FURTHER DATA ON THE DETERMINATION OF FLUORESCENCE DECAY TIME ON THE BASE OF NEPORENT'S MODIFIED RELATION

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STEPANOV's modified relation [1—2] has been used chiefly to study the relation between the luminescence spectrum and the yield function [3—4], and calculations about the *decay time* can only be found in our paper [5].

In the following we wish to give a short account on further results concerning the decay time τ of some solutions, obtained with the aid of our measurements of the fluorescence spectrum $f_q(v)$[1], the molar decadic extinction coefficient $\varepsilon(v)$, the quantum yield function $\eta(v)$, and the absolute quantum yield η, using NEPORENT's modified relation

$$\frac{c^2 \eta_m^2 f_q(v) L \cdot 10^{-3}}{8\pi n^2 \tau v^2 \eta(v)\,\varepsilon(v)\log 10} = \exp\left(-\frac{h(v-v_e)}{kT}\right). \tag{1}$$

In this equation v means the frequency, n the refractive index of the solution, c the velocity of light, L, h and k Loschmidt's, Planck's and Boltzmann's constants, respectively, v_e the frequency of pure electronic transition, and T the temperature of the system. The values τ_c of τ, calculated with the aid of (1) have been compared with the experimental values τ_m given in [6].

Some difficulties in the comparison arose from the fact that there is a little incertainty in the determination of v_e [7]. Therefore, we determined the values of v_e with different methods, namely, on the base of BLOKHINTSEV's mirror symmetry relation [10], NEPORENT's method based on „area normalization", and the functions $\varphi(v)$ given by DOMBI, KETSKEMÉTY and KOZMA [9] (from the spectra $f_q(v)$ and $\varepsilon(v)$ separately). Then, we calculated τ for different frequencies v with the values of v_e obtained by the four methods mentioned above. (The four values of v_e agreed within 1%.) The best agreement between the calculated τ_c and measured τ_m was obtained for v_e corresponding to the extreme value of the function $\varphi(v)$[2] calculated on the base of the fluorescence spectrum.

The results of our calculations are given in Table I, which contains also the values of τ_m measured in [6] corrected for secondary fluorescence.

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[1] $\displaystyle\int_0^\infty f_q(v)\,\mathrm{d}v = 1$

[2] $\varphi(v) = \text{const. } v^{-3} f_q(v) \exp(hv/2kT$

According to the table, a good accordance with the measured τ_m can be found for these solutions at any frequency in the overlapping interval of the fluorescence and absorption spectra. This shows the usefulness of Eq. (1).

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Table I

Fluorescein $5 \cdot 10^{-5}$ mole/l H$_2$O, 1% NaOH		Fluorescein $1 \cdot 10^{-4}$ mole/l C$_2$H$_5$OH, 1% NaOH		Fluorescein $1 \cdot 10^{-4}$ mole/l Glycerol, 1% NaOH		Eosin $5 \cdot 10^{-5}$ mole/l C$_2$H$_5$OH, $5 \cdot 10^{-3}$ mole/l NaOH	
ν (10^{14} sec^{-1})	τ_c (10^{-9} sec)	ν (10^{14} sec^{-1})	τ_c (10^{-9} sec)	ν (10^{14} sec^{-1})	τ_c (10^{-9} sec)	ν (10^{14} sec^{-1})	τ_c (10^{-9} sec)
5,800	3,9	5,775	3,9	5,825	2,3	5,500	2,9
5,920	3,8	5,800	3,7	5,850	2,2	5,550	2,3
5,950	3,8	5,820	3,4	5,870	2,2	5,600	2,2
$\nu_e = 5,970$	3,7	$\nu_e = 5,855$	3,2	$\nu_e = 5,910$	2,2	5,625	2,2
6,010	3,6	5,900	3,3	5,950	2,2	$\nu_e = 5,665$	2,3
6,050	3,5	5,925	3,2	5,975	2,1	5,705	2,4
6,150	3,8	5,950	3,1	6,000	2,1	5,725	2,6
		5,975	3,2	6,025	2,2		
		6,000	3,4	6,050	2,1		
$\tau_m = 3,9 \cdot 10^{-9}$ sec		$\tau_m = 3,3 \cdot 10^{-9}$ sec		$\tau_m = 2,2 \cdot 10^{-9}$ sec		$\tau_m = 2,4 \cdot 10^{-9}$ sec	

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