

## FURTHER INVESTIGATIONS ON THE UPPER LIMIT OF FLUORESCENCE YIELD

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According to a formula given in an earlier paper of the authors, the frequency at which the drop in fluorescence yield begins is completely determined by the position and shape of the emission spectrum. The validity of the formula obtained by a thermodynamical method is confirmed by results of recent investigations on several solutions.

1. In a former paper [1] the authors investigated the changes in entropy occurring in fluorescence processes and came to the result that in the case of very small exciting intensities the energy yield  $\eta$  of fluorescence satisfies the inequality

$$\eta \cong \sqrt{\frac{\Delta v_f}{\Delta v} \frac{v_0^2}{v^2}} e^{h(v-v_0)/2kT} (\cong I(v)). \quad (1)$$

Here  $v$  is the frequency of excitation,  $\Delta v_f = 1/f(v_0)$  is approximately the half-width of the normalized energy spectrum  $f(v)$  of fluorescence,  $\Delta v$  denotes the half-width of the exciting band ( $\Delta v \ll \Delta v_f$ ),  $k$  the Boltzmann constant,  $T$  the absolute temperature of the solution; the frequency  $v_0$  is determined by the equation

$$v_0^{-4} \exp(hv_0/kT) f(v_0) = \int_0^{\infty} v'^{-4} \exp(hv'/kT) / [f(v')]^2 dv'. \quad (2)$$

In deriving and applying inequality (1), besides purely mathematical simplifications and neglects, the following assumptions of physical character were made: *a*) A very small quantity of the solution is in contact with a body of great dimensions and good thermal conductivity; its surface is supposed to be black and the part of the exciting energy which is converted into heat is radiated by this body. *b*) The spectral intensity of the exciting light as well as that of the fluorescence (positive and negative) is small compared to the spectral intensity of the black body radiation of temperature  $T$  and it tends to zero in limit. *c*) It is supposed that the inequality (1) obtained for the limiting case remains valid for great intensities of excitation and fluorescence, as long as the intensity of fluorescence is proportional to that of the excitation.

As it is to be seen from inequality (1), the drop in yield within the anti-Stokes region begins at frequency  $v_0$  and according to (2), this frequency is completely determined by the shape and spectral position of the fluorescence spectrum at a given temperature  $T$ .

Table I.

No	Fluorescent compound and concentration (in mole/liter)	Solvent	(in $10^{12} \text{ s}^{-1}$ )	$\lambda_c$ (in $\text{m}\mu$ )	$\nu_0$ (in $10^{12} \text{ s}^{-1}$ )
1	Esculin $1 \cdot 10^{-4}$	Ethanol 90%, Water 10% $5 \cdot 10^{-3}$ mole/liter NaOH	712	421	685
2	Al-Morin $1 \cdot 10^{-3}$	Ethanol; 2% acetic acid	652	460	614
3	Trypaflavine $1 \cdot 10^{-4}$	Ethanol; $2 \cdot 10^{-3}$ mole/liter HCl	634	473	618
4	Auroposphin $1 \cdot 10^{-4}$	Ethanol 90%, Glycerol 10% $3 \cdot 10^{-3}$ mole/liter HCl	626	479	614
5	Flavophosphin $1 \cdot 10^{-4}$	Ethanol 90%, Glycerol 10% $3 \cdot 10^{-3}$ mole/liter HCl	620	484	611
6	Rhoduline orange $1 \cdot 10^{-3}$	Ethanol; $5 \cdot 10^{-3}$ mole/liter HCl	595	504	580
7	Fluorescein $1 \cdot 10^{-4}$	Ethanol; 1% NaOH	590	509	579
8	Eosin $4 \cdot 10^{-4}$	Ethanol 80%, Water 20% $5 \cdot 10^{-3}$ mole/liter NaOH	565	531	556
9	Rose bengale $1 \cdot 10^{-3}$	Ethanol; $5 \cdot 10^{-3}$ mole/liter NaOH	537	559	531
10	Rhodamine B $1 \cdot 10^{-3}$	Ethanol; $3 \cdot 10^{-3}$ mole/liter HCl	531	565	523

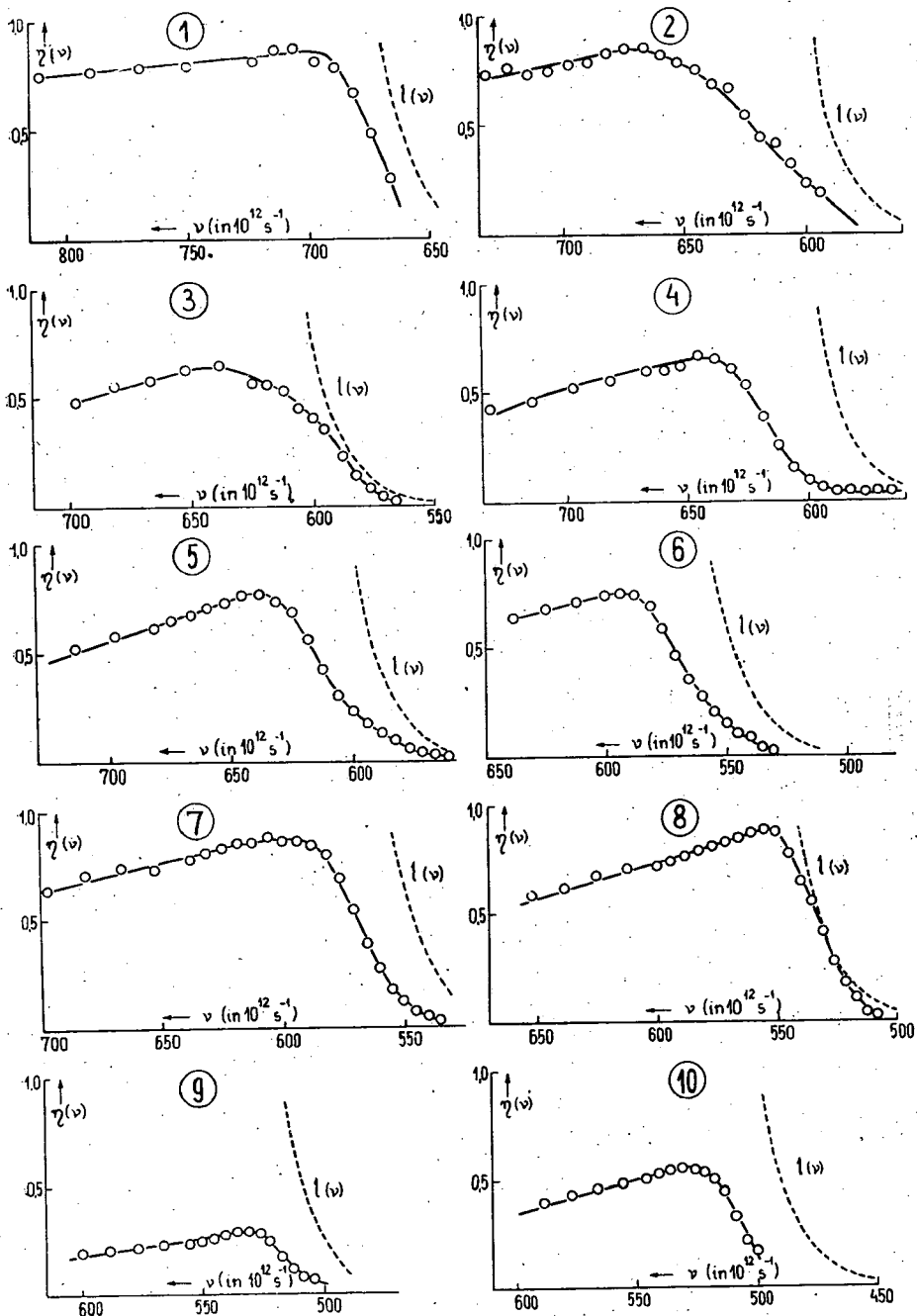


Fig. 1

If the emission spectrum of the solution can be described [2] by

$$f(\nu) = N\nu^4 \exp(-h\nu/2kT) \operatorname{sech} [a(\nu - \nu_0)], \quad (3)$$

the integrand in Eq. (2) is equal to  $N^2\nu'^4 \operatorname{sech}^2 [a(\nu' - \nu_0)]$ ; thus  $\nu_0$ , giving the spectral region of the drop in fluorescence yield, is led back to  $a$  and  $\nu_0$  by Eq. (2) because the normalization coefficient  $N$  is completely determined by the parameter  $a$  and the frequency  $\nu_0$  of pure electronic transition at a given temperature.

2. In order to check the validity of inequality (1), the energy yields  $\eta$ , shown in Fig. 1 by circles and solid lines, have been determined with the experimental method described in [3] for the solutions given in Table I. The limiting functions  $l(\nu)$ , calculated from the experimental fluorescence spectra and equal to the expression on the right of inequality (1), are shown by dotted lines in Fig. 1. In calculating  $l(\nu)$ , the value of  $\sqrt{\Delta\nu_f}/\Delta\nu$  has been taken equal to 3 according to the experimental conditions. It can be seen that the limitation given by inequality (1) is fulfilled for the solutions investigated, emitting fluorescence in rather different spectral regions of the visible spectrum.

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#### References

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### О ВЫСШЕЙ ГРАНИЦЕ ВЫХОДА ФЛЮОРЕСЦИРУЮЩИХ РАСТВОРОВ

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То частота, у которой начинается падение выхода флуоресценции, по заданной формуле в одной предыдущей работе авторов, с положением и формой спектра флуоресценции практически полностью определена. По термодинамическим путем полученную формулу, результаты новых экспериментальных исследований в случае многих растворов, подтверждают.