Anhang I

Zur Lösung der Integrale werden folgende Gleichungen verwendet: $\mathrm{d}\tau = \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi\,\mathrm{d}\psi/8\,\pi^2$ ist das Volumelement des Orientierungskonfigurationsraums; die Integration erfolgt in den Grenzen $0 \leqq \vartheta \leqq \pi$; $0 \leqq \varphi \leqq 2\,\pi$; $0 \leqq \psi \leqq 2\,\pi$. l_i, l_l' und l_m'' sind die Richtungskosinus zwischen den Achsen ($i, l, m = 1, 2, 3$) eines molekülfesten kartesischen Koordinatensystems und den drei Achsen eines raumfesten kartesischen Koordinatensystems. Weiterhin ist

$$\delta_{ij} = \begin{cases} 1 & \text{für} \quad i = j\,, \\ 0 & \text{für} \quad i \neq j\,. \end{cases}$$

$$\int \mathrm{d}\tau = 1; \quad \int l_i\,\mathrm{d}\tau = 0; \quad \int l_i\,l_j\,\mathrm{d}\tau = \tfrac{1}{3}\,\delta_{ij}; \quad \int l_i\,l_j\,l_k\,\mathrm{d}\tau = \int l_i'\,l_j'\,l_k\,\mathrm{d}\tau = 0;$$

$$\int l_i\,l_j\,l_k\,l_l\,\mathrm{d}\tau = \tfrac{1}{15}\,(\delta_{ij}\,\delta_{kl} + \delta_{ik}\,\delta_{jl} + \delta_{jk}\,\delta_{il})\,; \quad \int l_i'\,l_j'\,l_k\,l_l\,\mathrm{d}\tau = \tfrac{1}{30}\,(4\,\delta_{ij}\,\delta_{kl} - \delta_{ik}\,\delta_{jl} - \delta_{il}\,\delta_{jk})\,;$$

$$\int l_i\,l_j\,l_k\,l_l\,l_m\,\mathrm{d}\tau = \int l_i\,l_j\,l_k\,l_l\,l_m'\,\mathrm{d}\tau = \int l_i'\,l_j'\,l_k\,l_l\,l_m\,\mathrm{d}\tau = \int l_i\,l_j\,l_k'\,l_l'\,l_m''\,\mathrm{d}\tau = 0;$$

$$\begin{aligned}\int l_i\,l_j\,l_k\,l_l\,l_m\,l_n\,\mathrm{d}\tau = \tfrac{1}{105}\big\{&\delta_{ij}(\delta_{kl}\,\delta_{mn} + \delta_{km}\,\delta_{ln} + \delta_{kn}\,\delta_{lm}) + \delta_{ik}(\delta_{jl}\,\delta_{mn} + \delta_{jn}\,\delta_{lm} + \delta_{jm}\,\delta_{ln}) \\ &+ \delta_{il}(\delta_{jk}\,\delta_{mn} + \delta_{jm}\,\delta_{kn} + \delta_{jn}\,\delta_{km}) + \delta_{im}(\delta_{jk}\,\delta_{ln} + \delta_{jl}\,\delta_{kn} + \delta_{jn}\,\delta_{kl}) + \delta_{in}(\delta_{jk}\,\delta_{lm} + \delta_{jl}\,\delta_{km} + \delta_{jm}\,\delta_{kl})\big\}\,;\end{aligned}$$

$$\begin{aligned}\int l_i'\,l_j'\,l_k\,l_l\,l_m\,l_n\,\mathrm{d}\tau = \tfrac{1}{210}\big\{&6\,\delta_{ij}(\delta_{kl}\,\delta_{mn} + \delta_{km}\,\delta_{ln} + \delta_{kn}\,\delta_{lm}) - \delta_{ik}(\delta_{jl}\,\delta_{mn} + \delta_{jn}\,\delta_{lm} + \delta_{jm}\,\delta_{ln}) \\ &- \delta_{il}(\delta_{jk}\,\delta_{mn} + \delta_{jm}\,\delta_{kn} + \delta_{jn}\,\delta_{km}) - \delta_{im}(\delta_{jk}\,\delta_{ln} + \delta_{jl}\,\delta_{kn} + \delta_{jn}\,\delta_{kl}) - \delta_{in}(\delta_{jk}\,\delta_{lm} + \delta_{jl}\,\delta_{km} + \delta_{jm}\,\delta_{kl})\big\}\,;\end{aligned}$$

$$\begin{aligned}\int l_i'\,l_j'\,l_k''\,l_l''\,l_m\,l_n\,\mathrm{d}\tau = \tfrac{1}{210}\big\{&16\,\delta_{ij}\,\delta_{kl}\,\delta_{mn} - 5\,[\delta_{ij}(\delta_{km}\,\delta_{nl} + \delta_{kn}\,\delta_{lm}) + \delta_{kl}(\delta_{im}\,\delta_{jn} + \delta_{in}\,\delta_{jm}) + \delta_{mn}(\delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk})] \\ &+ 2\,[\delta_{il}(\delta_{jn}\,\delta_{km} + \delta_{jm}\,\delta_{kn}) + \delta_{ik}(\delta_{jm}\,\delta_{ln} + \delta_{jn}\,\delta_{lm}) + \delta_{im}(\delta_{jl}\,\delta_{kn} + \delta_{jn}\,\delta_{kl}) + \delta_{in}(\delta_{jk}\,\delta_{lm} + \delta_{jm}\,\delta_{lk})]\big\}\,.\end{aligned}$$

Alle anderen Integrale mit Kombinationen von bis zu sieben l werden Null.

Polarization and Decay of Fluorescence of Solutions

By R. K. Bauer

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(Z. Naturforschg. **18 a**, 718—724 [1963]; eingegangen am 12. März 1963)

Measurements of the polarization and the mean decay periods $\tau^{\parallel}$ and $\tau\perp$ of fluorescence components $I^{\parallel}$ and $I\perp$ parallel and perpendicular to the electric vector of plane polarized exciting light were performed for uranin dye solutions in glycerol diluted with methyl alcohol, ethyl alcohol and water. From these measurements the volume v of the dye molecule together with its solvation shell and the limiting emission anisotropy r_0 for solutions of various viscosities were calculated. Both v and r_0 appeared to be in general not constant and dependent on the nature of the solvent. If, as observed in one case, v and r_0 are substantially constant, a good agreement between experimental values $\tau^{\parallel}/\tau$ and $\tau\perp/\tau$ and those evaluated from the equations of Jablonski is obtained (τ being the mean duration of the fluorescence emitted in all directions).

The fluorescence emitted by solutions is in general partly polarized. The degree of polarization depends on certain depolarization factors such as Brownian rotations and torsional vibrations of luminescent molecules. Jabłoński [1, 2] has shown that rotational depolarization influences the course of decay of particular fluorescent components. Assuming an exponential decrease of the emission anisotropy [3], (such a decrease follows from the theory of depolarization by thermal rotations of luminescent molecules given by Perrin [5–7], of Brownian movements of spherical particles), Jabłoński developed some

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[1] A. Jabłoński, Z. Phys. **95**, 53 [1935].

[2] A. Jabłoński, Z. Phys. **103**, 526 [1936].

[3] It is convenient to describe polarization in terms of emission anisotropy $\bar{r} = (I^{\parallel} - I\perp)/(I^{\parallel} + 2\,I\perp)$ instead of the familiar degree of polarization $\bar{p} = (I^{\parallel} - I\perp)/(I^{\parallel} + I\perp)$, $I^{\parallel}$ and $I\perp$ being the components of fluorescence parallel and perpendicular to the electric vector of the plane polarized exciting light (Jabłoński [4]).

[4] A. Jabłoński, Bull. Acad. Pol. Sci., Ser. Math. Astr. Phys. **8**, 258, 655 [1960].

[5] F. Perrin, Ann. Phys., Paris **12**, 169 [1929].

[6] F. Perrin, J. de Phys. **5**, 497 [1934].

[7] F. Perrin, Acta Phys. Polon. **5**, 335 [1936].

equations for the course and the mean duration of various components of luminescence decay, particularly for the components perpendicular and parallel to the electric vector of the plane polarized exciting light. Jabłoński 's theory was checked experimentally by Szymanowski [8] and Kessel [9], but the agreement appeared to be rather qualitative. The aim of this paper is to find the reasons for the disagreement between theory and previous experimental results and to gain, by more accurate measurements of polarization and mean decay times, new informations concerning the properties of fluorescent solutions.

Theory

Let an isotropic fluorescent solution be excited with plane polarized primary light. Providing that the decay of total (emitted in all directions) fluorescence intensity I follows the simple exponential law [10]

$$I(t)=I_0 \exp(-t/\tau). \qquad (1)$$

Jabłoński [11] gets for the parallel and perpendicular components of light intensity

$$I^{\parallel}(t)=(I_0/3)\,[1+2\,r(t)]\exp(-t/\tau),$$
$$I^{\perp}(t)=(I_0/3)\,[1-r(t)]\exp(-t/\tau), \qquad (2)$$

and for the mean duration of $I(t)$ the following relation:

$$\tau=\frac{\tau^{\parallel}(1+2\,\bar{r})+2\,\tau^{\perp}(1-\bar{r})}{3}, \qquad (3)$$

$r(t)$ being the decrease function of emission anisotropy, $\bar{r}$ the mean value of emission anisotropy, and $\tau^{\parallel}$, $\tau^{\perp}$ the mean durations of the parallel and perpendicular components of fluorescence. It follows from equations (2) that the decay of the components depends on the course of $r(t)$ and in general does not follow the simple exponential law. Equation (3) is independent of the explicit form of $r(t)$ and allows us to evaluate τ, if the values $\tau^{\parallel}$, $\tau^{\perp}$ and $\bar{r}$ are known. It follows from the above mentioned theory of Perrin that, provided the rotations of luminescent molecules are governed by laws of Brownian rotations of spherical particles,

$$r(t)=r_0 \exp(-\varphi\,t), \qquad (4)$$

where r_0 denotes the value of $r(t)$ for $t=0$ and $\varphi=k\,T/v\,\eta$, v being the volume of the luminescent molecule together with its solvation shell, η the coefficient of viscosity, and $k\,T$ having the usual meaning.

From equations (1), (2) and (4) one obtains

$$\bar{r}=r_0/(1+\varphi\,\tau). \qquad (5)$$

Equations (2) and (4) lead to

$$I^{\parallel}(t)=(I_0/3)\,[1+2\,r_0\exp(-\varphi\,t)]\exp(-t/\tau),$$
$$I^{\perp}(t)=(I_0/3)\,[1-\;r_0\exp(-\varphi\,t)]\exp(-t/\tau). \qquad (6)$$

The mean durations of $I^{\parallel}(t)$ and $I^{\perp}(t)$ resulting from equation (6) by use of (5) are

$$\tau^{\parallel}=\tau\;(r_0+2\,\bar{r}^2)/(r_0+2\,r_0\,\bar{r}), \qquad (7)$$

$$\tau^{\perp}=\tau\;(r_0-\bar{r}^2)/(r_0-r_0\,\bar{r}), \qquad (8)$$

and hence (Jabłoński [11])

$$r_0=\frac{2\,\bar{r}^2\,\tau}{\tau^{\parallel}(1+2\,\bar{r})-\tau}=\frac{\bar{r}^2\,\tau}{\tau-\tau^{\perp}(1-\bar{r})}. \qquad (9)$$

All the quantities appearing on the right side of equation (9) can be measured directly. It becomes thus possible to obtain values of r_0 for any solution without extrapolation of $\bar{r}$ [eq. (5)] to $\varphi\to 0$ ($\eta\to\infty$). Moreover, if $\bar{r}$ is obtained from measurements of polarization of fluorescence, and if then τ and r_0 determined by fluorometric measurements, φ can be calculated by means of eq. (5). Since $\varphi=k\,T/v\,\eta$, also v the volume of molecule with its solvation shell, can be determined for each solution.

Measurements of the mean value of the emission anisotropy and of the mean duration of the parallel and perpendicular components of the fluorescent ligth in a wide range of viscosities make it possible to check the theory of Jabłoński.

Experimental

A) Purification of glycerol and measurements of the viscosity coefficient

As a solvent for fluorescent dyes glycerol was chosen because of its high coefficient of viscosity which may be reduced by various diluents. Since the coefficient of viscosity of glycerol is dependent on the water content it was necessary to purify the glycerol to free it from water. Commercial glycerol with 8% waser pas purified, by a method described previously by Kessel [9], by double distillation in vacuum (10^{-4} mm Hg) at a tem-

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[8] W. Szymanowski, Z. Phys. **95**, 466 [1935].

[9] W. Kessel, Z. Phys. **103**, 125 [1936].

[10] Equation (1) is correct only if the luminescence energy level is directly excited through light absorption, i. e. without the intermediary of other levels.

[11] A. Jabłoński, Z. Naturforschg. **16 a**, 1 [1961].

perature of 165 °C. Measurements of the viscosity and the density of the distilled glycerol showed that the water content was less than 0.2%. The dye was uranin and its concentration in all solutions was 10^{-5} g/g. Dyed glycerol was mixed with various amounts of dyed water, ethyl alcohol and methyl alcohol. Several solutions of uranin with various viscosity coefficients were made. The viscosity coefficient was measured at a temperature of 20 °C with a precision HOEPPLER viscositymeter. The temperature was stabilized to ±0.1 °C. The time of fall of the ball was measured with an accuracy of 0.1 sec. The density of the solutions was found by a pycnometer with an accuracy of 0.001 g/cm³. The accuracy of the viscosity coefficient measurements was 1%.

B) Fluorometer and polarimeter

To measure the mean duration of fluorescence a fluorometer, based on the principle of measuring the "phase difference" between the modulated exciting light and the fluorescence, was built (BAUER and ROZWADOWSKI [12]). In this fluorometer an ultrasonic light modulator utilizing the effect of birefrigence produced in fused quartz by ultrasonic waves was employed. Such a modulator is much more luminous than those so far used in fluorometers. The fluorometer allows to measure the mean duration of fluorescence with errors not greater than $5 \cdot 10^{-11}$ sec. The emission anisotropy was measured with a photoelectric polarimeter similar to that of WILLE [13]. To increase the sensitivity of the WILLE polarimeter a BILLINGS light modulator and a "lock-in-amplifier" were used (BAUER and ROZWADOWSKI [14]). In this way the accuracy $5 \cdot 10^{-5}$ of the measurements of emission anisotropy was obtained even when the photocurrent was as low as $6 \cdot 10^{-13}$ A.

The parallel and plane polarized exciting light beam from a 50 W bulb passed an optical system and a Zeiss light filter BG 12/2. The emission was observed through a Zeiss light filter OG 1/1 (a complementary filter to BG 12/2). The desired fluorescence component was chosen by turning a Zeiss polaroid "Bernotar".

As JABLOŃSKI [1, 2] had shown, there exists a component decaying according to the simple exponential law with a decay time equal to that of the decay of the total emitted light. With polarized exciting light this decay time is that of the fluorescence component making an angle equal ~55° with $I^{\parallel}$ ($\tau_{55^\circ} = \tau$).

Results

A) Fluorescence of uranin in glycerol diluted with methyl alcohol

Fourteen different solutions of uranin in glycerol diluted with methyl alcohol were prepared. The emission anisotropy of each of them was measured

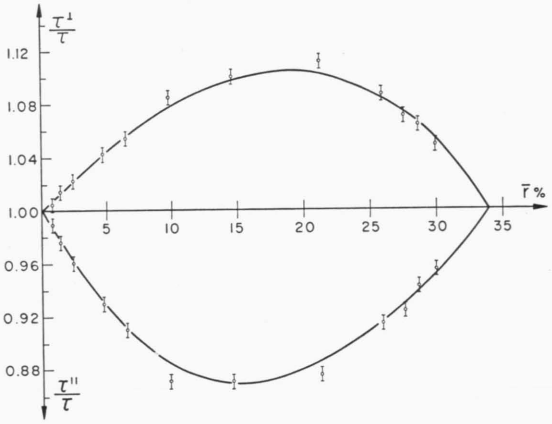

Fig. 1. Experimental and theoretical (solid line) values of $\tau^{\parallel}/\tau$ and $\tau\perp/\tau$ versus $\bar{r}$ for the fluorescence of uranin solutions in glycerol diluted with methyl alcohol.

Nr.	% CH_2HO	η	$\bar{r}$	$\tau\parallel$	$\tau\perp$	τ_{55}	$\tau\parallel/\tau_{55}$	$\tau\perp/\tau_{55}$
1	0	1397	0.2998	4.46	4.9	4.67	0.955	1.049
2	10	567.3	0.2875	4.40	4.97	4.67	0.942	1.064
3	15	355.3	0.2761	4.35	5.0	4.71	0.924	1.072
4	20	213	0.2592	4.26	5.07	4.66	0.914	1.087
5	30	83.7	0.2137	4.13	5.24	4.71	0.876	1.112
6	40	29	0.1461	4.26	5.38	4.89	0.871	1.100
7	50	13.3	0.985	4.28	5.33	4.91	0.871	1.085
8	60	6.65	0.653	4.41	5.12	4.85	0.909	1.055
9	70	4.15	0.482	4.48	5.03	4.82	0.929	1.043
10	80	1.95	0.248	4.56	4.86	4.75	0.960	1.023
11	85	1.42	0.203	4.59	4.81	4.73	0.970	1.016
12	90	1.09	0.154	4.60	4.78	4.71	0.976	1.014
13	95	0.796	0.117	4.62	4.73	4.69	0.985	1.008
14	100	0.632	0.0895	4.64	4.71	4.69	0.989	1.004

Table 1. Decay periods in 10^{-9} sec., emission anisotropy and viscosity coefficient in centipoises for the fluorescence of uranin solutions in glycerol diluted with methyl alcohol.

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[12] R. BAUER and M. ROZWADOWSKI, Bull. Acad. Pol. Sci., Ser. Math. Astr. Phys. **8**, 655 [1960].

[13] A. WILLE, Optik **9**, 84 [1954].

[14] R. BAUER and M. ROZWADOWSKI, Optik **18**, 37 [1961].

three times; the average results are given in Table 1. The decay periods $\tau^{\parallel}$, $\tau^{\perp}$ and τ_{55} of each solution were also measured three times and are also given in Table 1. The accuracy of the emission anisotropy measurements is 10^{-3} and that of decay periods $5 \cdot 10^{-11}$ sec. Fig. 1 shows the experimentally observed ratios $\tau^{\parallel}/\tau$ and $\tau^{\perp}/\tau$ plotted against $\bar{r}$. The solid curves are calculated from equations (7) and (8) for $r_0 = 0.34$. The agreement between the observations and theory is very good. Values of τ calculated from equation (3) are compared with those given by the experiment and satisfactory agreement is obtained. Thus a quantitative experimental confirmation of eqs. (3), (7) and (8) is gained.

It has been found that values of r_0 calculated by means of equation (9) can be obtained only for $\bar{r}$ values larger than 0.14 (leading to $r_0 = 0.34$). For values of $\bar{r}$ less than 0.14 the denominator of equation (9) becomes smaller than the accuracy of the measurements of τ, and the error in the calculated value of r_0 becomes then greater than r_0 itself.

B) Fluorescence of uranin in glycerol diluted with ethyl alcohol

Eleven different solutions of uranin in glycerol diluted with ethyl alcohol were prepared. The same measurements as in section A were performed, with results which do not differ qualitatively from those de- those given by equations (7) and (8), calculated using $r_0 = 0.34$. It can be seen that a serious discrepancy exists between the above eqs. and experi- scribed in section A. The results are given in Table 2 and plotted in Fig. 2. The solid curves in Fig. 2 are experimental data, we find the variation shown in Table 3 and plotted in Fig. 3. We see that r_0 de- ment. An improved fit is obtained for $r_0 = 0.32$ as shown by the dotted curves, but even then a serious discrepancy remains for values of $\bar{r} < 0.2$. The only way in which this discrepancy may be removed is to

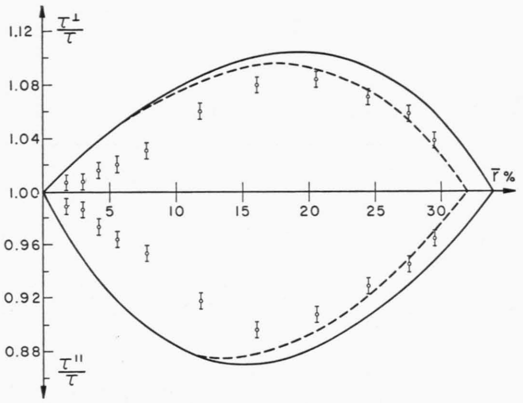

Fig. 2. Experimental and theoretical values of $\tau^{\parallel}/\tau$ and $\tau\perp/\tau$ versus $\bar{r}$ for the fluorescence of uranin solutions in glycerol diluted with ethyl alcohol. The solid curve is calculated for $r_0 = 0.34$, the dotted curve for $r_0 = 0.32$.

assume that r_0 ist not constant, at least in this case. Indeed, if we calculate r_0 from equation (9) and the creases with increasing concentration of ethyl alcohol in glycerol and that the decrease is very rapid between 50 and 70 mol/mol% of ethyl alcohol. Once r_0 is determined it is possible to calculate the depolarization probability $\varphi = k\,T/v\,\eta$. From this and the measured values the volume v of the luminescent molecule together with its solvation shell was calculated (Table 3 and Fig. 3). Surprisingly, the volume v increases almost exponentially with the alcohol concentration. Although, as shown in Fig. 3 the uncertainty in r_0 and v is rather large when the

Nr.	% C_2H_5OH	η	$\bar{r}$	$\tau\parallel$	$\tau\perp$	τ_{55}	$\tau\parallel/\tau_{55}$	$\tau\perp/\tau_{55}$
1	0	1295	0.2947	4.41	4.80	4.57	0.965	1.039
2	10	140.8	0.2758	4.30	4.82	4.55	0.945	1.059
3	20	58.95	0.2443	4.20	4.84	4.52	0.929	1.071
4	30	26.06	0.2050	4.09	4.88	4.51	0.907	1.082
5	40	13.20	0.1611	4.03	4.85	4.49	0.987	1.080
6	50	6.764	0.1182	4.11	4.75	4.48	0.917	1.060
7	60	4.146	0.0774	4.24	4.61	4.47	0.949	1.031
8	70	2.732	0.0549	4.30	4.55	4.46	0.964	1.020
9	80	2.002	0.04202	4.32	4.51	4.44	0.973	1.016
10	90	1.495	0.02988	4.37	4.46	4.43	0.986	1.007
11	100	1.036	0.01782	4.37	4.45	4.42	0.989	1.007

Table 2. Decay periods in 10^{-9} sec., emission anisotropy and viscosity coefficient in centipoises for the fluorescence of uranin solutions in glycerol diluted with ethyl alcohol.

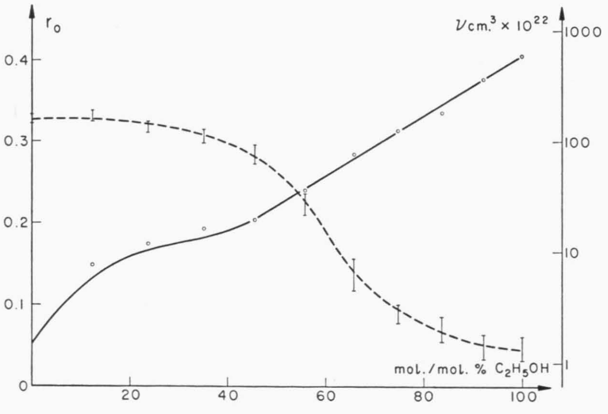

Fig. 3. Calculated values of r_0 and v for the fluorescence of uranin solutions in glycerol diluted with ethyl alcohol as functions of the ethyl alcohol content in glycerol.

Nr.	Vol. % C_2H_5OH	Mol/mol % C_2H_5OH	r_0	$\varphi \cdot 10^7$	$v \cdot 10^{-22}$ cm^3
1	0	0	0.32	2.2	1.3
2	10	12.2	0.32	4.1	7.0
3	20	23.8	0.31	6.1	11.2
4	30	34.9	0.30	10.4	15.0
5	40	45.5	0.28	16.3	18.4
6	50	55.6	0.21	17.5	33.8
7	60	65.2	0.12	13.5	72.2
8	70	74.5	0.08	12.3	118.0
9	80	83.3	0.06	12.8	162.0
10	90	91.8	0.04	7.6	338.0
11	100	100	0.03	7.1	540.0

Table 3. Calculated values of r_0, v, and φ for the fluorescence of uranin solutions in glycerol diluted with ethyl alcohol.

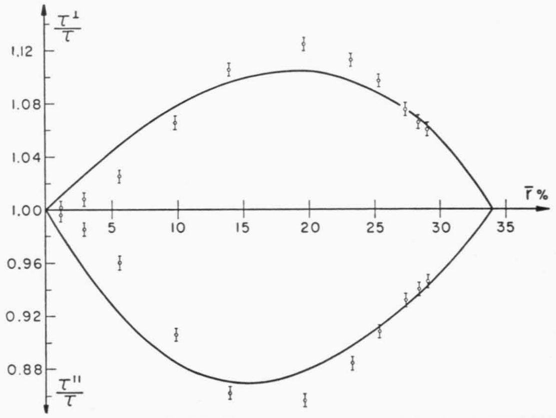

Fig. 4. Experimental and theoretical values of $\tau^{\parallel}/\tau$ and $\tau\perp/\tau$ versus $\bar{r}$ for the fluorescence of uranin solution in glycerol diluted with water. The solid curve is calculated for $r_0 = 0.34$.

ethyl alcohol content in the solution is great, it is almost certain that the observed behaviour of v is anomalous. The reason for this anomaly may be the 5% water content in commercial ethyl alcohol. To prove this supposition similar experiments were carried out with uranin solutions in glycerol with water.

C) *Fluorescence of uranin in glycerol diluted with water*

Similar measurements as in Sections A und B were performed with uranin solutions in glycerol diluted with water. The results of measurements of emission anisotropy and mean decay periods (Table 4) are qualitatively similar to the previous ones and to results obtained by Kessel [9]. There is, however, as shown in Fig. 4, a greater difference between the theoretical and experimental values of $\tau^{\parallel}/\tau$ and $\tau\perp/\tau$ than that observed for fluorescence of uranin in glycerol with ethyl alcohol. The calculated values of r_0, φ and v are tabulated in Table 5 and plotted in Fig. 5 as a function of water content in mol/mol% in glycerol. The values of r_0 decrease very abruptly and those for v increase very markedly when the water content reaches about 85 mol/mol%.

Nr.	% H_2O	η	$\bar{r}$	$\tau\parallel$	$\tau\perp$	τ_{55}	$\tau\parallel/\tau_{55}$	$\tau\perp/\tau_{55}$
1	0	1215	0.290	4.41	4.94	4.66	0.946	1.060
2	10	453.5	0.284	4.38	4.97	4.66	0.940	1.067
3	20	226.3	0.274	4.34	5.01	4.66	0.931	1.075
4	30	101.1	0.254	4.23	5.11	4.66	0.908	1.097
5	40	59.5	0.232	4.13	5.20	4.67	0.884	1.113
6	50	32.4	0.196	4.05	5.32	4.73	0.865	1.125
7	60	18.1	0.139	4.20	5.38	4.87	0.862	1.105
8	70	10.1	0.098	4.39	5.17	4.85	0.905	1.066
9	80	5.21	0.056	4.62	4.93	4.81	0.960	1.025
10	90	2.62	0.029	4.71	4.82	4.78	0.985	1.008
11	100	1.48	0.0116	4.75	4.78	4.77	0.996	1.002

Table 4. Decay periods in 10^{-9} sec., emission anisotropy and viscosity coefficient in centipoises for the fluorescence of uranin solutions in glycerol diluted with water.

Nr.	Vol. % H_2O	Mol/mol % H_2O	r_0	$\varphi \cdot 10^7$	$v \cdot 10^{-22}$ cm^3
1	0	0	0.34	3.7	0.9
2	10	31.2	0.34	4.3	2.1
3	20	50.5	0.34	5.2	3.4
4	30	63.5	0.35	8.2	4.9
5	40	73.1	0.36	12.4	5.5
6	50	80.5	0.39	22.0	5.7
7	60	85.9	0.38	36.2	6.1
8	70	90.6	0.24	29.4	13.0
9	80	94.4	0.09	14.1	60.0
10	90	97.6	0.04	7.9	200.0
11	100	100	0.014	4.3	640.0

Table 5. Calculated values of r_0, v, and φ for the fluorescence of uranin solutions in glycerol diluted with water.

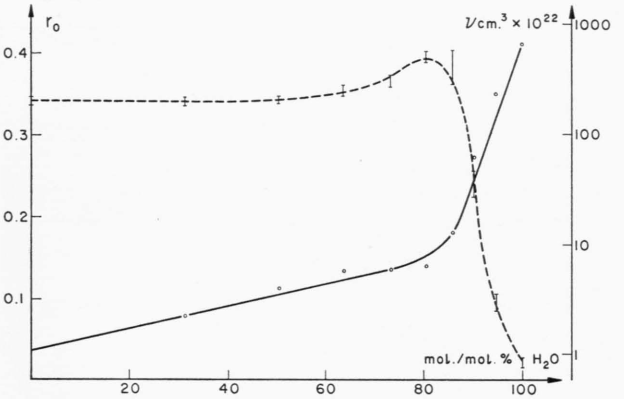

Fig. 5. Calculated values of r_0 and v for the fluorescence of uranin in glycerol diluted with water as functions of water content in glycerol.

Discussion

It follows from above experimental results that r_0 is constant if uranin in glycerol is diluted with methyl alcohol but varies if the diluent is ethyl alcohol or water and the amount of the diluent is varied. In fact in the case of uranin in glycerol diluted with ethyl alcohol r_0 varies from 0.32 to 0.03 as the relative amount of ethyl alcohol in the solvent varies from zero to 100%. This corresponds to a variation of the diameter of the uranin molecule together with its solvation shell from 6.4 Å to 48 Å. A similar behaviour of r_0 has been observed previously (Bauer und Szczurek [15]) in tests of the theory of Perrin.

Equation (5) can be written in the form

$$1/r = (1 + k\,T\,\tau/v\,\eta)\;r_0^{-1} \qquad (10)$$

which is equivalent to a relation given by Perrin in his theory of depolarization by thermal rotations. If we assume, with Perrin, that τ, v and r_0 are constants independent of T and the relative concentration of the constituents of the solvent, then $1/\bar{r}$ must be a linear function of $1/\eta$. Perrin goes further and assumes that r_0 is a constant characteristic of the dye molecule only and is therefore the same for all diluents. In the previous investigations (Bauer and Szczurek [15]) a linear relation between $1/\bar{r}$ and $1/\eta$ is indeed found for uranin in glycerol diluted with methyl alcohol, while a serious departure from linearity is observed when the diluent is either ethyl alcohol or water. Jabłoński [4, 11, 16] has suggested that, apart from Brownian rotations of luminescent molecules and from transfer of excitation energy between such molecules, depolarization is also caused by their torsional vibrations. The rotations of the dye molecules influence the course of $r(t)$, the torsional vibrations, however, only reduce r_0, the limiting value of $r(t)$. Since the torsional vibrations depend on the nature of the solvation shell of the dye molecule, it follows that r_0 is not a molecular constant but is dependent on the temperature and on the nature of the solvent.

The question remains as to why r_0 and v vary over such a wide range when the diluent is either ethyl alcohol or water, but are constant when the diluent is methyl alcohol. Water molecules are almost totally absent in the methyl alcohol solutions but present in the commercial ethyl alcohol used here and, of course, in water solutions, so, it is probable that the above mentioned different behaviour of r_0 and v may be ascribed by the large dipole moment of the water molecules forming the solvation shell. Experiments to test this point should involve waterless ethyl alcohol and methyl alcohol containing water. Reports given in a previous paper (Bauer and Szczurek [15]) show that in the case of uranin in glycerol + waterless ethyl alcohol, the relation between $1/\bar{r}$ and $1/\eta$ is indeed linear. In the meantime, however, it may be of interest to speculate as to how water molecules may give rise to the observed behaviour of r_0 and v. Water dissolves the alcohols much better than it does uranin and, hence, water molecules may form a solvation shell around alcohol molecules and these clusters in turn form a

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[15] R. Bauer and T. Szczurek, Acta Phys. Polon. **22**, 29 [1962].

[16] A. Jabłoński, Proc. Int. Conf. on Luminescence, New York, October 1961; in press.

solvation envelope around the dye molecules. Because of their large dipole moment, the water molecules forming the solvation shell may exist in long chains and thus form envelopes of large diameter. The structure of the solvation envelope has a direct effect on the torsional vibrations (on the average value of the torque moment acting on a molecule) of luminescent molecules and hence on r_0.

It should be emphasized that the equations from which r_0 and v are obtained, are based on the assumptions of PERRIN. The present results are therefore wholly correct only if (a) the dye molecule with its solvation shell is spherical in shape, (b) the decay of the luminescence is exponential and (c) the decrease of the emission anisotropy is exponential. It is known that the assumptions (a) and (c) are only approximately valid; nevertheless we feel that the behaviour of r_0 and v presented here represents, at least qualitatively, the true picture.

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Das Fluoreszenzspektrum von Naphthalin-Kristallen zwischen 2° und 100°K

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The fluorescence spectrum of naphthalene crystals has been investigated between 2 and 100 °K with a spectral resolving power of nearly 10^4. The spectrum of naphthalene purified by extreme zone refining contains almost exclusively the bands of the intrinsic fluorescence starting at 31 476 cm^{-1}. This spectrum is analyzed completely in terms of the well known RAMAN freqencies of the naphthalene molecule. — The temperature dependence of bandwidth, bandshape, quantum yield and absorption edge is determined by the coupling with the thermal lattice vibrations. The essential properties are well described by the exciton theories.

1. Aufgabenstellung

Obwohl es schon eine große Zahl von Untersuchungen der Fluoreszenzspektren organischer Molekülkristalle gibt, sind gerade einige ihrer wichtigsten Eigenschaften noch nicht geklärt. Besonders zwei Fragen stehen im Mittelpunkt des Interesses: Wie sieht das Spektrum der Eigenfluoreszenz eines Kristalls aus, und: Wie erfolgt die Energieübertragung und die sensibilisierte Fluoreszenz von Gastmolekülen in Molekülkristallen?

Beide Fragen hängen eng miteinander zusammen, und man wird sie nur gemeinsam beantworten können. Es zeigt sich, daß auch hier wie so oft in der Festkörperphysik das Problem der Reinheit und der Reinigung entscheidend ist.

Naphthalin-Kristalle erscheinen zum Studium solcher Fragen sehr gut geeignet, weil ihr Fluoreszenzspektrum bei tiefer Temperatur aus scharfen Linien besteht und deshalb gut zu analysieren ist. — Im folgenden wird über Messungen an Fluoreszenzspektren von Naphthalin-Kristallen verschiedener Reinheit berichtet. Dabei gelingt zum ersten Male eine genaue Analyse der Eigenfluoreszenz. Außerdem wird der Einfluß der sensibilisierten Fluoreszenz von Verunreinigungen auf die Kristall-Fluoreszenzspektren hier besonders deutlich.

Als wichtiges methodisches Hilfsmittel erweist sich die Messung der Temperaturabhängigkeit der Spektren von Kristallen verschiedener Reinheit zwischen 2 und ca. 100 °K mit einem Auflösungsvermögen von annähernd 10^4.

2. Übersicht über die Literatur

Die Literatur über Fluoreszenz- und Absorptionsspektren von Naphthalinkristallen bis 1957 ist in [1] zusammengestellt; weitere zusammenfassende Darstellungen in [2–4]. Seitdem kamen einige wichtige Arbeiten hinzu. Das Absorptionsspektrum wurde

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[2] A. S. DAVYDOV, Theory of Molecular Excitons, translated by M. KASHA and M. OPPENHEIMER, McGraw-Hill Co., New York 1962.

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[4] R. M. HOCHSTRASSER, Rev. Mod. Phys. **34**, 531 [1962].