EMISSION ANISOTROPY OF FLUORESCENCE OF AROMATIC HYDROCARBONS II

By R. K. Bauer

Physics Department, N. Copernicus University, Toruń*

(Received December 5, 1968)

The absorption polarization spectra of tetracene, anthracene and 5-aminoacridine were measured. The depolarization of the fluorescence light of these solutions becomes more dependent on the frequency of the exciting light with higher dye concentration (except for 5-aminoacridine solutions). A certain relationship was found between the structure of absorption and emission spectra of these hydrocarbon solutions and the magnitude of the depolarization of fluorescence excited with light of frequencies higher than that of the 0—0 transition. The probability of electronic energy transfer between dye molecules from higher vibrational levels is larger when the vibrational structure of the spectra is more pronounced, *i.e.* when there is less coupling between the vibrational levels. This behaviour may be explained by assuming that tetracene and anthracene molecules are partly "weakly" coupled .At higher concentrations of the dye molecules and shorter mean distances between them a certain kind of complex is formed. Energy transfers between complexed molecules are more probable than between "very weakly" coupled ones. An assumption of weak coupling between the dye molecules explains the observed vibrational structure of the polarization spectrum of tetracene and anthracene solutions, because in this kind of coupling the energy transfer rate is proportional to the population of the vibrational levels in both excited and unexcited molecules.

Introduction

An earlier paper [1] dealt with the dependence of emission anisotropy of the fluorescence of anthracence solutions on the wavelength of exciting light. It was conjectured there that the probability of energy transfer from higher vibrational levels to other molecules of the same kind increases together with an increase of dye concentration in the solution. The present work broadens the range of research on the dependence of fluorescence depolarization on wavelength of exciting light, with measurements being made of the absorption polarization spectra of anthracene, tetracene and 5-aminoacridine within a large range of dye concentrations. Similar measurements were performed by Zimmermann and Joop [2, 3] using high concentrations of aromatic hydrocarbons in ethyl alcohol. The emission anisotropy of fluorescence of aromatic hydrocarbon solutions of concentrations equal to about 10^{-4} M demonstrates a sharp drop when shorter wavelengths are used for excitation (relative to

* Address: Toruń, ul. Grudziądzka 5, Polska.

the wavelength corresponding to the 0—0 transition). This considerable decrease of emission anisotropy cannot be a result of an increase in the local temperature of the luminescence centres [4]. It may be supposed that the effect mentioned is due to the formation of stable dimers. Photodimerization of anthracene and tetracene had been observed by many authors [5–9]. The absorption spectra of dianthracene and ditetracene do not have a vibrational structure and are strongly shifted towards shorter wavelengths ($\lambda_{max} = 250$ mμ), as compared with the monomer spectra ($\lambda_{max} = 360$ mμ and $\lambda_{max} = 460$ mμ for anthracene and tetracene, respectively). The fluorescence spectra behave similarly ($\lambda_{max} = 320$ mμ, compared with $\lambda_{max} = 400$ mμ and $\lambda_{max} = 480$ mμ for anthracene and tetracene, respectively). Hence, it is possible to induce fluorescence of monomers without exciting dianthracene and ditetracene. Chandross and Ferguson found, however, that pseudodimers of anthracene form in solvents which become glassy at a temperature of 77°K. When a solution of dianthracene is illuminated with light of a wavelength of 253.7 mμ the dianthracene bonding becomes disrupted due to photodissociation, but the freed anthracene molecules remain close to each other in the frozen solution, forming a so-called "sandwich-dimer". This kind of pseudodimer has an absorption spectrum which is more diffuse and shifted slightly towards the longer wavelengths as compared with the monomer spectrum, and the fluorescence spectrum loses its vibrational structure. Its maximum is in the vinicity of 480 mμ. If the solution is heated and then refrozen, a monomeric absorption and emission spectrum is observed. Finally, there is a third type of anthracene dimer which forms in a 3:1 solution of isopentane and methylcyclohexane under the influence of light at temperatures higher than −160°C. The emission spectrum of this type of pseudodimer is highly diffuse, but does not lose its vibrational structure entirely. These pseudodimers are also unstable dissociate temperatures at which the solutions are no longer inflexible.

In order to avoid changes in the concentration of monomers due to the formation of stable dimers, the measurements described herein were made with the weakest possible intensities of exciting light during the several seconds required for reading the instruments. The absorption and emission spectra measured thus did not display any changes.

Results of measurements

Analyses of the emission and absorption spectra and measurements of the emission anisotropy of fluorescence were performed for tetracene in paraffin oil, and anthracene and 5-aminoacridine in anhydrous glycerol with 10 per cent of methyl alcohol added. The concentrations used were 3×10^{-4}, 10^{-4}, 3×10^{-5}, 10^{-5} and 3×10^{-6} M, at temperatures of the solution of 20 and −60°C. Figure 1 presents the emission and absorption spectra of the aromatic hydrocarbons examined. The width of the vibrational bands of these spectra depends on the interaction between the fluorescing molecules and the solvent molecules. The spectra of 5-aminoacridine dissolved in glycerol with an addition of 10% CH_3OH have the least distinct vibrational structure. This is a result of the stronger interaction of the nitrogen atom (substituting the atom of carbon at position 1 in the anthracene molecule) and NH_2 group (substituting the hydrogen atom at position 5) with the glycerol and methyl

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

alcohol, as compared with the corresponding atoms of the anthracene molecules. Owing to the very small dipole moment of paraffin oil, as compared with that of glycerol and methyl alcohol, the width of the vibrational bands and their mutual overlapping in the absorption and emission spectra of the tetracene solution is the smallest. With a change in the dye concentration from 3×10^{-6} to 3×10^{-4} M there is no change in the intensity distribution of the emission and absorption spectra.

A paper by Nieporent [11] and another by Terenin [12] deal with the effect of wavelength of exciting light and temperature on the spectral distribution, vield and transfer of vibrational excitation energy by collisions with perturbing atoms in the vapours of fluorescing

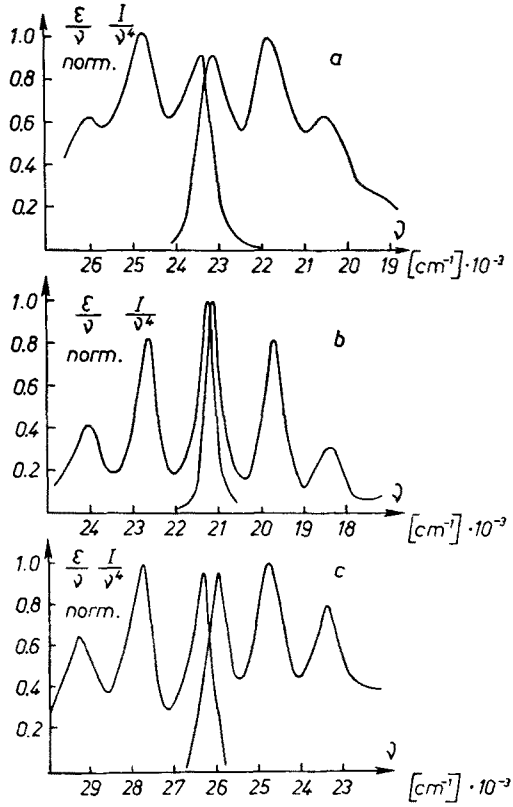

Fig. 1. Absorption and emission spectra of a solution of: *a*) 5-aminoacridine in glycerol, *b*) tetracene in paraffin oil, *c*) anthracene in glycerol

molecules. Their results indicate that in complex multi-atom molecules, which are characterized by their continuous emission and absorption spectra, there is strong coupling between the different vibrational degrees of freedom. Nieporent considered that the probability $W = 1/\tau'$ (where τ' is the relaxation time of the vibrational energy) of the intramolecular relaxation of vibrational energy is one of the essential features of a molecule, which determines the width of the vibrational bands in this emission and absorption spectra. According to the terminology used

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

by Nieporent [13], a molecule is complex (hence, has structureless emission and absorption spectra) if $W > 1/\tau$ (τ stands for the mean lifetime in the excited state); however, the narrower the vibrational bands, the lower is the probability W. Of the examined molecules, the highest probability of intramolecular relaxation of vibrational energy exists in 5-aminoacridine the lowest in tetracene.

The emission anisotropy measurements were performed with a polarimeter described in ref. [1]. Because the emission anisotropy of fluorescence of anthracene and tetracene solutions depends on the wavelength of the emitted light [2] as well as that of the exciting light, the emission anisotropy measurements required the use of absorption filters letting through only the shortest wavelength vibrational band of the fluorescence spectrum (near the 0—0 transition). The results of emission anisotropy measurements for the tetracene, anthracene and 5-aminoacridine solutions, with different wave numbers of exciting light, are shown in Figs 2 to 4. The emission anisotropy of fluorescence of tetracene, anthracene and 5-aminoacridine depends on the wavelength of the exciting light; for tetracene and anthracene this dependence is stronger when the concentration is higher, whereas for 5-aminoacridine the polarization spectra for different concentrations are approximately parallel. For example, when solutions cooled to −60°C are excited by light of a frequency ν, higher than the frequency of the 0—0 transition (ν_{0-0}) by 3000 cm^{-1}, the emission anisotropy drops in comparison with the value of emission anisotropy when the solutions are excited by light of frequency ν_{0-0} down to: *a*) 56.4% for tetracene at a concentration of 3×10^{-6} M, and 36.2% at 3×10^{-4} M, *b*) 97% for anthracene at a concentration of 3×10^{-6} M, and 57.6% at 3×10^{-4} M, *c*) 84.4% for aminoacridine at a concentration of 3×10^{-6} M, and 81.8%

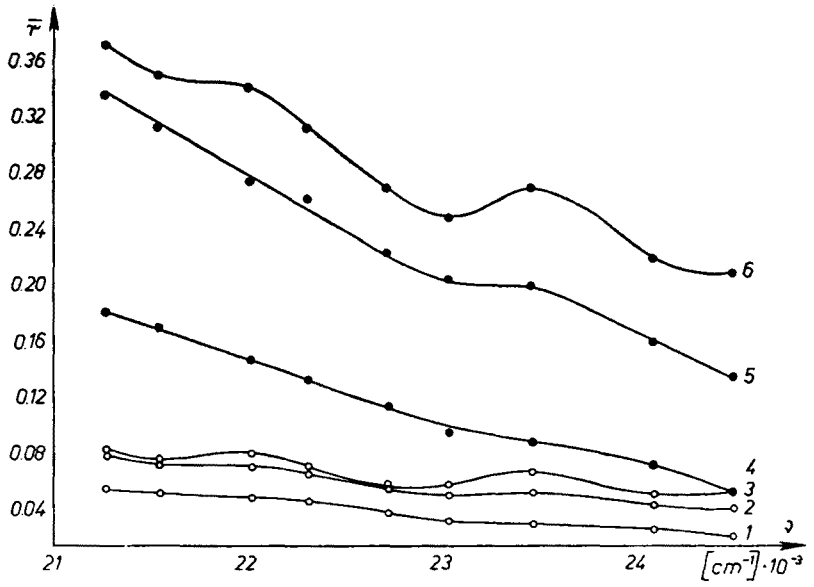

Fig. 2. Absorption polarization spectrum of tetracene dissolved in paraffin oil

1. 3×10^{-4}M, *2*. 3×10^{-5}M, *3*. 3×10^{-6}M } 20°C

4. 3×10^{-4}M, *5*. 3×10^{-5}M, *6*. 3×10^{-6}M } −60°C

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

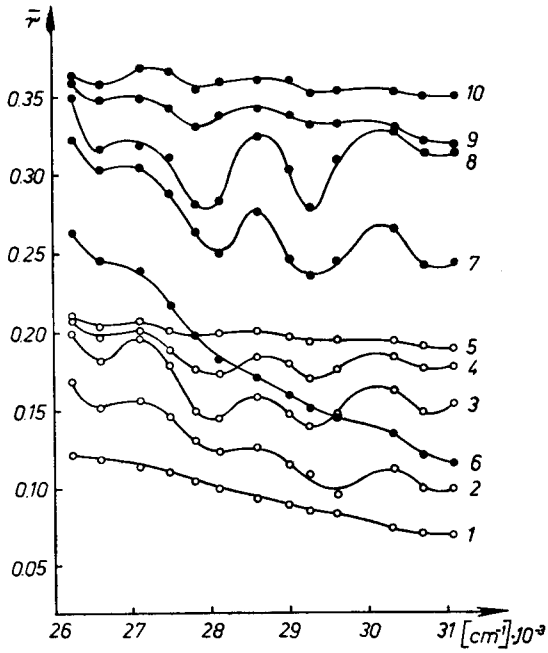

Fig. 3. Absorption polarization spectrum of anthracene dissolved in glycerol

1. 3×10^{-4}M
2. 10^{-4}M
3. 3×10^{-5}M
4. 10^{-5}M
5. 3×10^{-6}M

} 20°C

6. 3×10^{-4}M
7. 10^{-4}M
8. 3×10^{-5}M
9. 10^{-5}M
10. 3×10^{-6}M

} −60°C

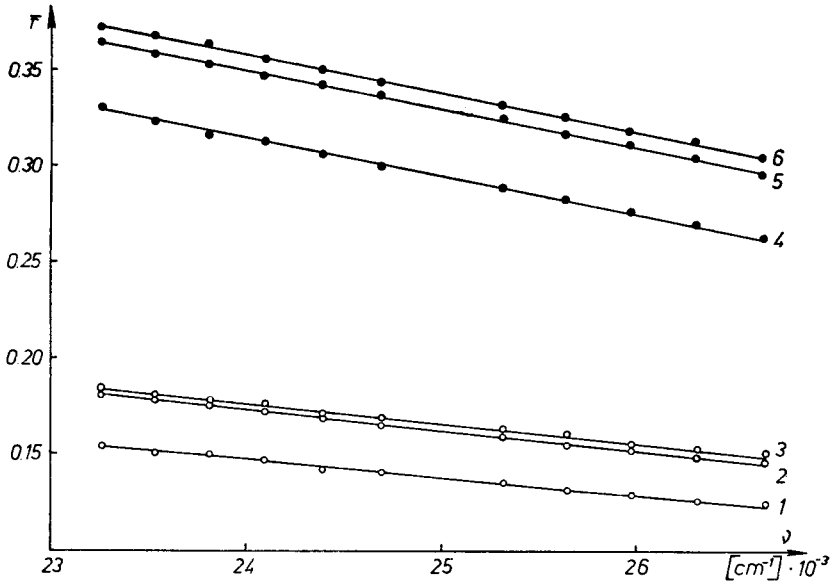

Fig. 4. Absorption polarization spectrum of 5-aminoacridine dissolved in glycerol

1. 3×10^{-1}M
2. 3×10^{-5}M
3. 3×10^{-6}M

} 20°C

4. 3×10^{-4}M
5. 3×10^{-5}M
6. 3×10^{-6}M

} −60°C

at 3×10^{-4} M. Similar results are also obtained when the polarization spectra are measured at 20°C. Hence, depolarization of fluorescence caused by excitation with light of a frequency higher than that of the 0—0 transition is greatest for the tetracene solutions, smaller for the anthracene solutions and weak for the 5-aminoacridine solutions.

The polarization spectrum of fluorescence of the anthracene solutions displays a certain structure, which is especially strong for the 3×10^{-5} and 10^{-4} M concentrations. This structure practically disappears for both the lower concentration (3×10^{-6} M) and higher concentration (3×10^{-4} M). The structure in the polarization spectrum of fluorescence of the tetracene solutions is less distinct, and is actually accentuated for the 3×10^{-6} M solution. Probably (by analogy to the anthracene solutions) the structure in the polarization spectrum of fluorescence of tetracene would disappear completely at lower concentrations. The sensitivity of the instruments used was too low to enable a measurement of the fluorescence of a solution with a lower concentration of tetracene. In paper [4], dealing with the local temperature of luminescence centres, it was shown that the use of excessively wide slits in the excitation monochromator (insufficient half-width of the spectral segment), or the use of sources of light with a continuous background spectrum superimposed by lines can be the cause of considerable deformation of the emission anisotropy *versus* ν curves. In order to avoid this systematic error, a high-pressure xenon lamp with a continuous emission spectrum was used, and the monochromator slits were chosen in such a way that the half-width of the spectral segment would not exceed 3 mμ. A comparison of the structures of the polarization spectrum and the absorption spectrum of the tetracene and anthracene solutions shows that when the fluorescence is excited by light of wavelengths corresponding to the individual absorption maxima, minima of emission anisotropy are obtained, and *vice versa*.

For the purpose of comparing the concentration depolarization of the examined luminescing substances, the size of the active sphere volume, introduced by Jabłoński [14], was calculated according to the approximate formula

$$\frac{r_0'}{\bar{r}} = 1 + \frac{1}{3}\nu'. \tag{1}$$

Here, r_0' is the emission anisotropy obtained by extrapolating the curve $1/\bar{r}(\nu')$ to zero concentration, $\bar{r}$ is the emission anisotropy obtained for different concentrations, and $\nu' = vn$ (v being the volume of the active sphere and n the number of molecules per cu. cm of solution). With exciting light of a frequency corresponding to the 0—0 transition the following values of active sphere volumes were obtained for solutions at —60 °C: *a*) tetracene 16.5×10^{-18} cu.cm, *b*) anthracene 6.6×10^{-18} cu.cm, and *c*) 5-aminoacridine 2.5×10^{-18} cu.cm. Identical calculations made for the values of active sphere volumes when the exciting light had a frequency higher by 3000 cm^{-1} did not give a single-valued result (for anthracene and tetracene), because the value of active sphere volume depends on the concentration of the dye in the solution. The values of v with fluorescence excited by frequencies $\nu = \nu_{0-0} + 3000$ cm^{-1} are as follows: *a*) tetracene (30 to 100)$\times10^{-18}$ cu.cm, *b*) anthracene (20 to 50)$\times10^{-18}$ cu.cm, and *c*) 5-aminoacridine 3×10^{-18} cu.cm. The mean

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

durations τ of fluorescence of anthracene solutions vary between 3.83 nsec to 4.04 nsec when the anthracene concentration increases from 3×10^{-6} to 3×10^{-4} M; the corresponding values for the tetracene solutions are 4.08 nsec and 4.72 nsec.

Interpretation of results

Since the conditions of the measurements excluded both the possibility of dianthracene and ditetracene formation, and that of excitation of their fluorescence, any influence of these dimers on the measurements of the emission anisotropy of fluorescence is entirely removed. Also, the pseudodimers which form in glasses at low temperatures, described in the introduction, could not be the cause of the observed dependence of emission anisotropy on exciting light wavelength, because the conditions of the measurements described here allowed relative motion of the dye molecules entering the composition of the examined solutions. (In Ref. [1] it was shown that there are depolarizing rotational thermal motions in glycerol with a 10% addition of methyl alcohol at a temperature of $-60°C$, however.)

The concentration-independent value of active sphere volume (calculated from the results of emission anisotropy measurements of fluorescence of tetracene, anthracene and 5-aminoacridine solutions excited with frequencies corresponding to the 0—0 transition) gives rise to the supposition that during excitation to the lowest vibrational state of the first excited electronic level the interaction leading to energy transfer and, hence, to fluorescence depolarization, is of the "dipole-dipole" type and "very weak". A theory of depolarization was elaborated by Förster [15, 16] for this peculiar type of interaction. According to Förster, the probability of energy transfer

$$n_s = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6 \tag{2}$$

is proportional to the sixth power of the ratio of a "critical distance" R_0 to the distance R between two molecules participating in the energy transfer. It is also inversely proportional to the mean lifetime in the excited state, τ. The quantity R_0 is the distance between two luminescence centers for which the transfer of energy from the initially excited molecule is equally probable as spontaneous emission of fluorescent light, and is equal to

$$R_0 = \frac{9 \ln 10 k^2 \eta_s}{128\pi^5 n^4 N} I_\nu. \tag{3}$$

Here, k is a dimensionless constant of the order of unity which depends on the alignment of the molecules, η_s is the quantum yield of fluorescence, n is the refractive index of the solution, N is the number of dye molecules per millimole, and $I_\nu = \int_0^\infty f_s(\varepsilon)\varepsilon_a(\nu)\frac{d\nu}{\nu^4}$ is known as the overlap integral. The function $f_s(\nu)$ appearing under the integral sign represents the dependence of relative fluorescence intensity on wave number (emission spectrum), and the function ε_a represents the dependence of the extinction coefficient on wave number (absorption spectrum). If the relaxation time of the vibrational energy were long enough,

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

and the probability of energy transfer from the higher vibrational states were higher than from the lower ones, then it would be possible on the basis of Eqs (2) and (3) to explain the dependence of fluorescence depolarization on the frequency of the exciting light as due to a change in the value of the overlap integral (and, hence, in R_0). The value of R_0 in the region of the concentrations applied is, according to Eriksen [24], equal to 0.7 R_J, where R_J is the radius of the active sphere. Increased depolarization of fluorescence of anthracene and tetracene solutions (enlargement of the interaction sphere, R_J and R_0) occurs not only at higher frequencies of the exciting light, but also when the concentration is increased, which is not implied in Eqs (2) and (3). The explanation for the structure of the polarization spectrum would be similar. Förster's theory (Eq. (3)), however, concerns energy transfer for "very weak" intermolecular coupling, when the relaxation time of vibrational energy (*i.e.* the time during which a Boltzmann distribution becomes established) is so short compared with the time in which energy is transferred between the molecules that the probability of transfers from the higher vibrational levels is negligible. Thus, the value of R_0 introduced by Förster is independent of the wavelength of the exciting light and independent of the concentration of luminescing substance in the solution. "Very weak" intermolecular coupling appears in 5-aminoacridine solutions. In these a slight dependence of emission anisotropy on exciting light orequency is observed, which is due to the higher local temperatures of the luminescence centres. Equations (2) and (3) are inapplicable, however, in the case of molecules for which the probability of relaxation of vibrational energy, $W < 1/\tau$, and the magnitude of the dipole-dipole interaction is large enough for rapid energy transfer [17], [18].

A classification of the types of energy transfer according to the magnitude of interaction was first given by Franck and Teller [19], and later by Förster [17, 18, 19] and Simpson and Peterson [21]. The intermolecular coupling may be "strong" if the intermolecular interaction considerably exceeds the interaction between the vibrational levels of a single molecule. With this kind of coupling the energy transfer takes place in a time shorter than the oscillation period, the electron excitation energy is delocalized, and the emission and absorption spectra of the coupled system are distinctly different from the spectra of non-coupled molecules. "Strong" coupling occurs primarily in crystals or between molecules forming dimers. "Weak" coupling occurs in solution when the intermolecular interaction is strong enough for the time of excitation energy transfer to be comparable with the relaxation time of the vibrational energy of the excited electronic level. The resonance condition for energy transfer is much more rigorous in the case of "weak" coupling than for "strong" coupling; thus, an energy transfer can only take place between molecules with suitable vibrational energy. The transfer of energy occurs after several periods of oscillation, the excitation energy is more localized, and the rate of energy transfer between the oscillatory states v and v' of the excited and unexcited molecule is

$$n'_{vv'} = \frac{4|U|S^2_{vv'}}{h} \tag{4}$$

where U is the interaction energy, and $S_{vv'}$ is the Franck–Condon factor of the $v—v'$ intermolecular transition. The rate $n_{vv'}$ depends on the vibrational quantum numbers

of both molecules. It is possible, however, to calculate the mean values of the transfer rate by summing the individual values of $n_{vv'}$ multiplied by the appropriate population probabilities g_v^* and $g_{v'}$ of the level v of the excited molecule and level v' of the unexcited molecule, obtaining

$$n = \frac{4|U|}{h} \sum S_{vv'}^2 g_v^* g_{v'}. \tag{5}$$

For dipole-dipole interaction the energy U is inversely proportional to the cube of the distance between the molecules taking part in the energy transfer ($\sim R^{-3}$), hence, the rate n is much greater than the rate of energy transfer for "very weak" coupling ($n_s \sim R^{-6}$).

"Weak" coupling only occurs between molecules with a distinct vibrational structure ($W < 1/\tau$). The interaction between complex molecules, for which vibrational energy relaxes much more quickly than the duration of a transfer of energy between molecules, is of the "very weak" type. When the coupling is "very weak", the energy transfer primarily proceeds from the lowest vibrational levels after attainment of thermal equilibrium with the environment.

The dependence of emission anisotropy of fluorescence of the tetracene and anthracene solutions on wavelength of exciting light indicates the existence of energy transfers from the higher vibrational levels; hence, it points to the participation of the so-called "weak" intermolecular coupling. The participation of "weak" coupling is larger when the concentration is higher and the mean distances between the dye molecules are smaller. This explains well the increasing dependendce of emission anisotropy on exciting light wavelength with increasing concentration. The existence of two mechanism of excitation energy transfer causes the volume of the interaction sphere to depend both on the frequency of the exciting light and on the concentration of anthracene and tetracene molecules in the solution, because an increase of these factors enlarges the probability of energy transfers between "weakly" coupled molecules.

The rate of energy transfer in the case of "weak" interaction is proportional to the product of population probabilities of vibrational levels of the excited and unexcited molecules. Because of this, the greatest depolarization (the highest rate of transfer) is observed when fluorescence is excited by light of wavelengths for which absorption reaches a maximum value. The explanation proposed here of the observed dependence of fluorescence emission anisotropy on wavelength of exciting light and the associated "vibrational structure" of the absorption polarization spectrum may also apply to the polarization of the fluorescence of other aromatic hydrocarbons, mainly investigated by Zimmermann and Joop [2], [3], and Dörr and Gropper [25]. Depolarization of fluorescence light by energy transfer when there is "weak" coupling is more probable, the smaller the intramolecular interaction. Therefore, the concentration depolarization (with exciting light frequency $\nu = \nu_{0-0} + 3000\text{cm}^{-1}$) is greatest in the case of the tetracene solution.

The partial de-localization of energy which occurs when there is "weak" interaction leads to a change in the emission spectrum. A theoretical elaboration of the problem of spectral changes with the appearance of vibronic coupling which occurs between coupled molecules had been given by Witkowski and Moffit [22] and Fulton and Goutermann [10].

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

Due to the vibronic coupling there is a splitting and shifting of the vibrational levels which lead to a shift of the centre of gravity of the spectra of coupled molecules as compared with the spectra of monomers. Chandross and Ferguson [7] investigated the absorption and emission spectra of anthracene pseudodimers, finding strong broadening and a shift towards the long wavelengths in the emission spectrum.

The emission spectra of anthracene and tetracene solutions excited by light of a frequency corresponding to the 0—0 transition and one some 3000 cm^{-1} higher are shown

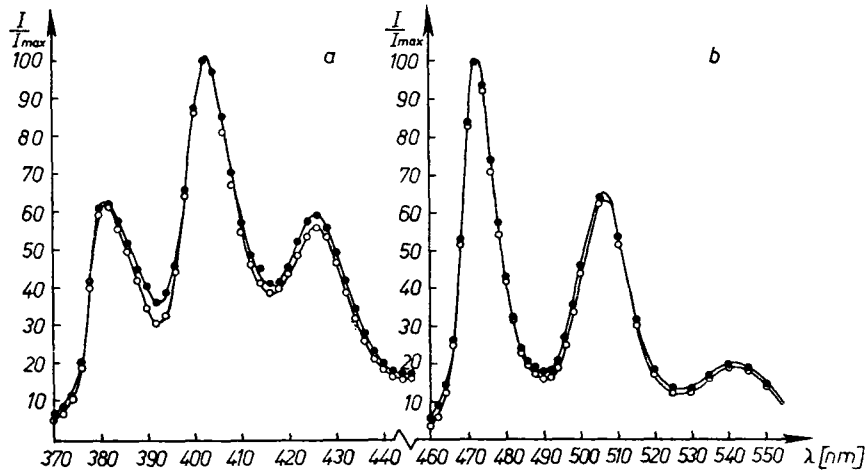

Fig. 5. Emission spectra *a*) solution of anthracene in glycerol, ● – exciting light wavelength 330 mμ, ○ – exciting light wavelength 382 mμ; *b*) solution of tetracene in paraffin oil, ● – exciting light wavelength 382 mμ, ○ – excitinglight wavelength 476 mμ

in Fig. 5. When excitating by light of the higher frequency, there is observed a certain broadening of the emission spectrum, and the minima between the three main vibrational maxima are not as deep. This effect is weak and in the range between 10^{-3} and 10^{-5} M is practically independ of concentration. Assuming that the emission spectrum broadening is caused by the overlapping of the fluorescence of non-coupled molecules and the fluorescence of molecules between which there is vibronic coupling[1], and analysing the

[1] Excitation of fluorescence with light of a frequency higher than ν_{0-0} probably leads to a rise in the local temperature of the luminescence center which may also result in a more diffuse emission spectrum. However, Bączyński (unpublished data), using different wavelengths of light to excite anthracene molecules which did not interact with each other, observed their quasi-linear emission spectrum (Szpolski effect) and did not observe this broadening. The problem of the dependence of emission spectra on local temperature of the centers was solved by Jabłoński [23]. He arrived at the conclusion that if the relaxation time of the local temperature of the luminescence centre is long enough and the temperature-dependence of both position and intensity distribution of the luminescence band is strong enough, one should expect a measurable dependence of emission spectrum on wavelength of exciting light. In a remark on his paper (in press) Jabłoński expresses his conviction that the emission spectrum is altered by makroscopic changes in temperature whereas during excitation of a dye molecule by light of a high frequency (compared with that corresponding to the 0—0 transition) only the temperature of the immediate environment of the luminescing molecule is altered.

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

emission spectrum from this point of view, it is possible to make a rough estimate of the intensity ratio I_1/I_0 (I_1 being the fluorescence intensity of molecules coupled "weakly" at the instant of emission, and I_0 the intensity of fluorescent light of non-coupled molecules) for the fluorescence of tetracene and anthracene. It is found to be equal to 0.1. An analysis of the emission spectra was made with the intensity of the exciting light known and with the assumption of identical absorption spectra and identical quantum yields of fluorescence for the non-coupled molecules and the molecules coupled "weakly" with each other. From the above estimate it follows, that about 10 per cent of the anthracene or tetracene molecules are "weakly" coupled at the instant of emission. Analysing in similar fashion the polarization spectra (for the same dye concentrations and for $\nu = \nu_{0-0} + +3000\ \mathrm{cm}^{-1}$) it was assumed that the fluorescent light emitted by mole- cules excited after a single transfer of energy is completely depolarized. The emission anisotropy of tetracene and anthracene solutions excited by frequences $\nu > \nu_{0-0}$ is smaller than that of the fluorescence excited by the frequency ν_{0-0}. This is so because there is an increase in the number of molecules excited by energy transfers from the higher vibrational levels. The ratio of the intensity of fluorescent light I_2 emitted by molecules excited by a transfer of energy from the higher vibrational levels to the intensity of fluorescent light I_0' emitted by molecules excited directly or by energy transfer between "very weakly" coupled molecules is

$$\frac{I_2}{I_0'} = \frac{\bar{r}_{0-0}}{\bar{r}} - 1. \tag{6}$$

Here, $\bar{r}_{0-0}$ is the emission anisotropy of fluorescence excited by light of frequency ν_{0-0}, and $\bar{r}$ is the corresponding value for frequency ν. The values of the ratio I_2/I_0' are *a*) 1.77 for a tetracene concentration of 3×10^{-4}M, and *b*) 0.73 for an anthracene concentration of 3×10^{-4}M. This means that when the tetracene solution is excited with light of a frequency $\nu = = \nu_{0-0} + 3000\ \mathrm{cm}^{-1}$, sixty four per cent of the molecules are excited by transfers of energy from the higher vibrational levels. The respective value for anthracene molecules is 43 per cent. The ratio I_1/I_0' is very large. No conclusions as regards the ratio of the relaxation time of vibrational energy to the lifetime in the excited state, can be drawn merely by knowing this ratio, because however, the transfer of energy from the higher vibrational levels when there is "weak" intermolecular coupling is much more probable than the transfer of energy from the lowest vibrational levels when there is "very weak" coupling.

Dye molecules coupled "weakly" with one another form a certain kind of complex. Their binding, however, is loose enough for them to maintain properties of monomers in the emission and absorption of light. As is already known, the emission and absorption spectra of tetracene and anthracene solutions are independent of dye concentration, and independently of the solution temperature there is observed an increase in the volume of the active sphere with increased dye concentration and exciting light frequency. It should be accepted, therefore, that "weak" coupling is not equivalent to a type of dimerization of tetracene or anthracene molecules in solution which allows for motion of molecules with respect to each other.

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

Summary

In investigations of the absorption polarization spectra of tetracene, anthracene and 5-aminoacridine solutions it was noticed that the emission anisotropy of fluorescence of these solutions depends on the wavelength of the exciting light. In the case of 5-aminoacridine this dependence has been explained by a rise in the local temperature of the luminescence centres. This, however, cannot be the cause of the remarkable depolarization of the fluorescence of the tetracene or anthracene solutions; moreover, the shape of the polarization spectrum here depends on the concentration of the fluorescing substance. To explain this it was proposed that apart from "very weak" coupling of the dipole-dipole type, for which the transfer of energy is primarily from the lowest vibrational level, there exists "weak" coupling in tetracene and anthracene molecules. Owing to the latter energy can migrate from the higher vibrational levels at a decidedly faster rate. The assumption of this mechanism of energy transfer explains the dependence of concentration depolarization on the wavelength of the exciting light and the observed "vibrational structure" of the polarization spectrum. Because of the participation of "weak" coupling between tetracene molecules or anthracene molecules the excitation energy is delocalized, and the spectrum of fluorescence emitted by coupled molecules should be strongly diffused and shifted towards longer wavelengths. A certain broadening of the emission spectra of tetracene and anthracene solutions is actually observed when fluorescence is excited with light of a frequency higher than ν_{0-0}. There is more "weak" coupling between tetracene molecules than between anthracene molecules, and practically none is observed between 5-aminoacridine molecules. At the same time, the vibrational structure is most distinct in the absorption and emission spectra of the tetracene solution, and weakest in the 5-aminoacridine solution. It is assumed, therefore that the probability of intramolecular interaction is sufficiently high in 5-aminoacridine molecules for a Boltzmann distribution of the vibrational energy to become established before there is an energy transfer. Thus, in this case an energy transfer from the higher vibrational states is barely probable and in practice proceeds from the lowest vibrational level.

I would like to express my heartfelt thanks to Docent Danuta Frąckowiak for her help and numerous discussions which aided me in interpreting the experimental results.

I am also grateful to Professor A. Jabłoński for many critical remarks on reading this paper.

REFERENCES

[1] R. Bauer, *Acta Phys. Polon.*, (in press 1969).
[2] H. Zimmermann, N. Joop, *Z. Elektrochem.*, **64,** 1215 (1960).
[3] H. Zimmermann, N. Joop, *Z. Elektrochem.*, **65,** 342 (1961).
[4] R. Bauer, H. Grudziński, A. Jabłoński, E. Lisicki, *Acta Phys. Polon.*, **33,** 803 (1968).
[5] J. B. Birks, J. H. Appleyard, R. Popoe, *Photochem. and Photobiol.*, **2,** 493 (1963).
[6] E. A. Chandross, *J. Chem. Phys.*, **43,** 4175 (1965).
[7] E. A. Chandross, F. Ferguson, E. G. McRae, *J. Chem. Phys.*, **45,** 3546 (1966).
[8] E. A. Chandross, J. Ferguson, *J. Chem. Phys.*, **45,** 3554 (1966).
[9] E. A. Chandross, J. Ferguson, *J. Chem. Phys.*, **45,** 3564 (1966).

[10] R. L. Fulton, M. Gouterman, *J. Chem. Phys.*, **35,** 1059 (1961); **40,** 2280 (1964).
[11] B. S. Nieporent, *Zh. Fiz. Chim.*, **24,** 1219 (1950).
[12] A. N. Terenin, *Izw. Akad. Nauk SSSR, Ser. Fiz.*, **9,** 305 (1945).
[13] B. S. Nieporent, *Izw. Akad. Nauk SSSR, Ser. Fiz.*, **15,** 533 (1951).
[14] A. Jabłoński, *Acta Phys. Polon.*, **14,** 295 (1955); *ibid.* **17,** 471 (1958).
[15] Th. Förster, *Ann. Phys.*, **2,** 55 (1948).
[16] Th. Förster, *Fluoreszenz Organischer Verbindungen*, Vandenhoek und Ruprecht, Göttingen 1951.
[17] Th. Förster, *Z. Elektrochem.*, **64,** 157 (1960).
[18] Th. Förster, *Faraday Soc. Disc.*, **27,** 7 (1959).
[19] J. Franck, E. Teller, *J. Chem. Phys.*, **6,** 861 (1958).
[20] Th. Förster, *Comprehensive Biochemistry*, Vol. 22, Elsevier, Amsterdam 1967.
[21] W. T. Simpson, D. L. Peterson, *J. Chem. Phys.*, **26,** 588 (1957).
[22] A. Witkowski, W. Moffit, *J. Chem. Phys.*, **33,** 872 (1960).
[23] A. Jabłoński, *Bull. Acad. Polon. Sci. Ser. Sci Math. Astron. Phys.*, **15,** 885 (1967) and a remark on this paper (in press).
[24] E. L. Eriksen, *Physica Norvegia*, **2,** 189 (1967).
[25] F. Dörr, H. Gropper, *Berichte Bunsenges. Phys. Chem.*, **67,** 46 (1963); *ibid.* **67,** 193 (1963).