

## YIELD OF ANTI-STOKES FLUORESCENCE OF DYE SOLUTIONS

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A new explanation is suggested of the much discussed phenomenon of the abrupt drop in the anti-Stokes region of the curve representing the quantum yield of fluorescence of dye solutions as a function of the wave-length of the exciting light. The writer believes that this drop is due to the long wave-length tail of the absorption band of non-luminescent dimers superimposed on that of (luminescent) monomers and even extending beyond it.

The yield of fluorescence of dye solutions as a function of the exciting wave-length was the subject of several investigations. Valentiner and Rössiger (1926) have shown that the yield of fluorescence of a solution of fluoresceine drops very rapidly as soon as the exciting wave-length exceeds a certain value. This result was confirmed by Vavilov (1927) and many others (Jabłoński 1932, Solomin 1941, Alentsev 1949). As Pringsheim (1949, p. 308) points out, "this phenomenon cannot be interpreted without introducing new assumptions. According to the potential curves (Jabłoński 1931, 1935) the long-wavelength branch of the absorption band is ascribed to molecules having a relatively high vibrational energy in the electronic ground state... There is no reason why these molecules, once they are lifted into the excited state, should have a smaller probability of subsequent fluorescence emission than any other excited molecules."

Vavilov (1937) and Jabłoński (1931) have suggested that the drop of the yield at greater wave-lengths of the exciting light may be due to a very weak "inactive" absorption band superimposed on the long wave-length tail of the main absorption band. Later Jabłoński (1933, 1935) has expressed the supposition that such a weak band may be possibly due to a forbidden transition from the ground state N of the molecule to its metastable state M. This last supposition has been, however, criticized by Pringsheim (1949, p. 308), who has pointed out that such an absorption band would be too weak to cause the observed decrease of the yield<sup>1</sup>. He has put forward instead the

<sup>1</sup> I should like to add here the following remark. In solid solutions in which phosphorescence and/or slow fluorescence appear, the transition probability of the forbidden transition N—M is almost  $10^8$  times smaller than the probability of transition of the F—N band (main band), as estimated on

following explanation: According to Franck and Rabinovitch the interaction of a molecule with its neighbours in liquids lasts considerably longer than a single collision in gases because of the so-called cage-effect; since the wings of the absorption bands in solutions are due to very strong perturbations, a molecule excited by absorption of light in the region of the wings possesses an especially great probability to be quenched.

The problem was also discussed from the point of view of thermodynamics.<sup>2</sup>

I should like to put forward another explanation of the phenomenon in question, which, I believe, will prove sufficient in several instances.

Most of the fluorescent molecules do polymerize. The polymerization of some of them is appreciable even at very low concentrations of the solutions. The presence of polymers, say dimers, in a solution manifests itself by their own absorption spectrum superimposed on that of monomers. If the relative concentration of dimers increases, the relative intensity of the bands belonging to dimers (D-bands) grows at cost of that of the bands belonging to monomers (M-bands), thus causing in cases in which dimers are not luminescent the diminution of the yield of fluorescence, i.e. the "self-quenching" of the fluorescence (cf. e.g. Pringsheim 1949, p. 353).

Although the absorption spectrum undergoes marked changes with the concentration of the solution, there is no reason indeed to suppose that the energy levels of monomers are shifted significantly when the concentration of the solution, and thus also the fraction of dimers, changes. If so, we must expect that, in cases in which only the monomers are luminescent, and, besides, the fluorescence spectrum consists of a single "band", the intensity distribution of fluorescence must be almost independent of the concentration of the solution, whereas the absorption spectrum should depend on concentration very considerably. Such behaviour of the solutions was actually observed in some instances. As an example we may quote the case of fluoresceine in aqueous solutions, in which, according to Levshin (1927), the intensity distribution of the fluorescence spectrum (but not that of the absorption spectrum) remains practically the same for all concentrations up to  $10^{-2}$  g/cm<sup>3</sup>. In cases in which the intensity distribution of the fluorescence spectrum changes with concentration, the spectrum may consist of a superposition of different bands, due

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ground of the duration of emission of these bands. This probability may be, however, greatly enhanced in such solutions in which disturbances caused by adjacent molecules of the solvent are large enough to quench thoroughly the phosphorescence and/or the slow fluorescence.

<sup>2</sup> Although the papers concerning this subject were partly not accessible to me, it seems nevertheless expedient to quote them here for the sake of completeness. Vavilov (1945, 1946) has expressed the view that the drop of yield in the anti-Stokes region is a necessary consequence of the second law of thermodynamics. His view was supported by a theory developed by Landau (1945), in which both the exciting light and that emitted by the luminescent body is assumed to be strongly monochromatic. According to Levshin (1951, p. 156), however, this theory cannot be applied to the case of solutions having broad absorption and emission bands. A further theory was given by Adirovich (1949). Pringsheim (1946) has challenged the above view of Vavilov. Apparently no final agreement was reached in this discussion.

to different electronic transitions, or, possibly, even to different (luminescent) polymers (cf. Pringsheim 1949, p. 359). If we accept the above assumption that the energy levels of the monomers remain unshifted when the concentration of the dye solution changes, we must conclude that at least in some cases also the proper absorption spectrum of monomers is rather insensible to the changes of the concentration, all the changes of the absorption spectrum being due to changes of the relative intensity of D- and M-bands.

The peak of the D-band appears in all instances known to me on the short wave-length side of the peak of the M-band. A closer inspection of the absorption curves of different solutions at various concentrations<sup>3</sup> shows, however, that the long wave-length tail of the D-band is superimposed on that of the M-band and even extends beyond it, as can be deduced from the fact that the larger the concentration of the dyes, and thus the fraction of dimers, the larger is the molar extinction coefficient of the long wave-length tail of the absorption spectrum, whereas the intensity of the M-peak becomes weaker, and, according to our assumption, the width of the M-band does not grow significantly. This being so, the yield of the fluorescence excited in this region of the spectrum (anti-Stokes excitation) must be low.

The observed fact that the drop of the yield in the anti-Stokes region becomes less rapid at higher temperatures of the solution (Vavilov 1943) can be explained as due to the "dissociation" of dimers into monomers (decrease of the proportion of dimers).

I believe that the explanation of the drop of yield in the anti-Stokes region suggested in this paper is the most plausible and simple.

#### КРАТКОЕ СОДЕРЖАНИЕ

А. Яблонский, *Выход антистоксовской флуоресценции растворов красителей*

Предложено новое объяснение явления резкого падения выхода флуоресценции при переходе от стоксовского к антистоксовскому возбуждению. Согласно с этим объяснением падение выхода вызвано наложением длинноволновой части абсорбционной полосы нелюминесцирующих димеров на длинноволновую часть абсорбционной полосы мономеров.

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<sup>3</sup> E.g. that of fluoresceine (Levshin 1927), that of eosin (Soederberg 1913), that of thionine (Rabinovich and Epstein 1941). Cf. also Pringsheim (1949, p. 354).

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