viscosity). Our experiments described above prove a fulfilment of these three conclusions.

As for a quantitative examination of the validity of Eq. (4), in lack of experimental data of $(T^* - T)_0$, τ and τ' we are restricted to estimations. We obtain an estimate for $(T^* - T)_0$ if we assume that the whole excess of the exciting energy as a value of $h(\nu_g - \nu_{e, \max})$ is converted into heat. In this case

$$(T^* - T)_0 \approx \frac{k' h (\nu_g - \nu_{e, \max}) \cdot N}{Mc}, \quad (5)$$

where $N = 6,02 \cdot 10^{23}$, $k' = 2,4 \cdot 10^{-8}$ cal/erg, h , M and c denote Planck's constant, molar weight and oscillation specific heat of the solute „gas”, respectively. In case of fluorescein dissolved in a glycerol-water mixture and quenched by KI (see [13]) $\nu_g = 6,89 \cdot 10^{14}$ s $^{-1}$, $\nu_{e, \max} = 5,75 \cdot 10^{14}$ s $^{-1}$ and $M = 332$ g. Taking a value of $c = 0,30$ cal/degree. g, Eq. (5) yields $(T^* - T)_0 \approx 100$ centigrade. With this value and the fluorometrically measured values of τ [28] (ranging from $2,3 \cdot 10^{-9}$ s to $5,05 \cdot 10^{-9}$ s) Eq. (4) gives $\tau' \approx 5,6 \cdot 10^{-9}$ s. In case of rhodamine B quenched by KI $\nu_g = 5,48 \cdot 10^{14}$ s $^{-1}$, $\nu_{e, \max} = 5,17 \cdot 10^{14}$ s $^{-1}$ and $M = 479$ g. Taking a value of $c = 0,10$ cal/degree. g, from equation (5) we obtain $(T^* - T)_0 \approx 70$ centigrade. With this value and with $\tau' = 5,6 \cdot 10^{-9}$ s equation (4) yields $\tau \approx 3,1 \cdot 10^{-9}$ s for the unquenched solution. For the sake of comparison it should be mentioned that $\tau = 4,2 \cdot 10^{-9}$ s is given in [29] for unquenched solution of rhodamine B in pure glycerol and an extrapolated value of the dielectric relaxation time of $\tau' \approx 10^{-9}$ s may be estimated from [30] for the glycerol-water mixture applied in our case. According to [31], $c = 0,16 - 0,50$ cal/degree. g is given for 3-6-tetramethyl-diamino-phtalimide, 3-aminophtalimide, β -naphthylamine, perylene and anthracene in vapour phase.

The similar order of magnitude of the dielectric relaxation time and the relaxation time introduced in Eq. (3) is to be expected, since both processes are governed by the weak thermal interaction.

Let us assume after JABŁOŃSKI [3] that the thermal interaction is realized as a heat conduction and consider the relaxation time in form of

$$\tau' = \frac{q\varrho c}{\lambda}, \quad (6)$$

where q is a surface through which the heat is transferred during the mean life time, ϱ , c and λ denote the density, the specific heat and the heat conductivity of the solvent. With the values $\tau' = 5 \cdot 10^{-9}$ s, $\varrho = 1$ g cm $^{-3}$, $\lambda = 5 \cdot 10^{-3}$ cal cm $^{-1}$ s $^{-1}$ degree $^{-1}$ and $c = 0,8$ cal g $^{-1}$ degree $^{-1}$, from Eq. (6) we obtain $q \approx 3 \cdot 10^{-11}$ cm 2 . A sphere of radius $r \approx 1,5 \cdot 10^{-5}$ cm would belong to this surface. This should mean that the local heat might be present in a sphere around the excited particles, the order of magnitude of its radius being 10^{-5} cm. Though we are aware of the oversimplified character of the above considerations we hope they may contribute to an explanation of the appearance of the local heat to some extent.

From a thermodynamical point of view it would be very interesting to treat the system of excited molecules in case of higher concentrations when the interaction between neighbouring solute particles is not to be neglected.

For a more precise investigation of the validity of Eq. (3) we ought to know the dependence of τ and τ' on the composition of solution and the exciting wavelength.

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К ПРИМЕНИМОСТИ СООТНОШЕНИЯ СТЕПАНОВА В СЛУЧАЕ ВЯЗКИХ, ФЛУОРЕСЦЕНЦИРУЮЩИХ РАСТВОРОВ

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Для спектров поглощения и испускание глицеринно-водных растворов родамина Б, потушенных KJ , а также для спектров поглощения и спектров испускания полученных разными возбуждающими длинными волнами, разных вязких глицеринно-этанольных растворов триафлавина, родулина оранжа и эозина, формула Степанова оказывается действительной. Для температуры T^* , полученной из формулы и которую можно считать температурой в окружении флуоресценцирующих частиц, в зависимости от концентрации тушителя, длины волн возбуждения и вязкости, можно сделать вывод, что в системе исследованных растворов часть избытка энергии возбуждения во время возбуждения не рассеивается, а в согласии с более ранними предложениями, до момента излучения, эта не полностью рассеянная энергия вызывает локальное нагревание.

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