

# THE INFLUENCE OF THE LOCAL TEMPERATURE OF LUMINESCENT CENTRES ON THE EMISSION ANISOTROPY OF FLUORESCENCE OF SOLUTIONS

BY H. GRUDZIŃSKI

Physics Department, Nicholas Copernicus University, Toruń\*

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The dependence of the emission anisotropy  $\bar{r}$  of fluorescence of solutions on the absorbed frequency  $\nu$  belonging to the region of one absorption band (thus involving the same electronic transition) has been attributed by Jabłoński to the influence of the local temperature of the luminescent centres on the depolarization factors, *viz.* the torsional vibrations and the Brownian rotations of these centres. Jabłoński's theory is based on the assumption that the local temperature relaxes exponentially in time and that the limiting emission anisotropy  $r_0$ , as well as "depolarization probability"  $\varphi$  by Brownian rotations are linear functions of the temperature.

In the present paper the dependence of  $\varphi$  on temperature is extended by including a term quadratic in temperature. In consequence, the dependence anisotropy  $\bar{r}$  of emission on  $\Delta\nu$  (the difference between the frequency of the exciting light and that of the purely electronic transition) is shown to be given by a 2nd order parabola. This form of  $\bar{r}$ -dependence on  $\Delta\nu$  agrees well with the experimental curves obtained for fluorescein and acriflavine in glycerol-water solutions.

The measurements of  $\bar{r} = \bar{r}(\Delta\nu)$  and of the mean decay time  $\tau$  make it possible to estimate on the basis of the expressions obtained, the relaxation times  $\theta$  of the local temperatures as well as the inverse of the heat capacities  $\sigma$  of the luminescent centres. The values obtained are  $\theta = 1.6 \times 10^{-11}$ s,  $\sigma = 5 \times 10^{-2}$  degree/cm<sup>-1</sup> and  $\theta = 3 \times 10^{-12}$ s,  $\sigma = 1 \times 10^{-1}$  degree/cm<sup>-1</sup> for fluorescein and acriflavine respectively, in glycerol + water solutions.

## Introduction

The dependence of the emission anisotropy (*EA*) of fluorescence of *polyatomic* molecules on the frequency of the *exciting light* in the region of one electronic absorption band, observed by many authors (*e. g.* [1-11]), has been interpreted by Jabłoński as due to the "initial shock" effect [12-14].

The energy of nuclear motion of the non-excited luminescent centres<sup>1</sup> in solution is in thermal equilibrium with the surrounding medium. The absorption of a photon by a

\* Address: Katedra Fizyki Doświadczalnej Uniwersytetu Mikołaja Kopernika, Toruń 1, Grudziądzka 5 Polska.

<sup>1</sup> luminescent centre — the *luminescent* molecule together with the neighbouring molecules of the *solvent*.

molecule causes, in general, a change of the nuclear motion energy of the molecule, according to the Franck-Condon principle, thus producing a transient violation of the thermal equilibrium of the centre with the surrounding medium. The above effect is called initial shock by Jabłoński.

The transient alteration of the nuclear motion energy, *i. e.* of the local temperature (see below), of luminescent centres caused by the absorption of light depends on the frequency  $\nu$  of the exciting light. Excitation of the *purely electronic* transition of the molecule with light of frequency  $\nu_{0-0}$  does not affect the "local temperature" of the centre. If, however,  $\nu > \nu_{0-0}$  the absorption of the photon causes an increase of the local temperature, if  $\nu < \nu_{0-0}$  its decrease. Therefore, owing to a transient violation of the thermal equilibrium for  $\nu \neq \nu_{0-0}$ , the energy of such thermal motions as torsional vibrations and Brownian rotations of the luminescent molecules also changes. These motions, as is well known, produce an at least partial depolarization of the photoluminescence of solutions; as the energy of these motions depends on the frequency  $\nu$  of the exciting light, the photoluminescence  $EA$  is also  $\nu$  dependent.

It follows mainly from the works of Neporent [15] that in "complex" polyatomic molecules characterized by continuous absorption and emission spectra (*i. e.*, with no traces of a vibrational structure), there is a strong enough probability of energy transfer between different vibrational degrees of freedom, that after the gaining of a certain *surplus* of vibrational energy by these molecules in the process of excitation, a distribution of vibrational energy corresponding to statistical equilibrium characterized by a certain temperature called vibrational temperature, is very quickly established. In the case of solutions, owing to a strong interaction of the luminescent molecule with the neighbouring solvent molecules, one may rather refer to the temperature of the luminescent centre, called by Jabłoński the *local temperature* of the luminescent centre  $T^*$ , and to the *heat capacity* of the centre,  $C^*$ .

It is believed that the time of establishment of the vibrational energy equilibrium between the degrees of freedom of the complex molecule is much shorter (of the order of a period of vibration, *i. e.*, about  $10^{-13}$  sec) than the lifetime of the molecule in the excited state (of the order of  $10^{-9}$  sec), so that, to a fairly good approximation, one can describe the vibrational energy of the molecule by the local temperature at the moment of excitation  $t = 0$ . For  $t > 0$ , owing to the interaction of the molecule with the solvent, this temperature tends to level itself to that of the surroundings. Jabłoński assumes that the *surplus*  $\Delta T$  of the local temperature over the temperature of the medium decreases exponentially with time (in accordance with Newton's law)

$$\Delta T(t) = \Delta T(0) \exp(-t/\theta), \quad (1)$$

where  $t$  is the time measured from the moment of excitation,  $\theta$  the relaxation time of the local temperature of the luminescent centres and  $\Delta T(0)$  the value of  $\Delta T$  at  $t = 0$ .

A further development of the theory of depolarization through initial shock was made by assuming as a first approximation a linear dependence on temperature of both the limiting  $EA$ ,  $r_0$ , and the probability of depolarization  $\varphi$  by Brownian rotations per unit time [14]. This approximation leads to a linear dependence of the  $EA$ ,  $\bar{r}$ , on the difference  $\Delta\nu$  between the frequency of the exciting light  $\nu$  and that of the *pure-electronic* transition  $\nu_{0-0}$ .

The expressions obtained allow the relaxation time of the local temperature of the luminescent centres  $\theta$  to be estimated from the measurements of  $\bar{r}(\Delta\nu)$  and of the mean duration of fluorescence, if the heat capacity of the vibrational degrees of freedom of the luminescent centres,  $C^*$ , is known. Such measurements were performed for solutions of *fluorescein*, *eosin* and *erythrosin* [14].

The results of further experiments showed that in order to obtain better agreement between theory and experiment one has to include terms up to the second order in the power series expansion of  $\varphi$  as a function of temperature. It follows from this paper that the expression for  $\bar{r}(\Delta\nu)$  obtained in this approximation agrees well with experiment and allows the determination of both  $\theta$  and  $C^*$  on the basis of the measurements mentioned above.

### Theoretical

In the case of excitation of photoluminescence with light of frequency equal to that of the pure-electronic transition  $\nu_{0-0}$ , the thermal equilibrium of the motions of the luminescent centre is not disturbed and the local temperature,  $T^*$ , is equal to the temperature of the solution,  $T_0$  ( $\Delta T = T^* - T_0 = 0$ ). Under these conditions the observed mean value of the  $EA$  of the fluorescence of solutions,  $\bar{r}$ , is equal to [13, 14]

$$\bar{r} = r_0 / (1 + \varphi\tau), \quad (2)$$

where  $r_0$  is the limiting  $EA$ ,  $\varphi$  the probability of depolarization through a Brownian rotation per unit time and  $\tau$  the mean duration of fluorescence. A change in the overall temperature of the solution influences the torsional vibrations and Brownian rotations of the molecules causing a decrease of  $r_0$  and an increase of  $\varphi$  with rising temperature and an increase of  $r_0$  and a decrease of  $\varphi$  with decreasing temperature.

In the first approximation a linear dependence of  $r_0$  on temperature variations is assumed [14]:

$$r_0(T_0 + \Delta T) = r_0(T_0) - a\Delta T \quad (3)$$

where  $r_0(T_0)$  is the limiting value of  $EA$  at temperature  $T_0$  and  $r_0(T_0 + \Delta T)$  that at temperature  $T_0 + \Delta T$ ,  $a$  being the proportionality factor. As has been shown [14], it is not necessary to find out the dependence of  $r_0$  on  $T$  experimentally to determine the coefficient  $a$ , the knowledge of  $r_0$  at the temperature  $T_0$  is sufficient for the case when same virtual linear oscillator is responsible for the absorption and emission of light in the molecule:

$$a = \Delta r_0 / \Delta T = (1.2u - 1.8u^2) / T_0,$$

where  $u$  is the dispersion of the sine of the angle between the momentary, variable direction of the transition moment and its equilibrium direction, and may be calculated from the expression

$$r_0 = 0.4 - 1.2u + 0.9u^2.$$

$r_0$  for temperature  $T_0$  is measured experimentally [16]. (We have neglected the zero point torsional vibrations in this discussion.) If the amplitude of torsional vibrations is not too

large the limiting  $EA$  does not differ much from the fundamental  $EA$ ,  $r_f$ , and thus  $u$  is small,  $a = 1.2 u/T_0$  and  $r_0 \approx 0.4 - 1.2u$ . Hence

$$a = \Delta r_0 / \Delta T = (0.4 - r_0) / T_0. \quad (4)$$

The value of  $r_0$  at temperature  $T_0$  is obtained from measurements of the  $EA$  of fluorescence  $\bar{r}$  observed at steady illumination with primary light of frequency  $\nu_{0-0}$  at temperature  $T_0$  of the solution by means of [16]:

$$r_0 = \frac{2\bar{r}^2 \tau}{\tau^{\parallel} (1 + 2\bar{r}) - \tau} = \frac{\bar{r}^2 \tau}{\tau - \tau^{\perp} (1 - \bar{r})}, \quad (5)$$

where  $\tau^{\parallel}$  is the mean duration of the fluorescence components parallel and  $\tau^{\perp}$  that perpendicular to the direction of the electric vector of the linearly polarized exciting light and  $\tau$  the mean duration of the total fluorescence ( $\tau$  is equal to that time measured for the fluorescence component making an angle of  $55^\circ$  with the direction of the electric vector of the exciting light).

According to [17, 18] the probability,  $\varphi$ , of depolarization by a Brownian rotation per unit time is

$$\varphi(T) = b \exp(-\varepsilon/T), \quad (6)$$

where  $b$  is constant for a given solution and  $\varepsilon \times k$  the activation energy for a Brownian rotation ( $k$  is the Boltzmann constant).

Excitation of a luminescent centre by light of frequency  $\nu \neq \nu_{0-0}$  causes a change of the local temperature of the centre influencing both  $r_0$  and  $\varphi$ . It is now assumed that a variation of the local temperature influences the depolarizing factors in the same way as does a variation of the temperature of the whole solution.

Accordingly an increase of the local temperature by  $\Delta T$  for  $\nu > \nu_{0-0}$  causes a decrease of  $r_0$  in agreement with Eq. (3). However the proportionality factor,  $a$ , will now be halved because the local temperature influences only the emission oscillator and not the absorption oscillator (a proof is given in [14]). Thus relation (3) will now become

$$r_0(T_0 + \Delta T) = r_0(T_0) - a\Delta T/2, \quad (7)$$

where  $\Delta T$  is the change in the *local temperature* of the luminescent centre.

Apart from this an increase in the local temperature by  $\Delta T$  causes an increase of  $\varphi$ . Expanding the function (6) into a Taylor series at the point  $T_0$  and limiting ourselves to terms up to the second order:

$$\varphi(T_0 + \Delta T) \approx \varphi(T_0) + b_1 \Delta T + b_2 \Delta T^2, \quad (8)$$

where

$$b_1 = \left. \frac{d\varphi}{dT} \right|_{T=T_0} = \varphi(T_0) \varepsilon / T_0^2, \quad (9)$$

$$b_2 = \left. \frac{1}{2} \frac{d^2\varphi}{dT^2} \right|_{T=T_0} = \frac{1}{2} \varphi(T_0) (\varepsilon/T_0 - 2) \varepsilon / T_0^3, \quad (10)$$

and  $\Delta T = T^* - T_0$  ( $T^*$  — the local temperature of the luminescent centre,  $T_0$  — the temperature of the surrounding medium) is the change in the local temperature of the luminescent centre.

Since, according to (1),  $\Delta T$  is a function of time  $t$ ,  $r_0$  and  $\varphi$  will also be functions of  $t$ ; thus, approximately:

$$r_0(t) \approx r_0 - \frac{1}{2} a \Delta T(0) \exp(-t/\theta) \quad (11)$$

$$\varphi(t) \approx \varphi(T_0) + b_1 \Delta T(0) \exp(-t/\theta) + b_2 \Delta T^2(0) \exp(-2t/\theta). \quad (12)$$

It was shown in [14] that in the general case when  $r_0$  and  $\varphi$  are functions of time, the dependence of  $EA$  on the time elapsing from the moment of excitation is described by the following expression

$$r(t) = r_0(t) \exp\left(-\int_0^t \varphi(t) dt\right). \quad (13)$$

Introducing (11) and (12) into (13) and denoting by  $r^*$  the  $EA$  of fluorescence excited with light of frequency  $\nu \neq \nu_{0-0}$ , one obtains the following equation describing the decay in time of the  $EA$ :

$$\begin{aligned} r^*(t) &= \left[ r_0(T_0) - \frac{1}{2} a \Delta T(0) e^{-t/\theta} \right] \times \\ &\times \exp \left[ - \int_0^t (\varphi(T_0) + b_1 \Delta T(0) e^{-t/\theta} + b_2 \Delta T^2(0) e^{-2t/\theta}) dt \right] \\ &= \left[ r_0(T_0) - \frac{a}{2} \Delta T(0) e^{-t/\theta} \right] e^{-\varphi(T_0)t} \times \\ &\times \exp \left[ - b_1 \Delta T(0) \theta (1 - e^{-t/\theta}) - b_2 \Delta T^2(0) \frac{\theta}{2} (1 - e^{-2t/\theta}) \right]. \end{aligned} \quad (14)$$

If  $b_1 \Delta T(0) \theta \ll 1$  and  $b_2 \Delta T^2(0) \theta / 2 \ll 1$ , then (14) becomes

$$\begin{aligned} r^*(t) &\approx \left[ r_0(T_0) - \frac{a}{2} \Delta T(0) e^{-t/\theta} \right] e^{-\varphi(T_0)t} \times \\ &\times \left[ 1 - b_1 \Delta T(0) \theta (1 - e^{-t/\theta}) - b_2 \Delta T^2(0) \frac{\theta}{2} (1 - e^{-2t/\theta}) \right], \end{aligned}$$

and since  $\frac{1}{2} a \Delta T(0) b_1 \Delta T(0) \theta \ll r_0 b_1 \Delta T(0) \theta$  and  $\frac{1}{2} a \Delta T(0) b_2 \Delta T^2(0) \theta \ll r_0 b_2 \Delta T^2(0) \theta$  one obtains

$$\begin{aligned} r^*(t) &\approx r_0(T_0) e^{-\varphi(T_0)t} - \frac{a}{2} \Delta T(0) e^{-(\varphi(T_0) + 1/\theta)t} - r_0(T_0) b_1 \Delta T(0) \theta e^{-\varphi(T_0)t} (1 - e^{-t/\theta}) - \\ &- r_0(T_0) b_2 \Delta T^2(0) \frac{\theta}{2} e^{-\varphi(T_0)t} (1 - e^{-2t/\theta}). \end{aligned} \quad (15)$$

The measured  $EA$  which is its mean value averaged over the entire decay time is then given by:

$$\bar{r}^* = \frac{1}{\tau} \int_0^{\infty} r^*(t) \exp(-t/\tau) dt. \quad (16)$$

Introducing (15) into (16) and carrying out the integration one obtains

$$\bar{r}^* = \frac{r_0(T_0)}{1 + \varphi(T_0)\tau} \left[ 1 - \frac{a\Delta T(0)}{2r_0} \frac{1 + \varphi(T_0)\tau}{1 + (\varphi(T_0) + 1/\theta)\tau} - \frac{b_1\Delta T(0)\tau}{1 + (\varphi(T_0) + 1/\theta)\tau} - \frac{b_2\Delta T^2(0)\tau}{1 + (\varphi(T_0) + 2/\theta)\tau} \right].$$

Taking into account the relationship

$$\frac{r_0(T_0)}{1 + \varphi(T_0)\tau} = \bar{r}(T_0) \equiv \bar{r} \quad (17)$$

giving the measured value of the  $EA$  at steady excitation of the solution at  $T_0$  with light of a frequency equal to that of the pure *electronic transition*  $\nu_{0-0}$ , and denoting  $r_0(T_0)$  by  $r_0$ , one finally arrives at:

$$\bar{r}^* = \bar{r} \left( 1 - \frac{a\Delta T(0)}{2\bar{r} \left( \frac{r_0}{\bar{r}} + \frac{\tau}{\theta} \right)} - \frac{b_1\tau\Delta T(0)}{\frac{r_0}{\bar{r}} + \frac{\tau}{\theta}} - \frac{b_2\tau\Delta T^2(0)}{\frac{r_0}{\bar{r}} + 2\frac{\tau}{\theta}} \right). \quad (18)$$

Denoting  $h/C^*$  by  $\sigma$ , where  $h$  is Planck's constant, one can express the increase of local temperature at  $t = 0$  as function of the difference  $\Delta\nu = \nu - \nu_{0-0}$

$$\Delta T(0) = \sigma(\nu - \nu_{0-0}) = \sigma\Delta\nu. \quad (19)$$

Introducing (19) into (18):

$$\bar{r}^*(\Delta\nu) = \bar{r} - \frac{(\bar{r}b_1\tau + a/2)\sigma}{r_0/\bar{r} + \tau/\theta} \Delta\nu - \frac{\bar{r}b_2\tau\sigma^2}{r_0/\bar{r} + 2\tau/\theta} \Delta\nu^2. \quad (20)$$

Thus  $\bar{r}^*$  as a function of  $\Delta\nu = \nu - \nu_{0-0}$  is, in this approximation, a second degree parabola which may be simply written as

$$\bar{r}^*(\Delta\nu) = \bar{r} - q_1\Delta\nu - q_2\Delta\nu^2. \quad (21)$$

By performing measurements of the dependence of the  $EA$ ,  $\bar{r}^*$ , on the frequency  $\nu$  of the exciting light and tracing a second degree parabolic curve through the experimental points using a least squares fit, one can see how well the approximation agrees with experiment and calculate the values of  $\bar{r}$ ,  $q_1$ ,  $q_2$ . Hence one may calculate  $\theta$  and  $\sigma$  by comparing coefficients of the same powers in Eqs (20) and (21), since the remaining quantities can be calculated if the values of  $r_0$  and  $\tau$  are determined experimentally at a few temperatures of solution ( $a$  is determined from equation (4),  $b_1$  and  $b_2$  on ground of Eqs (8), (9), (10) determining by means of Eq. (2)):

$$q_1 = \frac{(\bar{r}b_1\tau + a/2)\sigma}{r_0/\bar{r} + \tau/\theta},$$

$$q_2 = \frac{\bar{r}b_2\tau\sigma^2}{r_0/\bar{r} + 2\tau/\theta}. \quad (22)$$

Eliminating  $\sigma$  one obtains the following quadratic equation with respect to  $\theta$ :

$$(r_0^2 - Ar_0\bar{r}\tau)\theta^2 + 2(r_0\bar{r}\tau - A(\bar{r}\tau)^2)\theta + (r\tau)^2 = 0,$$

where

$$A = \left(\frac{b_1'}{q_1}\right)^2 \frac{q_2}{b_2} \bar{r}$$

and

$$b_1' = b_1 + a\bar{r}\tau/2.$$

The roots of the equation are

$$\theta_{1,2} = \frac{-[r_0\bar{r}\tau - A(\bar{r}\tau)^2] \pm (A^2\bar{r}^4\tau^4 - A\bar{r}^3\tau^3r_0)^{1/2}}{r_0^2 - Ar_0\bar{r}\tau}.$$

From numerical calculations, only one of these roots is positive (and thus has physical meaning). It is conveniently expressed in the form:

$$\theta = \frac{r_0\varrho - A\varrho^2 + (A^2\varrho^4 - Ar_0\varrho^3)^{1/2}}{Ar_0\varrho - r_0^2} \quad (23)$$

where  $\varrho = \bar{r}\tau$ .

Knowing  $\theta$  one can calculate  $\sigma$  from Eqs (22):

$$\sigma = \frac{b_1' q_2}{b_2 q_1} \frac{r_0\theta + 2\varrho}{r_0\theta + \varrho}. \quad (24)$$

### Experimental

Two dyes were investigated: fluorescein (BDH) and acriflavine (Allied Chemicals) dissolved in mixtures of *glycerol* and water. The following abbreviations are used in all tables:

- $F_1$  fluorescein in 10% water + 90% glycerol
- $F_2$  fluorescein in 20% water + 80% glycerol
- $F_3$  fluorescein in 30% water + 70% glycerol
- $F_4$  fluorescein in 40% water + 60% glycerol
- $A_1$  acriflavine in 10% water + 90% glycerol
- $A_2$  acriflavine in 20% water + 80% glycerol
- $A_3$  acriflavine in 30% water + 70% glycerol
- $A_4$  acriflavine in 40% water + 60% glycerol

Glycerol and water were both purified by double distillation.

The dye concentration  $3 \times 10^{-5}$  mol/l was sufficiently low that the effects of secondary fluorescence and of the migration of the excitation energy between the fluorescent molecules on *EA* and on the mean durations of fluorescence could be neglected [9], [19].

In order to make sure that only one ionic form of fluorescein was present in the solution NaOH was added to the solvent, its concentration being such as to give  $pH = 10$ . At this  $pH$  the almost exclusively predominant ionic form of fluorescein is the doubly charged negative ion [20]. Similarly acriflavine in solutions of  $pH \leq 7$  occurs in the form of singly charged positive ions [21].

Fluorescent solutions thus prepared were placed in rectangular hermetically sealed glass cuvettes. Their absorption and emission spectra were investigated with a standard set of apparatus.

The measurements of the  $EA$  of fluorescence were carried out by means of the Bauer-Rozwadowski polarimeter [36]. A xenon lamp was used as the source of exciting light which was passed through a Hilger-Müller double monochromator. The transmitted band width amounted to about 30 Å.

The mean durations of fluorescence were measured by means of the Bauer-Rozwadowski fluorometer [22].

### Results

The frequency of the purely electronic transition (which appears in Equation (19)), necessary for performing the calculations, was determined on the basis of the law of mirror-symmetry of absorption and fluorescence spectra. These spectra are presented in Figs 1-8. On the abscissa the frequency of light absorbed and emitted by solution is given in  $\text{cm}^{-1}$ . The ordinate represents the intensity of the emitted light of frequency  $\nu$  divided by  $\nu^4$  and the absorption coefficient  $\epsilon(\nu)$  divided by the frequency  $\nu$  of the absorbed light. The absorption and emission spectra are both normalised to unity at their respective maxima. When the units are chosen in this particular way, the frequency corresponding to the intersection of the curves is equal to the frequency of the *purely electronic* transition [23-27], provided the mirror-symmetry of the fluorescence spectrum and the long-wave part of the absorption spectrum is fulfilled.

The frequency of the purely electronic transition of molecules in solutions in not too large a range of temperatures is practically constant [26, 28, 29]. Therefore the absorption and fluorescence spectral measurements were carried out for one temperature (293°K) only, and the frequency  $\nu_{0-0}$  of the purely electronic transition obtained for this temperature was assumed to be the same for 313, 333 and 353°K. The frequencies of the purely electronic transitions are indicated in the figures by an arrow with a subscript  $\nu_{0-0}$ .

As is seen from the graphs, the absorption and fluorescence spectra of the solutions investigated do not show any traces of vibrational structure. They thus belong to the class of *complex polyatomic molecules* (in the nomenclature of Neporent [15]) which are characterized by a vibrational energy distribution corresponding to the state of equilibrium at a given local temperature.

The results of the measurements of the dependence of  $EA$ ,  $\bar{\tau}$  on  $\Delta\nu$  are also presented in Figs 1-8. The points represent the value of  $\bar{\tau}$  measured directly by a polarimeter for a given frequency of exciting light, while the solid curve is a second order parabola (*cf.* Eq.



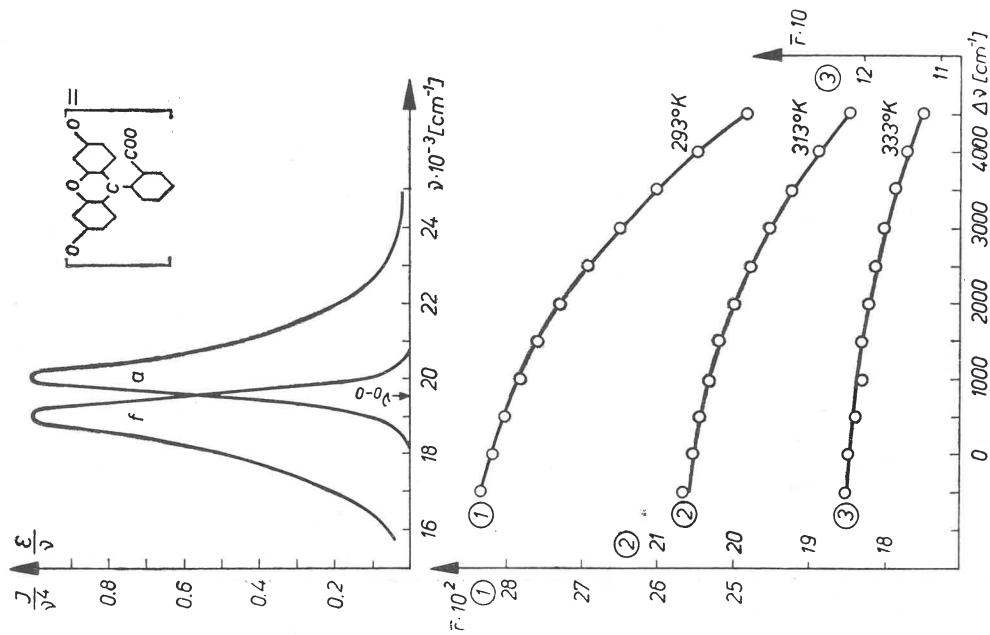


Fig. 1

Fig. 1. Absorption spectrum (a) and fluorescence spectrum (f) and dependence of emission anisotropy ( $\bar{r}$ ) on  $\Delta\lambda = \nu_{\text{exc}} - \nu_{\text{em}}$  for fluorescein in 90% glycerol + 10% water

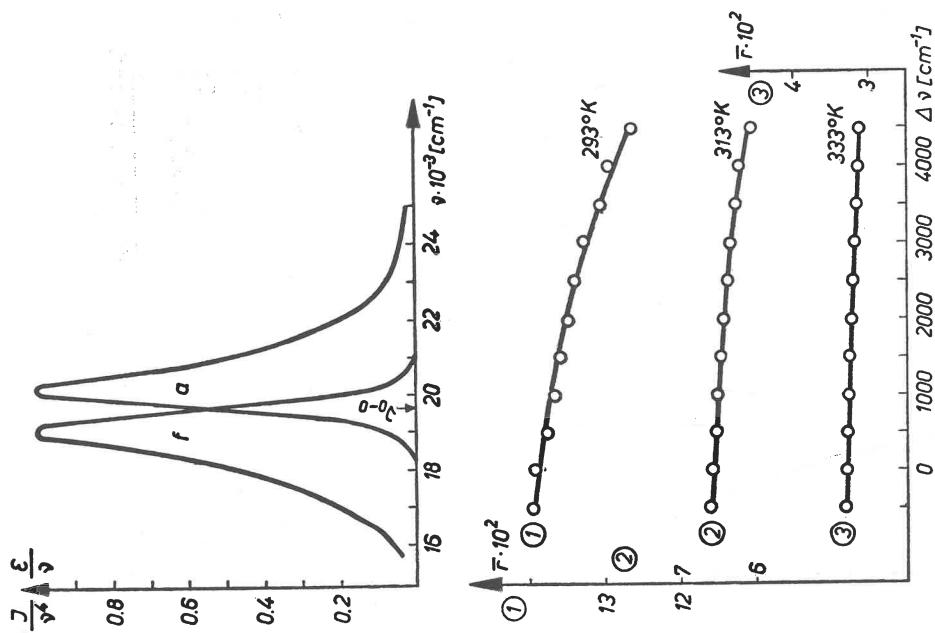


Fig. 2

Fig. 2. As Fig. 1 but for 80% glycerol + 20% water

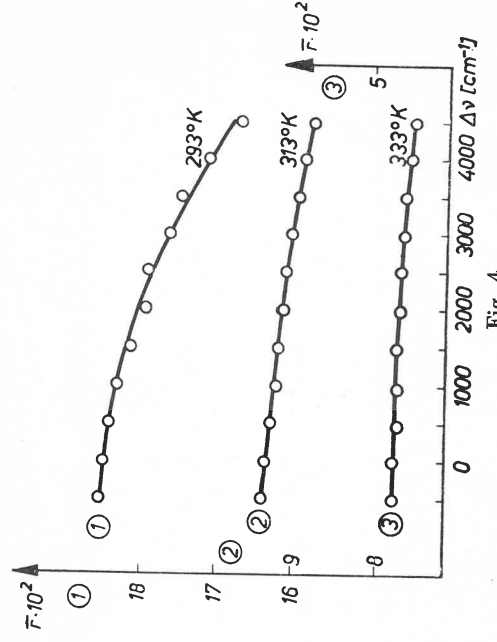
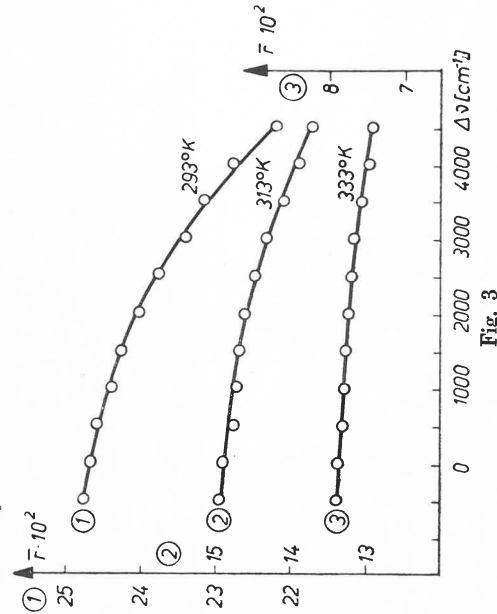
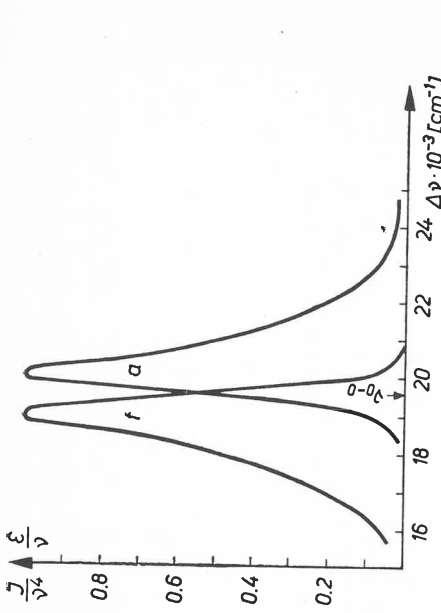
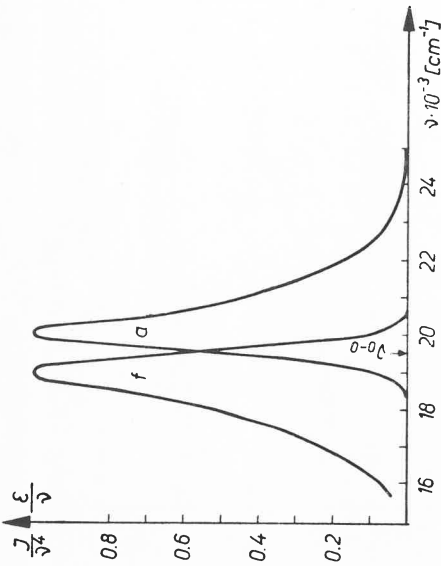


Fig. 3

Fig. 3. As Fig. 1 but for 70% glycerol + 30% water

Fig. 4. As Fig. 1 but for 60% glycerol + 40% water

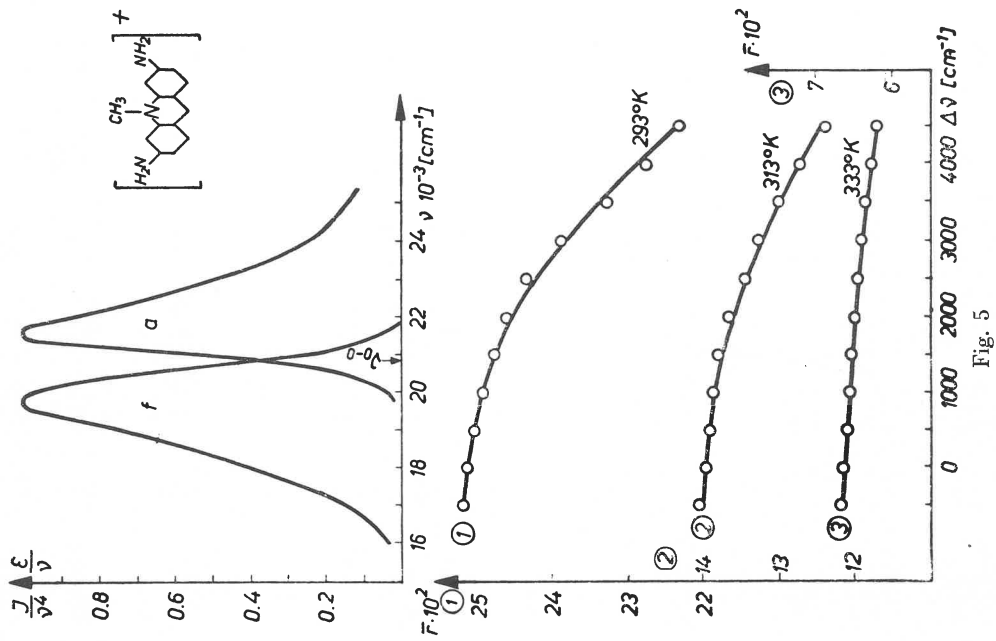


Fig. 5

Fig. 5. As Fig. 1 but for acriflavine in 90% glycerol + 10% water  
 Fig. 6. As Fig. 5 but for 80% glycerol + 20% water

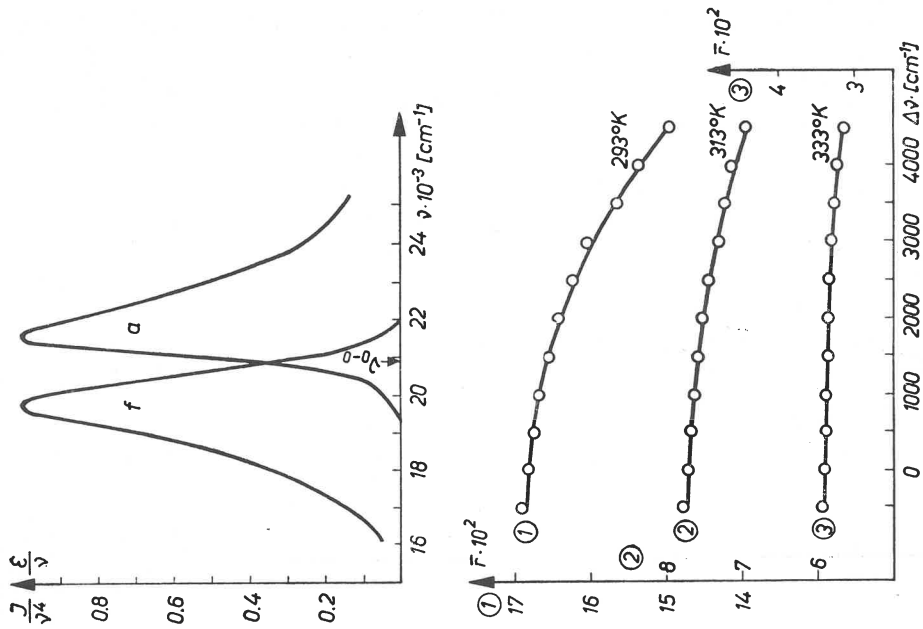


Fig. 6

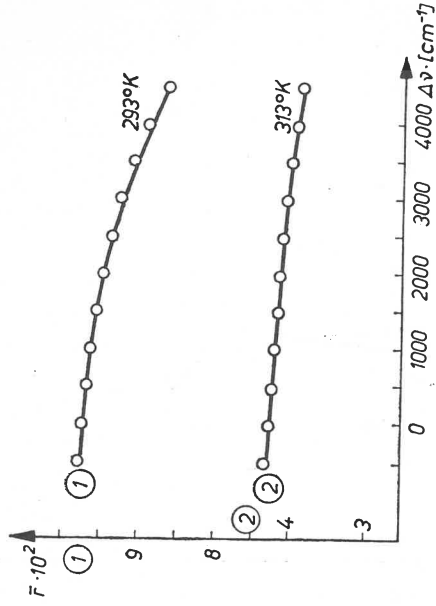
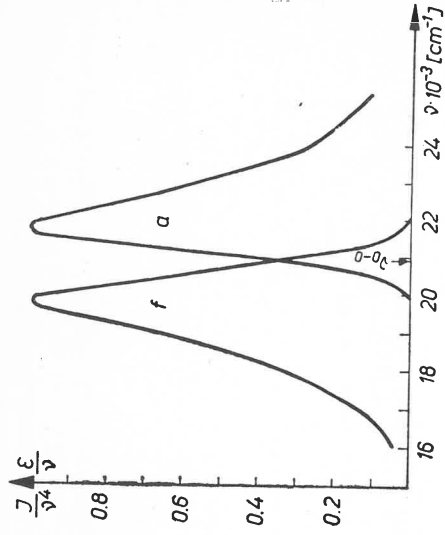


Fig. 8

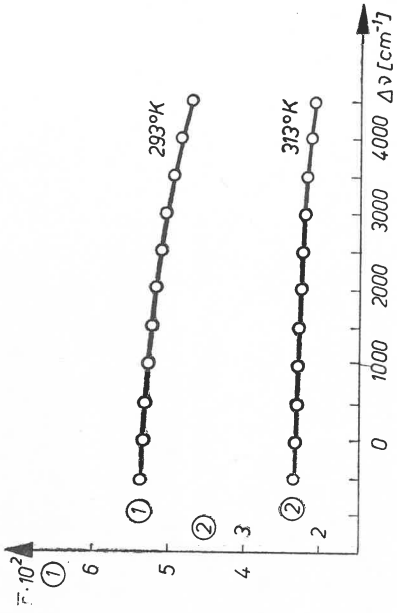
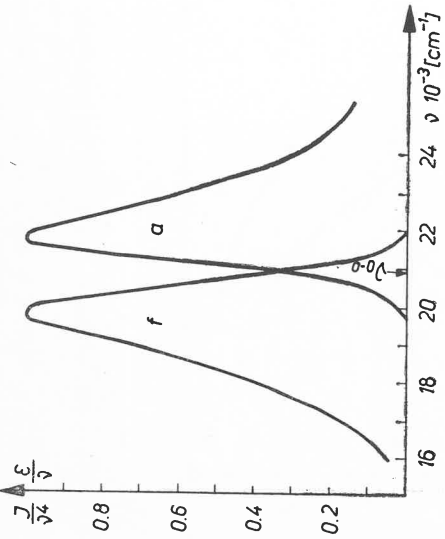


Fig. 7

Fig. 7. As Fig. 5 but for 70% glycerol + 30% water

Fig. 8. As Fig. 5 but for 60% glycerol + 40% water

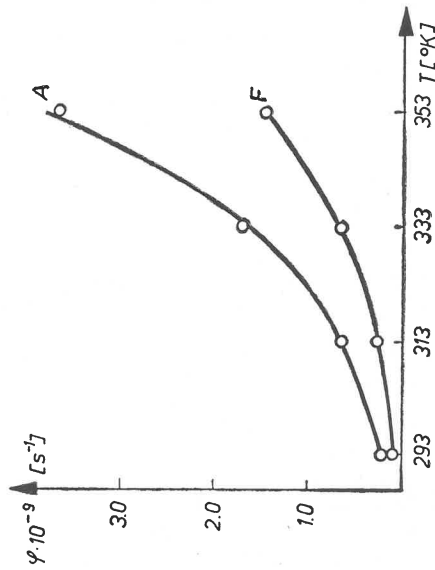
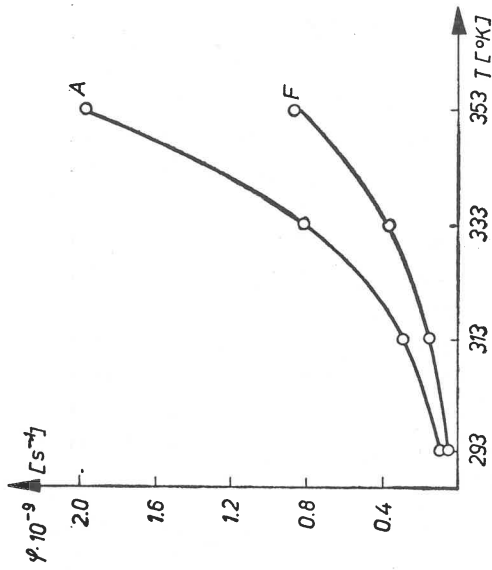


Fig. 9

Fig. 9. Dependence on temperature ( $T$ ) of the probability of depolarization by Brownian rotations per unit time ( $\phi$ ) for fluorescein ( $F$ ) and acriflavine ( $A$ ) in 90% glycerol + 10% water (upper figure) and 80% glycerol + 20% water (lower figure)

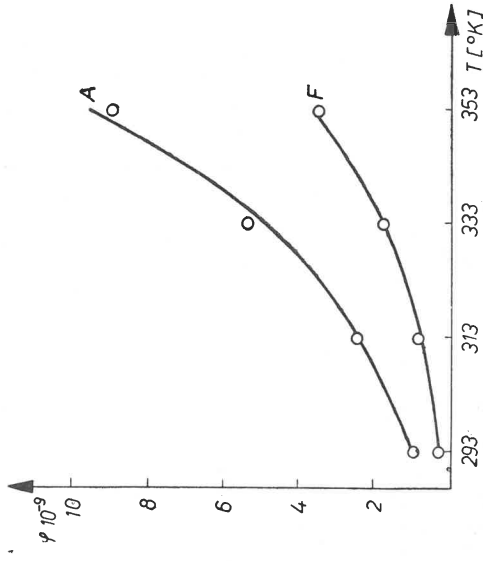
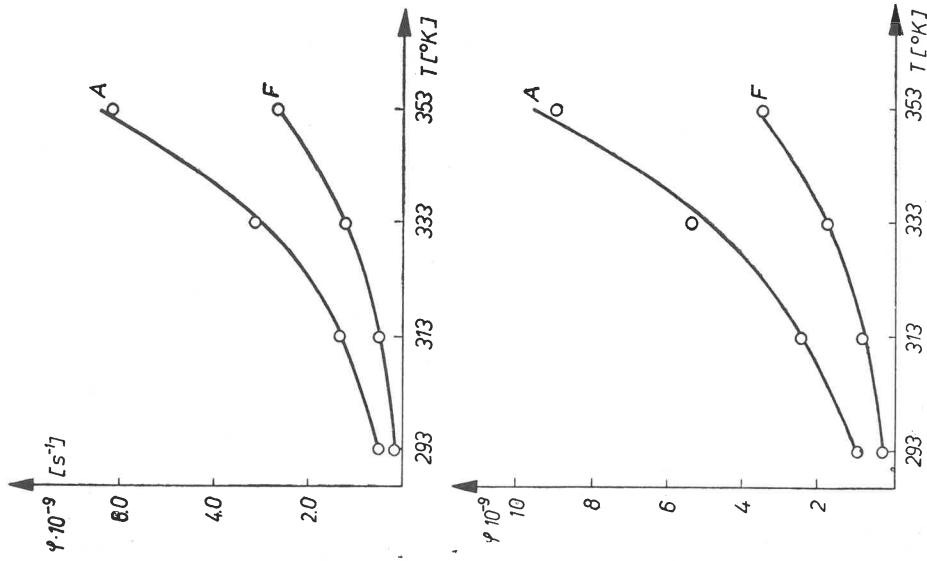


Fig. 10

Fig. 10. As Fig. 9 but for 70% glycerol + 30% water (upper figure) and 60% glycerol + 40% water (lower figure)

TABLE I

	$\bar{r}$	$q_1 \cdot 10^6$ [cm]	$q_2 \cdot 10^{10}$ [cm <sup>2</sup> ]	$\tau$ [ns]	$\tau^{\parallel}$ [ns]	$\tau^{\perp}$ [ns]	$r_0(\parallel)$	$r_0(\perp)$	$\langle r_0 \rangle$	$r_0(293) - a \cdot \Delta T$	$\varphi_{\text{exp}} \cdot 10^{-9}$ [s <sup>-1</sup> ]	$\varphi_{\text{int}} \cdot 10^{-9}$ [s <sup>-1</sup> ]	
1	2	3	4	5	6	7	8	9	10	11	12	13	
$F_1$	293 °K	0.2842	2.0343	11.7910	5.60	5.07	6.18	0.38	0.38	0.38	0.380	0.0596	0.0571
	313 °K	0.2076	0.2224	7.9212	5.58	4.87	6.25	0.37	0.38	0.38	0.379	0.1480	0.1569
	333 °K	0.1223	0.5829	3.2227	5.56	4.83	6.09	0.37	0.39	0.38	0.377	0.3745	0.3818
	353 °K	0.0640			5.60	5.07	5.92	0.39	0.39	0.39	0.376	0.8705	0.8400
$F_2$	293 °K	0.2464	1.3069	8.8561	5.80	5.16	6.43	0.37	0.37	0.37	0.380	0.0935	0.0946
	313 °K	0.1490	0.4989	4.4024	5.79	5.00	6.41	0.37	0.38	0.38	0.379	0.2693	0.2645
	333 °K	0.0787	0.3902	1.2169	5.79	5.16	6.18	0.39	0.37	0.38	0.377	0.6548	0.6541
	353 °K	0.0400			5.80	5.43	6.02	0.29	0.45	0.37	0.376	1.4487	1.4596
$F_3$	293 °K	0.1851	0.7896	6.4576	5.72	4.97	6.37	0.36	0.37	0.37	0.380	0.1850	0.1907
	313 °K	0.0936	0.1987	2.6545	5.69	5.01	6.13	0.39	0.37	0.38	0.379	0.5357	0.5138
	333 °K	0.0472	0.1523	0.7106	5.61	5.19	5.85	0.36	0.35	0.35	0.377	1.2464	1.2289
	353 °K	0.0243			5.58	5.23	5.79				0.376	2.5949	2.6626
$F_4$	293 °K	0.1393	1.2087	3.1106	5.78	4.98	6.37	0.38	0.38	0.38	0.380	0.2990	0.3114
	313 °K	0.0659	0.2616	1.6500	5.68	5.14	6.01	0.36	0.37	0.37	0.379	0.8365	0.788
	333 °K	0.0331	0.3030	0.1727	5.73	5.40	5.91				0.377	1.8126	1.7868
	353 °K	0.0177			5.67	5.50	5.77				0.376	3.5723	3.6891

(21)) fitted<sup>2</sup> to the experimental points by the method of least squares. The number at the left of every curve gives the corresponding number of the scale on which the value of  $EA \bar{r}$  is to be read. At the right-hand side the temperature (in °K) of the solution of which the  $EA$  was measured is given (the temperature was controlled with a Hoespler thermostat to an accuracy of  $\pm 0.1$  °K). The reproducibility of the  $EA$ ,  $\bar{r}$ , measurement is  $\pm 1\%$  of the value. All the points lie, within experimental error, on a curve  $\bar{r} = \bar{r} - q_1 \Delta\nu - q_2 \Delta\nu^2$ . This justifies the approximations introduced while deriving Eq. (20) and shows that the dependence of  $EA$  on the exciting frequency can be satisfactorily explained by the influence of the local temperature of centres on torsional vibrations and Brownian rotations of luminescent molecules.

The values of  $\bar{r}$ ,  $q_1$  and  $q_2$  obtained from the  $\bar{r}(\Delta\nu)$  experimental curves of the form (21) make it possible to calculate  $\theta$  and  $\sigma$  by means of Eqs (23) and (24). The values of  $\bar{r}$ ,  $q_1$  and  $q_2$  are given in Tables I and II, where the  $\tau$ ,  $\tau^{\parallel}$  and  $\tau^{\perp}$  necessary for calculation of  $r_0$  (by means of Eq. (5)) and of  $\varphi$  (by means of Eq. (17)) and their temperature dependence, are also set out. The dependence of  $\varphi$  on temperature is presented in Figs 9 and 10. The points denote the values of  $\varphi_{\text{exp}}$  calculated from experimental data, whereas the solid curve is the plot of  $\varphi_{\text{int}}(T) = b \exp(-\varepsilon/T)$  fitted to the points by the method of least squares. The values of  $\varphi_{\text{exp}}$  and  $\varphi_{\text{int}}$  ( $\varphi_{\text{int}} = \varphi_{\text{interpolated}}$ ) are also given in Tables I and II.

<sup>2</sup> All the numerical calculations in this paper were carried out on the Odra 1003 computer in the Computing Centre of the Chair of Mathematics of the Nicholas Copernicus University in Toruń.

TABLE II

	$\bar{r}$	$q_1 \cdot 10^6$ [cm]	$q_2 \cdot 10^{10}$ [cm <sup>2</sup> ]	$\tau$ [ns]	$\tau_{  }$ [ns]	$\tau_{\perp}$ [ns]	$r_0^{(  )}$	$r_0^{(\perp)}$	$\langle r_0 \rangle$	$r_0(293) - a \cdot \Delta T$	$\varphi_{\text{exp}} \cdot 10^{-9}$ [s <sup>-1</sup> ]	$\varphi_{\text{int}} \cdot 10^{-9}$ [s <sup>-1</sup> ]	
1	2	3	4	5	6	7	8	9	10	11	12	13	
$A_1$	293 °K	0.2510	1.2316	6.1000	5.59	5.01	6.22	0.36	0.38	0.37	0.370	0.0848	0.0873
	313 °K	0.1397	0.0173	7.2312	5.53	4.76	6.08	0.39	0.36	0.37	0.368	0.2954	0.2841
	333 °K	0.0665	0.4198	1.1953	0.52	4.99	5.84	0.37	0.36	0.36	0.366	0.8163	0.8023
	353 °K	0.0310			5.49	5.20	5.65	0.33	0.35	0.34	0.364	1.9608	2.0141
$A_2$	293 °K	0.1682	0.1949	8.5683	5.77	5.00	6.41	0.36	0.37	0.37	0.370	0.2079	0.2168
	313 °K	0.0774	0.4787	2.7557	5.62	5.03	5.99	0.36	0.36	0.36	0.368	0.6678	0.6363
	333 °K	0.0342	0.7184	0.8709	5.67	5.34	5.85	0.38	0.33	0.36	0.366	1.7089	1.6412
	353 °K	0.0171			5.56	5.37	5.68				0.365	3.6286	3.8021
$A_3$	293 °K	0.0970	0.2202	4.7152	5.83	5.14	6.29	0.36	0.37	0.37	0.370	0.4827	0.5028
	313 °K	0.0423	0.4592	0.9301	5.64	5.25	5.86	0.37	0.36	0.36	0.368	1.3656	1.3078
	333 °K	0.0192			5.69	5.48	5.82				0.366	3.1779	3.0330
	353 °K	0.0103			5.63	5.52	5.69				0.364	6.0873	6.3944
$A_4$	293 °K	0.0535	0.3557	2.1552	6.02	5.53	6.31	0.38	0.36	0.37	0.370	0.9825	1.0269
	313 °K	0.0233	0.1548	0.7249	5.99	5.74	6.14	0.36		0.36	0.368	2.4653	2.3834
	333 °K	0.0112			5.85	5.73	5.94				0.366	5.4102	5.000
	353 °K	0.0068			5.85	5.77	5.92				0.364	9.0064	9.6441

TABLE III

	$F_1$	$F_2$	$F_3$	$F_4$	$A_1$	$A_2$	$A_3$	$A_4$
1	2	3	4	5	6	7	8	9
$b \cdot 10^{-15}$ [s <sup>-1</sup> ]	0.4222	0.9299	1.0383	0.6446	0.1123	4.5180	1.5817	0.5426
$\varepsilon \cdot 10^{-4}$ [grad]	0.4634	0.4718	0.4545	0.4261	0.4510	0.4938	0.4384	0.3861
$E = k \cdot \varepsilon$ [eV]	0.399	0.406	0.391	0.367	0.466	0.425	0.378	0.333

These curves show that the function (6) describes well the dependence on temperature of the probability of depolarization by Brownian rotations per unit time. The empirical constants  $b$  and  $\varepsilon$  chosen by the method of least squares, are shown in Table III. In the third row of the table the *activation energy* of Brownian rotations  $E = k\varepsilon$  (where  $k$  is the Boltzmann constant) is given. This energy decreases, for a given kind of molecule, with the decrease in percentage of glycerol *i.e.* with the decrease of solvent viscosity. The course of this change depends on the kind of fluorescent compound employed (the *activation energy* of Brownian rotations decreases faster with viscosity for acriflavine than for fluorescein). It also follows from Figs 9 and 10 that in a solvent with a similar percentage of glycerol

TABLE IV

	$b_1 \cdot 10^{-7}$ [s <sup>-1</sup> /grad]	$b_2 \cdot 10^{-5}$ [s <sup>-1</sup> /grad <sup>2</sup> ]	$\theta \cdot 10^{11}$ [s]	$\sigma \cdot 10^2$ [grad/ cm <sup>-1</sup> ]		$b_1 \cdot 10^{-7}$ [s <sup>-1</sup> /grad]	$b_2 \cdot 10^{-5}$ [s <sup>-1</sup> /grad <sup>2</sup> ]	$\theta \cdot 10^{12}$ [s]	$\sigma \cdot 10^1$ [grad/ cm <sup>-1</sup> ]	
	1	2	3	4	5	6	7	8	9	10
$F_1$	293 °K	0.3083	0.7270	4.81	4.89	293 °K	0.5503	1.5460	2.00	1.85
	313 °K	0.7423	1.5183	0.72	8.39	$A_1$ 313 °K	1.5690	3.8305	4.60	0.70
	333 °K	1.5957	2.8549	0.49	6.17	333 °K	3.9141	8.3720	6.12	0.27
$F_2$	293 °K	0.5196	1.2504	1.83	5.62	293 °K	1.2468	3.1602	0.27	3.47
	313 °K	1.2739	2.6603	0.31	8.44	$A_2$ 313 °K	3.2072	7.0576	3.70	0.52
	333 °K	2.7829	5.0840	0.53	3.41	333 °K	7.3082	14.0766	0.23	1.26
$F_3$	293 °K	1.0095	2.3275	0.60	7.09	293 °K	2.5673	5.6785	0.46	1.94
	313 °K	2.3833	4.7663	5.59	0.88	$A_3$ 313 °K	5.8521	11.2230	8.96	0.21
	333 °K	5.0361	8.8071	0.12	5.33	333 °K				
$F_4$	293 °K	1.5460	3.3089	2.37	2.39	293 °K	4.6184	8.8093	2.27	0.63
	313 °K	3.4309	6.3649	0.17	6.79	$A_4$ 313 °K	9.3933	15.5090	1.25	0.57
	333 °K	6.8660	11.1297	2.00	0.69	333 °K				

TABLE V

	$\langle \theta \rangle$	$\langle \sigma \rangle$
Fluorescein	$1.63 \cdot 10^{-11}$ s	$5 \cdot 10^{-2}$ grad/cm <sup>-1</sup>
Acryflavie	$3 \cdot 10^{-12}$ s	$1 \cdot 10^{-1}$ grad/cm <sup>-1</sup>

and water at the same temperature  $T$  (*i.e.* of the same viscosity  $\eta$ ),  $\varphi$  for acriflavine is always larger than for fluorescein. This indicates that the volume of the acriflavine molecule together with its solvation shell is smaller than for fluorescein  $v_A < v_F$  (from Perrin's expression:  $\varphi = kT/v\eta$  [30]).

The values of relaxation times,  $\theta$ , of the local temperature of luminescent centres and reciprocals of the heat capacity of these centres,  $\sigma$ , calculated on the basis of the Eqs (23) and (24), for all fluorescent solutions at temperatures 293, 313, 333 °K, are set out in Table IV. Inspection of the values  $\theta$  and  $\sigma$  given there leads to the conclusion that only a rough estimate of their magnitude is possible. Therefore  $\langle \theta \rangle$  and  $\langle \sigma \rangle$ , *i.e.* the values of  $\theta$  and  $\sigma$  averaged over the above mentioned three temperatures are given in Table V.  $\langle \theta \rangle$  and  $\langle \sigma \rangle$  are sufficient to demonstrate the influence of the individual properties of the fluorescent molecules on  $\theta$  and  $\sigma$ . However the determination of their dependence on temperature (which was varied within rather narrow limits) and on the variation of the composition of the solvent is beyond the capacity of the method. Nevertheless, comparison of the structural formulae and  $v$ 's of fluorescein and acriflavine molecules (Figs 1 and 5) shows that the luminescent centre with the larger number of degrees freedom (fluorescein) has the higher *heat capacity*.



The relaxation time of the local temperature for fluorescein is longer than that for acriflavine. This is partly due to the larger heat capacity of fluorescein but also the different "thermal conductivity" (owing to the difference in their interaction<sup>3</sup> with the solvent) on which the velocity of the energy flow from one subset (the fluorescent molecule) to another (the solvent molecules) depends; according to de Groot [31] the relaxation time is directly proportional to the heat capacity of the subset of higher temperature and inversely proportional to the thermal conductivity coefficient between the subsets.

The vibrational heat capacities of the fluorescent molecules in vapours may be determined by two methods:

1) the method of Neporent [15], from the curves of the quantum yield of fluorescence as a function of the frequency of the exciting light and temperature, and

2) on the basis of the Stepanov relationship [32] between the absorption and fluorescence spectra.

The reciprocal values of the heat capacity obtained by these methods lie between  $1 \times 10^{-2}$  and  $5 \times 10^{-2}$  deg/cm and they depend on the kind of molecule ([33] p. 155). The agreement between the results obtained by these two methods is satisfactory. The vibrational heat capacities in solutions have not yet been measured. Within the (poor) accuracy with the heat capacities of luminescent centres in solutions were determined here, one may consider them to agree reasonably well with those obtained for fluorescent molecules in vapours.

The relaxation times for solutions,  $\theta$ , obtained here are much shorter than those (about  $5 \times 10^{-9}$  sec) previously published [34, 35].

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<sup>3</sup> It has also been shown (14) that the atomic masses of the substituents of the molecule influence the relaxation time.

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