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Pioneers in Photochemistry Part 1

From the Perrin Diagram to the Jabłoński Diagram.

1. Introduction

In the preface to his book "Fluorescence and Phosphorescence" [Pr49], Pringsheim wrote in December 1948: »It is curious to see how inclined one is to assume that research did not begin much before 1936.« With a slight variation of this quotation I should like to say: "It is curious to see how inclined one is to assume that our present understanding of the triplet state began with Jabłoński's Note in Nature in 1933." In that Note [Ja33b] Jabłoński published the precursor of the diagram, which today is called "Jabłoński diagram". The aim of this article is to let the reader see Jabłoński's Note in the context of preceding work by F. Perrin, S.I. Vavilov and P. Pringsheim and by Jabłoński himself.

My interest in this subject was roused in 1990 when I prepared a lecture with the title "The metastable triplet state of aromatic compounds; phosphorescence and delayed fluorescence". In the introduction I sketched the way from the Jabłoński diagram to the Lewis-Kasha diagram [Le44]. This way has been described by Kasha himself in his article "50 Years of the Jabłoński Diagram" [Ka87]. (Kasha had given a lecture with the same title at the "International Symposium on Molecular Luminescence and Photophysics – Half a Century of the Jabłoński Diagram" in Toruń, Poland, 1986.) The name "Perrin" does not occur in Kasha's article. In the printed lectures held at that symposium, only Leach [Lea87] mentioned the work of Francis Perrin [Pe29]. Jabłoński does not cite F. Perrin in his Note [Ja33b], and in his full paper [Ja35a] he cites F. Perrin only in a footnote; the cited work is not Perrin's treatise of 1929 [Pe29], but his later booklet "Durée élémentaire d'émission lumineuse" [Pe31]. Fortunately this booklet was available in the Library of the University of Göttingen. Having read this booklet [Pe31] and later also the treatise [Pe29] I came to the conclusion that part of the credit traditionally given to Jabłoński might be due to F. Perrin.

Lewis and Kasha published their famous article "Phosphorescence and the Triplet State" [Le44] in December 1944. Fifty years later, November 17 and 18, 1994, a Joint Meeting of the French and German Photochemistry Groups took place in Strasbourg. I took the opportunity to present my view of that time on the history of the Lewis-Kasha diagram. The title of my short lecture was "50 Years of Lewis-Kasha Scheme and 65 Years of Perrin Scheme".

After my lecture I was encouraged by several participants to write an article on the same subject for the EPA Newsletter. About a year ago I started to collect additional literature for this purpose. The material of interest became so extensive that I decided to treat in this first part only the development leading to the Jabłoński diagram.

The structure of the article is as follows: In section 2 the state of knowledge on fluorescence and phosphorescence in 1928 is outlined. The first main objective of my article is to give the reader an idea of the scope and depth of F. Perrin's treatise [Pe29] (section 3). I believe that this can be achieved best by long quotations from the original with a minimum of comments. Section 4 is an attempt to let the reader see Jabłoński's Note [Ja33b] in its historical context, i.e. in the context of Vavilov's rule and the quantum yield of the anti-Stokes fluorescence from dyes. In section 5

Jabłoński's Note in Nature [Ja33b] is reprinted and discussed. In section 6, three aspects of Jabłoński's famous paper "Über den Mechanismus der Photolumineszenz von Farbstoffphosphoren" [[On the mechanism of the photoluminescence of dye phosphors]] [Ja35a] are treated: The impact of his paper on the later work by Lewis, Lipkin and Magel [Le41], his disagreement with Pringsheim, and his reference to earlier work by F. Perrin. Finally, section 7, the Conclusion, is the attempt of a balanced appreciation of the merits of F. Perrin and A. Jabłoński.

As far as possible I shall adhere to a chronological order. In most quotations I have tried to remain typographically as close as possible to the originals. Quotations are marked by the quotation marks » «. At the end of a quotation the page number is given in braces { }. My own additions in a quotation are marked by single brackets [], and my own emphasis of a passage is indicated by underlining. Most of the literature of interest here is written in French and in German. In particular Vavilov and Jabłoński wrote many of their articles in impeccable German. To my regret, in order to reduce this article to a reasonable length, I had to omit most quotations of original texts in French and in German. My English translations of quotations are enclosed in double brackets [[]]. A question mark [?] will indicate that I am not sure whether my translation is adequate.

In any work on the history of science, the author has to cope with the problem of changes in terminology. In the table below the present terminology is compared with that in the cited literature. Whenever a confusion will be likely, the present customary term will be added in brackets.

Present terminology	prompt fluorescence $S_1 \rightarrow S_0$	delayed fluorescence $S_1 \rightarrow S_0$ (E-type DF)	phosphorescence $T_1 \rightarrow S_0$
Pringsheim & Vavilov [Pr26]	fluorescence	phosphorescence	phosphorescence
Pringsheim [Pr28]	fluorescence	phosphorescence	phosphorescence
F. Perrin [Pe29]	fluorescence	phosphorescence	fluorescence of long duration
J. Perrin [Pe36]	fluorescence	phosphorescence, delayed fluorescence	fluorescence of long duration
Jabłoński [Ja33b]	fluorescence, F-N band	phosphorescence at room temperature, F-N band	phosphorescence at low temperatures, M-N band
Lewis, Lipkin & Magel [Le41]	fluorescence, $F \rightarrow N$	alpha phosphorescence, $F \rightarrow N$	beta phosphorescence, $P \rightarrow N$
Lewis & Kasha [Le44]	fluorescence, $S' \rightarrow S$	fluorescence, $S' \rightarrow S$	phosphorescence, $T \rightarrow S$

2. Precursors

2.1. Wiedemann (1888): Transformation of fluorescence into phosphorescence. In 1888 Wiedemann published an article [Wi1888] that strongly influenced later research on fluorescence and phosphorescence from organic dyes. The distinction between fluorescence and phosphorescence was originally an experimental one. Fluorescence was a luminescence that disappeared simultaneously with the end of excitation; the decay of a phosphorescence was slow and could be observed with a Becquerel phosphoroscope. In Wiedemann's article, item (2) is of particular interest:

[[2. Transformation of fluorescence into phosphorescence.

Up to now with liquids only fluorescence has been observed, and with solid bodies only phosphorescence.

Starting from the idea that the rapid decay of the fluorescence results from collisions and the [mutual] influence of molecules of the same kind, it seemed interesting to me to investigate whether it would not be possible to convert the fluorescence into a phosphorescence by the gradual addition of colloidal substances. As a result, first of all the following was found:

Nearly all substances that luminesce by incident light in solutions do this in the solid state as well as in the liquid state, if one mixes their solutions with solutions of gelatin and lets them dry up if necessary. ...

Whereas, however, the aqueous solutions luminesce only during the incidence of the light, i.e. fluoresce, the dried solutions with added gelatin continue to luminesce for some time, i.e. they phosphoresce.

This property can be very nicely observed with eosin, quinine sulfate, esculin, acridine hydrochloride, fluorescein. A particularly long afterglow of several seconds is exhibited by acridine hydrochloride and quinine sulfate. ...

Gelatin containing small amounts of glycerol shows upon addition of fluorescent substances a clear phosphorescence; the gelatin is still entirely plastic and is, therefore, on the borderline between liquids and solids.]] (pp. 448-449)

»Diese Versuche zeigen, dass man einen fluorescirenden Körper in einen phosphorescirenden dadurch umwandeln kann, dass man die freie Beweglichkeit seiner Moleküle mehr und mehr beschränkt.« (p. 450)

[[These experiments show that one can transform a fluorescent body into a phosphorescent by more and more restricting the free mobility of its molecules.]]

I call the last quotation "**Wiedemann's dogma**". This dogma was believed to be true for more than 50 years. The scientific reasoning of Lewis [Le41] and Terenin [Te43] was still influenced by it. As will be shown below, F. Perrin [Pe26,Pe29] was the first to question the general validity of this dogma (cf. § 59 in section 3). Vavilov and Levshin [Va26] demonstrated that the transition from fluorescence to phosphorescence is not a gradual one (section 2.4 below).

2.2. Pringsheim: Reviews of the literature on luminescence and his own research. Peter Pringsheim (1881-1963) was professor of physics in Berlin. He had to leave Germany in 1933, went to Brussels, and finally in 1940 to the United States [Ob64,Fr64]. In the context of the present article, his importance is threefold:

First, Pringsheim was a highly respected authority in the field of luminescence. At the first international conference on luminescence in Warsaw in 1936 he was elected president [Pr36a]. In particular his book "Fluoreszenz und Phosphoreszenz im Lichte der neueren Atomtheorie" [Pr28] defines the level of knowledge in the middle of 1927. Everybody working in the field of luminescence knew this book. By his review "Anregung von Lichtemission durch Einstrahlung" [Pr33] he had a strong influence on Jabłoński [Ja33b]. His later book "Fluorescence and Phosphorescence" [Pr49] has been the most comprehensive source of information on the history of that field of research.

Second, Pringsheim worked himself on the phosphorescence of dyes [Pr26,Pr36c] (see 2.3 below). At the conference in Warsaw in 1936 the invited lecture on fluorescence and phosphorescence from adsorbed dyes was given by him [Pr36b].

Third, in the controversy on the possibility of a fluorescence energy yield greater than unity, Pringsheim advanced from the beginning the right argument in favor of this possibility. This topic will be treated in some detail in section 4 in the context of Vavilov's rule.

2.3. Pringsheim and Vavilov (1926): Polarized and unpolarized phosphorescence of solid dye solutions. Two types of phosphorescence were known at that time, for which Lewis et al. [Le41] later used the terms "alpha phosphorescence" (= E-type delayed fluorescence) and "beta phosphorescence" (= phosphorescence $T_1 \rightarrow S_0$). Pringsheim and Vavilov [Pr26] were close to the idea that the same long-lived state is responsible for both kinds of phosphorescence. Their paper [Pr26] was known to F. Perrin [Pr29] and Jabłoński [Ja35a]. From the style of [Pr26] one may

conclude that the paper was written by Pringsheim; in general he was a very cautious scientist and liked to leave questions open. Unfortunately the authors use the same term "phosphorescence" for both types of phosphorescence, and there is no itemization of the main results. In the following I first quote a longer passage from [Pr26] and then give a few comments.

[All phenomena observed by us can be summarized as follows: the dyes investigated by us possess in their luminescence spectrum two bands respectively groups of bands, which differ principally. The first, which we call the "fluorescence band", occurs alone, as long as the substance is dissolved in liquid media and hence exhibits only fluorescence¹⁾; if the solvent is viscous enough, then this band is partially polarized in the known way. It survives in solid solvents, possibly with small spectral shifts, possesses now a certain ability of afterglow and is homogeneously polarized in fluorescence [prompt fluorescence] and [alpha] phosphorescence [= E-type delayed fluorescence $S_1 \rightarrow S_0$]. But now an additional band occurs, which is always shifted to longer wavelengths, the "[beta] phosphorescence band" [phosphorescence $T_1 \rightarrow S_0$], whose intensity, compared with that of the fluorescence band, is only weak during the excitation, but relatively stronger during the afterglow and nearly alone present at low temperature; this [beta] phosphorescence band is always completely unpolarized; in esculin sugar and in still higher degree in rhodamin sugar, already at room temperature the state is given, which is normally reached only at -180° . Since the two band groups are not sharply separated but always overlap, not only the polarization of the total radiation will depend on the predominance of the one or the other band, but – with spectral selection – also the degree of polarization will decrease, when one passes in the emission spectrum from the short-wave part, where the polarized fluorescence band dominates, to the long-wave range, in which the [beta] phosphorescence band contributes more to the luminescence.] [p. 711-712]

(a) In the footnote¹⁾ Pringsheim and Vavilov refer to a paper by Gaviola [Ga26] and write that the duration of the afterglow does not exceed the order of 10^{-8} sec even in viscous solvents like glycerol. I have not been able to understand how this conclusion can be drawn from Gaviola's results. F. Perrin mentions that the lifetime of the metastable state of eosin in glycerol is of the order of 1 ms (cf. section 3, § 62 and [Pe24]).

(b) The authors report that both types of phosphorescence have the same lifetime and that this fact cannot be accidental.

(c) The authors also mention that the spectra of both types of phosphorescence have similar structures and that also this fact cannot be accidental (the same final state in emission).

(d) The lifetimes of the beta phosphorescence at -180°C of fluorescein (5 s), eosin (= tetra-bromo-fluorescein) (10 ms), and erythrosin (= tetraiodo-fluorescein) (1 ms) are a nice example of an intramolecular heavy-atom effect.

(e) The lack of phosphorescence polarization will be explained by F. Perrin [Pe29, §§ 38, 49]. Later Jabłoński [Ja35b, Ja35c] and Pringsheim [Pr36b, Pr36c] will show that the phosphorescence can be even negatively polarized.

In conclusion, this paper by Pringsheim and Vavilov [Pr26] and, as will be shown in detail, F. Perrin's treatise [Pe29] are the closest approaches to Jabłoński's final assignment of the beta phosphorescence to the direct radiative transition from a metastable state to the ground state.

2.4. Vavilov and Levshin (1926): The relations between fluorescence and phosphorescence in solid and liquid media. Vavilov's and Levshin's paper [Va26] is important in two respects:

(1) In contradiction to "Wiedemann's dogma" [Wi1888] they concluded that phosphorescence and fluorescence in solid and viscous media probably correspond to two different physical processes, between which there is no continual transition.

(2) They found no short-lived prompt component in the luminescence from uranyl salts. This negative result was important for F. Perrin's correct view that the true radiative lifetime of excited states can be very long, of the order of a millisecond at least (cf. section 3, § 59).

3. F. Perrin (1929, 1931): Metastable state of dye molecules

In the obituary on Francis Perrin (1901-1992) Charpak [Ch93] writes: »Francis Perrin est né le 17 août 1901 à Paris. Il a grandi dans un rare climat de richesse intellectuelle. Fils de Jean Perrin qui apporta une preuve décisive de l'existence des atomes, il vécut dans une famille étroitement liée à des amis, tous humanistes, idéalistes, qui décidèrent d'éduquer eux-mêmes leurs enfants parmi lesquels nombreux furent ceux qui contribuèrent à la richesse intellectuelle de la France.« [[Francis Perrin was born August 17, 1901 in Paris. He grew up in a rare climate of intellectual richness. Son of Jean Perrin [Nobel Prize in physics 1926] who furnished a decisive proof of the existence of atoms, he lived in a family closely joined with friends, all humanists, idealists, who decided to educate their children themselves, among whom those were numerous who contributed to the intellectual richness of France.]]



F. Perrin (in the thirties) [RV96]



A. Jabłoński (1935)

F. Perrin is referring also to this intellectual richness when he writes in the acknowledgment of his treatise "La Fluorescence des Solutions" [Pe29]: »J'ai eu le très rare bonheur de faire ce travail au côté de mon père dans son laboratoire ; en tant que disciple je tiens à exprimer ici ma profonde reconnaissance pour tout ce que je lui dois. [[I had the very rare good luck to do this work at the side of my father in his laboratory; as his disciple I would like to express here my deep gratitude for all that I owe to him.]] It is obvious that Francis Perrin got the subject of his research and many important ideas from his father Jean Perrin. Two examples may suffice to justify this assertion. First, the essentially correct explanation of E-type delayed fluorescence was given by J. Perrin, and the energy histograms used by F. Perrin had been introduced by J. Perrin before. Second, F. Perrin's work on the connection between orientational relaxation, fluorescence polarization and fluorescence lifetime is likely to have started from J. Perrin's work on rotational Brownian motion of microscopic particles. In the present context, however, it is not always important to whom, father or son, credit should be given. Whenever credit is to be given to his father, F. Perrin seems to have done this

himself. F. Perrin went far beyond the work of his father. He was the less common case of a theoretical physicist who started his career as an experimentalist.

In 1929 Francis Perrin published his great treatise «**La Fluorescence des Solutions**» [Pe29]. The subtitle is: «**Induction Moléculaire. – Polarisation et Durée d'Émission. – Photochimie.**» [[Molecular induction^{#1} – Polarization and Duration of an Emission. – Photochemistry.]]. On 28th April 1931 F. Perrin gave a public lecture with the title «**Fluorescence**» and with the subtitle «**durée élémentaire d'émission lumineuse**» [[elementary duration of light emission]]. This subtitle denotes what Perrin considered his most important contribution. The published lecture [Pe31] is a shortened version of [Pe29]. The treatise [Pe29] seems to be identical with F. Perrin's thesis of 1928 (which has not been accessible to me). The treatise is a systematic introduction into the photophysics of dye molecules in solutions. It is 105 pages long and subdivided into seven chapters and 63 paragraphs (§). To give the reader an idea of the scope of the treatise, first its complete summary is quoted in my translation. After the summary mainly those paragraphs of the treatise are mentioned or quoted, which are of interest in connection with Jabłoński's later work [Ja33b,Ja35a].

[[SUMMARY. – This treatise begins with a survey of the experimental properties that define the fluorescences^{#2} and their theoretical interpretation (§§ 1-20).

The essential difference between fluorescence and phosphorescence is not based on a more or less long persistence of an emission, since from this point of view a nearly continuous sequence of intermediates links the shortest fluorescences with the longest phosphorescences.

A fluorescence is essentially associated with a simple passage of molecules, having absorbed the incident light, through an excited state from which the emission takes place due to an internal instability; and if this state is not directly attained at the absorption, the intermediate transformations must take place nearly instantaneously and borrow no energy from the medium (rapid decay of a mechanical oscillation produced simultaneously with the electronic excitation [= rapid vibrational relaxation of a primary vibronic state]). The mean duration of a fluorescence is, therefore, the lifetime τ of molecules in an excited state susceptible to a spontaneous transformation by emission; it is in addition equal to the inverse τ_0 of the coefficient of the instantaneous probability of this emission; precisely one has, with p denoting the luminescence yield (as number of photons),

$$\tau = p\tau_0$$

and this relation permits to characterize a true fluorescence.

If on the contrary the excited molecules pass, between absorption and emission, through an intermediate, stable or metastable state and can no longer reach the emissive state without getting from the medium a certain amount of energy, then the luminescence is a phosphorescence, characterized by the unlimited increase^{#3} of the duration of the emission at low temperatures.

From the wave aspect necessarily associated with the quantum aspect, the duration of a fluorescence represents the attenuation constant of the elementary wave trains, whereas the duration of a phosphorescence has no fundamental significance.

The return to the normal state of an excited molecule can take place not only by light emission but also by interaction with another material system and production of kinetic energy. These mechanisms intervene by diminishing simultaneously the luminescence yield of a fluorescence and the mean duration of its emission. Thus a molecule can be deactivated by the presence of a ground state molecule of the same species in its neighborhood [= concentration quenching], or more generally [by the presence] of a synchronous molecule^{#4}; this induced deactivation by resonance must be

^{#1}Molecular induction here means long-range intermolecular energy transfer due to dipole-dipole interaction (Förster energy transfer). Cf. also footnote #4 below.

^{#2}The plural of the noun fluorescence is not usual; here it is preferable to ignore that inconvenient practice.

^{#3}The concept of a metastable state of infinite lifetime at $T = 0\text{ K}$ will be revised in § 61.

^{#4}A synchronous molecule is a molecule that can absorb the fluorescence emitted from a neighboring molecule. J. Perrin and F. Perrin discovered the intermolecular energy transfer over large intermolecular distances. Their work is the precursor of Förster's later work on electric dipole-dipole energy transfer. For this reason, this type of energy transfer has been occasionally called Perrin-Förster energy transfer.

connected with the possibility of a transfer of excitation energy from one molecule to another. I have shown that another kind of induced deactivation occurs in the inhibition of fluorescences by certain colorless substances (iodides, phenols); the molecules of these substances, easily oxidizable and all having antioxidant properties, possess a weakly bound electron, and the deactivations produced by them result without doubt from a mechanism, which is very similar to the collisions of the second kind with free electrons, envisaged by Klein and Rosseland (§§21-26).

The light reemitted by fluorescent solutions is in general partially polarized. The study of this polarization proofs, firstly, with more certainty than Wiener's experiment alone, that the excitation of the fluorescence is due to the action of only the local oscillating electric field of the incident wave. On the other hand, the variations of the polarization as a function of the viscosity η of the solvent permit to calculate the mean duration of an emission, τ . By using the exact laws of rotational Brownian motion, I have shown that the degree of polarization, p , of the fluorescence light observed perpendicularly to the electric vector of a polarized excitation wave has the value

$$p = p_0 \frac{1}{1 + (1 - \frac{1}{3} p_0) \frac{RT}{V\eta} \tau}$$

V being the total volume of the N [$= N_A$] molecules of a gram molecule [$= \text{mol}$] of the dissolved fluorescent substance, and p_0 the value which the polarization would have if the molecules did not rotate. This formula permits to deduce the values of the fundamental polarization p_0 and of the mean life τ of the excited molecules from measurements of the fluorescence polarization for the same substance dissolved in different solvents. It is in general verified satisfactorily (§§ 27-60).

The values of the mean emission durations thus obtained are for the majority of the brilliantly fluorescing dyes of the order of 0.5×10^{-8} sec, in a rather satisfactory accord with the evaluation from classical electromagnetic theory. But I found that certain fluorescent substances exhibit much longer emission durations (25×10^{-8} [sec] for anthracene⁵⁵). On the other hand I have given new arguments for admitting that the still much longer luminescence from uranyl salts is a simple fluorescence, and I have indicated, how such durations of elementary light emission, which are much longer than those foreseen by classical theory, can be easily interpreted by wave mechanics (§§ 61-62).

Finally, I summarize in a last paragraph the explanations (that I have been able to deduce from my research on the fluorescence) of certain phenomena in chemical kinetics, in particular of certain negative catalyses in photochemical reactions and in chain reactions (autooxidations).]]

Chapter I (§§ 1-2, pp. 171-179) introduces the basic scientific terms: fluorescence, phosphorescence, Stokes rule, excited states, lifetime of emissions, spontaneous emission, radiative lifetime of excited states, etc.

Chapter II [[Theories of fluorescence]] (§§ 3-20, pp. 179-206) is the most important one in the present context. In §§ 3-4 the application of classical electromagnetic theory to the excitation and the decay of a fluorescence is treated. It is shown that, although the right order of magnitude is obtained for the short radiative lifetime of the fluorescent state of typical dyes, classical electromagnetic theory offers neither an explanation for much longer radiative lifetimes nor one for the Stokes shift of the fluorescence.

In §§ 5-20 the old quantum theory is applied to fluorescence. In § 6 the concept of an excited state is introduced. In this respect it is noteworthy that F. Perrin always takes into account the possibility of *states with different multiplicities*. The statement in the following quotation from § 7 is of fundamental importance in Perrin's reasoning:

§ 7. »Absorption et émission. — ... Lorsqu'une transformation quantique d'activation ou de désactivation est possible suivant un certain processus, il est naturel d'admettre que la transformation inverse est possible suivant le processus exactement inverse. Par exemple, si une activation est

⁵⁵This lifetime is by a factor of 50 too long. From the description of the experiments in § 56 follows that Perrin had no suitable well-defined solvent for the investigation of the polarization of the fluorescence from anthracene.

possible par absorption de lumière, la désactivation correspondante doit pouvoir se faire par émission spontanée. « [[If a quantum transformation of activation or deactivation is possible according to a certain process, it is natural to admit that the inverse transformation is possible according to the exactly inverse process. For example, if an excitation is possible by absorption of light, the corresponding deactivation by spontaneous [light] emission has to be a possible process.]]

The translated titles of the subsequent paragraphs are: § 8. Fluorescence; § 9. Photochemical reactions; § 10. Quantum relation; § 11. Optical resonances [in monatomic vapors, the frequency of the emitted light is equal to that of the absorbed light]; § 12. Change of frequency [vibrational relaxation of a primary vibronic state and radiative transition to a final vibrational state]; § 13. Electronic excitation and molecular vibrations; § 14. Influence of temperature [overlap of absorption band and emission band at higher temperatures, explanation of anti-Stokes fluorescence]. § 15. Deactivation without emission; light yield. [Perrin defines the light yield as the quantum yield p , i.e. the number of emitted photons divided by the number of absorbed photons. Among the processes responsible for $p < 1$ he mentions concentration quenching and quenching by other substances.]

§ 16. »Relation entre la vie moyenne et le rendement lumineux.« [[Relation between the mean life and the light yield.]] In this paragraph F. Perrin derives the important relation

$$(15) \quad \tau = \rho \tau_0$$

already mentioned in the Summary. By this relation J. Perrin and F. Perrin define a fluorescence as opposed to a phosphorescence (cf. § 20 below).

In § 17 (The correspondence principle and the mean life of excited molecules) Perrin discusses among other things the wave-particle dualism of light. The subsequent §§ 18-20 are very important in connection with Jabłoński's later postulate of a metastable state [Ja33b] and Lewis' later interpretation of the metastable state as a triplet state [Le41, Le44].

§ 18. »Relation entre la vie moyenne maximum et le pouvoir absorbant. – Une telle relation résulte immédiatement de la démonstration de la loi de Planck par Einstein. ... « [[Relation between the maximum mean lifetime [= radiative lifetime] and the absorption strength. – Such a relation immediately results from the demonstration of Planck's law by Einstein [Ei17]. ...]]

[In Perrin's equation (27) below τ_0 is the radiative lifetime, g is the degeneracy coefficient, ν is the frequency, n is the refractive index, c is the velocity of light and α_ν is the absorption cross-section at the frequency ν .]

$$»(27) \quad \frac{1}{\tau_0} = \frac{1}{g} \frac{8\pi\nu^2 n^2}{c^2} \int \alpha_\nu d\nu .$$

Cette formule très remarquable est malheureusement d'application difficile et incertaine. Sa démonstration suppose en effet l'existence de seulement deux états stationnaires bien définis ; elle n'est donc valable en toute rigueur que pour les résonances optiques, mais alors l'étroitesse extrême des raies d'absorption rend très difficile la détermination de la courbe de variation du coefficient d'absorption α_ν en fonction de la fréquence. Dans le cas des solutions fluorescentes l'étalement spectral de la bande d'absorption rend aisée cette détermination, mais par suite du passage par des états intermédiaires oscillants la formule ne peut plus être rigoureuse.

D'autre part on ne connaît pas en général le coefficient g , rapport des probabilités *a priori* des deux états considérés, ou d'après les principes de la statistique quantique, des degrés de multiplicité de ces états.

J'ai pourtant essayé d'appliquer la formule (27) à la fluorescéine en solution aqueuse ; la détermination spectrophotométrique de la courbe d'absorption m'a donné (en admettant que $g = 1$)

$$\tau_0 = 0,65 \cdot 10^{-8} \text{ sec.}$$

Nous verrons que cette valeur est voisine de la vraie valeur.

[[The application of this remarkable formula is difficult and uncertain, unfortunately. Its demonstration supposes the existence of only two well-defined stationary states; it is, therefore, rigorously

valid only for optical resonances, but here the extreme narrowness of absorption lines renders very difficult the determination of the curve of the variation of the absorption coefficient as function of the frequency. In the case of fluorescent solutions, the spectral extent of the absorption band renders this determination easy, but, because of the passage through intermediate vibrational states, the formula cannot be rigorously valid.

On the other hand, in general one does not know the coefficient g , the ratio of the *a priori* probabilities of the two considered states, or according to the principles of quantum statistics, the multiplicities of these states.

Nevertheless I tried to apply the formula (27) to fluorescein in aqueous solution; the spectrophotometric determination of the absorption curve gave me (by assuming $g = 1$)

$$\tau_0 = 0.65 \times 10^{-8} \text{ sec.}$$

We will see that this value is close to the true value.]]

Eq. (26) is a precursor of the Strickler-Berg formula. With the last statement Perrin refers to his indirect determination of τ from the dependence of the degree of polarization on the viscosity of the solvent (cf. § 51 below) and on the direct phase-fluorometric determination of τ by Gaviola [3].

§ 19. »Etats métastables. Phosphorescence. — Lorsqu'un état activé peut être atteint directement, à partir de l'état normal, par absorption de lumière, réciproquement le retour à l'état normal est possible par émission spontanée de lumière. Mais il existe des états activés, dits *métastables*, pour lesquels aucune transformation de ce genre n'est possible ; le retour à l'état normal ne peut alors se produire que par interaction avec d'autres molécules (désactivation induite) ou par passage intermédiaire par un autre état activé d'énergie interne plus grande. L'existence de ces états métastables, prévues théoriquement par Bohr, comme conséquence du principe de correspondance, a été démontrée expérimentalement dans plusieurs cas (hélium, mercure,...). Tous les principes de sélection en spectroscopie expriment d'ailleurs l'impossibilité de certaines transformations quantiques par rayonnement.«

[[Metastable states. Phosphorescence. If an excited state can be reached directly from the normal state by absorption of light, conversely the return to the normal state is possible by spontaneous emission of light. But there are excited states, called *metastable*, for which no transformation of this kind is possible. The return to the normal state can take place only by interaction with other molecules (induced deactivation) or by intermediate passage through another excited state of higher internal energy. The existence of these metastable states, anticipated theoretically by Bohr as a consequence of the correspondence principle, has been demonstrated experimentally in several cases (helium, mercury,...). All selection principles in spectroscopy express, by the way, the impossibility of certain quantum transformations by radiation.]]

The immediately following paragraph contains Jean Perrin's explanation of an E-type delayed fluorescence (F. Perrin mentions J. Perrin without giving a specific reference):

[[It may occur that a molecule that has passed to a first excited state α by light absorption, undergoes, either spontaneously or by reaction with other molecules, a transformation bringing it into a state α that is metastable or even completely stable, from which the return to the normal state is possible only by repassing the first excited state or an analogous state with an internal energy a little higher than that of the state α . A molecule having attained such a state will subsist there until an external cause, collision or radiation, will bring to it the energy ϵ necessary for its return to the primary excited state, from where it will be able to return to the normal state by emitting a light quantum. If that energy ϵ is not too large, it can be supplied by the thermal energy of the medium; thus the considered substance will exhibit two photoluminescences, a prompt fluorescence [»fluorescence directe«] and a delayed fluorescence [»fluorescence retardée«], by the transition to the state α . The duration, separating on the average the absorption and the emission for this second photoluminescence, will essentially depend on the rapidity with which the medium will supply the energy increment ϵ ; consequently it will be the longer the lower the temperature, tending to infinity

at absolute zero. Hence this luminescence will have the properties of a typical phosphorescence, of which we thus obtain a theoretical interpretation (Jean Perrin), which can be represented by the following scheme, where for simplicity we have omitted intervening vibrational states. One will notice that, if the state α is stable, the phosphorescence will be a veritable reversible photochemical reaction.]]

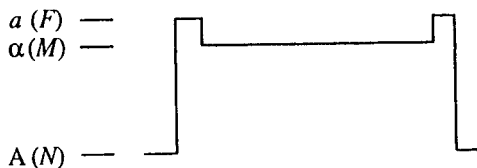


Figure 1. Perrin's diagram ([Pe29], Fig. 4) for the explanation of the delayed fluorescence $a \rightarrow A$ by the intermediate passage through a metastable state α . For comparison Jablonski's state symbols N , M and F [Ja33a] have been added in parentheses. The Perrin diagram is an energy histogram, the horizontal axis representing the time.

[[The average life of the molecule in the intermediate state has no relation to the phenomenon of light emission; hence, in general, in a phosphorescence, there will be no relation between the duration of the emission and the light yield. In particular an increase of temperature can much diminish the duration of an emission without sensitively modifying the yield; and if the elevation of temperature is produced, after an excitation, in a very short time relative to the duration of the emission, one will observe the phenomenon of thermoluminescence, which characterizes a phosphorescence most simply.]] – This text will be commented in connection with § 20.

§ 20. [[Theoretical distinction between fluorescence and phosphorescence. – Thus the experimental property which we have adopted to distinguish the phosphorescences from the fluorescences, that is, the unlimited increase of the duration of an emission at low temperatures, has a simple theoretical meaning, which we can summarize by the following statements:

Every photoluminescence corresponds to a cycle of quantum transformations of excited molecules or sensitive groups.

If all these transformations do not borrow energy from the medium in an essential way, and if all traversed states are capable of spontaneous transformation by light emission, the phenomenon is a fluorescence.

If, on the contrary, the transformed molecules pass, between absorption and emission, through an intermediate stable or metastable state, and thus are no longer able to reach the emitting state without receiving a certain amount of energy from the medium, or if a dissociation followed by recombination takes place, there is phosphorescence.

The duration [= lifetime] of a fluorescence is the duration of the elementary wave emission (length of a wave train) and must vary in first approximation only proportionally to the light yield, whereas the duration of a phosphorescence has no direct relation to these quantities and has no simple fundamental significance.]]

In the preceding §§ 19 and 20 F. Perrin discusses three different thermally activated processes that may cause a "phosphorescence": (1) An E-type delayed fluorescence in the present sense resulting from the intermediate passage through a metastable state. In §§ 19 and 20 he still assumes that the lifetime of a metastable state becomes infinite at very low temperature. (2) A delayed fluorescence due to a reversible photochemical reaction. This possibility was originally favored by J. Perrin [PeJ26, p. 387]. 12 years later Franck and Livingston [Fr41] publish their tautomer hypothesis, which is a paraphrase of the reversible photochemical reaction considered by Perrin (in [Fr41] the papers by J. Perrin, F. Perrin, and Jabłoński are not cited). (3) A delayed fluorescence resulting from photoionization and recombination. The latter type of delayed fluorescence was well known from combined investigations of photoluminescence and electrical photoconductivity of many inorganic substances.

A phosphorescence in the present sense ($T_1 \rightarrow S_0$) is not discussed, since Perrin still regarded the radiative transition $\alpha \rightarrow A$ as strictly forbidden. One has to admit that a reader having read §§ 19 and 20 cannot expect that Perrin will revise his view in this point 68 pages later in § 61.

In **Chapter III**, »Induction moléculaire«, (§§ 21-26, pp. 206-213) Perrin treats three different energy transfer processes: (1) Quenching of a fluorescence by long-range resonance energy transfer to molecules of the same kind (energy migration and concentration quenching) or to molecules of a different kind, whose absorption spectrum overlaps with the emission spectrum of fluorescent molecules (§§ 22-23). (2) A quenching process in which the colorless energy acceptor is photoionized (but the energy donor does not act as electron acceptor) (§§ 24,25). (3) The internal conversion of a higher excited state into the lowest excited state is treated as intramolecular energy transfer from one electronic oscillator to another (§ 26).

Chapter IV »Polarisation de la fluorescence des solutions« (§§ 27-40, pp. 213-230) is the first of three chapters on fluorescence polarization. In connection with the aim of the present paper, § 38 is of particular interest because of its reference to the paper by Pringsheim and Vavilov [Pr26] (cf. section 2.3).

§ 38. [[Wavelengths of observation and excitation. – The polarization of the fluorescence light is in general uniform in the whole emission band, and consequently does not depend on the color filter chosen for observation.

However, for certain substances (erythrosin,...) the emission band comprises two partial bands; one of them corresponds to a phosphorescence, which becomes rather long-lived and relatively more important at low temperature (liquid air); the polarization is then different for these two bands (which can overlap); it is, with the exception of vitreous media, zero for the phosphorescence band (P. Pringsheim [24]).

In the same way, if one excites the fluorescence of a solution by monochromatic light, one finds that the polarization varies little or not at all as long as the used wavelength is in the main absorption band adjacent to the emission band, but if the excitation is produced by light of a significantly shorter wavelength, the polarization often takes a smaller value (V. L. Levshin [7]).

We will give below [§ 57 Investigation of chlorophyll] a remarkable example of these variations for which we shall propose a theoretical interpretation [cf. § 49].]

The quoted § 38 shows that the phosphorescence (in the present meaning) was known to Perrin. The aspect of interest to him was the different polarization of the phosphorescence ($T_1 \rightarrow S_0$). He drew the right conclusion that the phosphorescence ($T_1 \rightarrow S_0$) has to be assigned to a different electronic transition, without speculating on its nature. Obviously, when he wrote § 38, he was still inhibited by the idea of an unlimited increase of the lifetime of a metastable state at very low temperature.

Chapter V, »Théorie de la polarisation de fluorescence des solutions« (§§ 41-50, pp. 231-252) contains the derivation of Perrin's famous formula (cf. the Summary and § 51 in Chapter VI below). In the present context, § 49 is supplementary to § 38.

§ 49. [[Distinct linear oscillators of absorption and emission. – We have assumed up to now that the oscillator of emission was also that which determines the probability of absorption. We will have to consider cases where it does not seem like that (excitation of the fluorescence by an absorption band not adjacent to the emission band). It is easy to calculate the depolarization that results from such a change of oscillator.

Let α be the angle between the two oscillators of absorption and emission, which are assumed to be fixed in the molecule. The transfer of excitation from the first to the second is equivalent to an angular displacement performed on the average for all positions of the molecule, corresponding to the same direction of the oscillator of absorption, symmetrically around that direction. Hence one will obtain the corresponding fundamental polarization by replacing in the formula (17) [in § 44],

used [again] in the preceding paragraph [§ 48], p_0 by $1/2$, p by p_0 , and u by $\cos^2 \alpha$, which yields after solving with respect to p_0

$$(22) \quad p_0 = \frac{3 \cos^2 \alpha - 1}{\cos^2 \alpha + 3}$$

This formula gives values for p_0 between $1/2$ and $-1/3$ (for $\alpha = \pi/2$). One sees that this mechanism could lead to negative values of the polarization, which means that the fluorescence light emitted perpendicularly to the electric vector of the incident wave would have its maximum electrical vibration in the plane perpendicular to that exciting electric vector.]]

Chapter VI [[Experimental verifications. Determination of mean emission lifetimes.]] (§§ 51-60, pp. 253-269). The first paragraph of chapter VI, § 51, is of general interest because it contains Perrin's famous polarization formula in its most useful form:

§ 51. - «Nous avons obtenu dans le chapitre précédent une formule fondamentale, qui relie la polarisation de fluorescence p d'une solution quelconque à trois constantes caractérisant des propriétés intrinsèques des molécules du corps fluorescent dissous: le volume moléculaire [= molaire ?] V , la polarisation fondamentale p_0 , et la vie moyenne τ dans l'état activé. Cette formule peut s'écrire:

$$(1) \quad \frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \tau \frac{RT}{V\eta}.$$

Elle exprime donc, qu'à une température donnée, si pour des solvants de viscosités différentes les quantités V , p_0 et τ ont les mêmes valeurs, l'inverse de la polarisation de fluorescence doit être une fonction linéaire de l'inverse de la viscosité.»

[[In the preceding chapter we have obtained a fundamental formula, which links the polarization of the fluorescence p of any solution to three characteristic constants of the intrinsic molecular properties of the dissolved substance: the molecular [= molar] volume V , the fundamental polarization p_0 , and the mean life τ in the activated state. This formula can be written: (1) $1/p = \dots$ (see above).

Thus it expresses that at a given temperature, if the quantities V , p_0 and τ have the same values for solvents of different viscosity, the reciprocal of the polarization of the fluorescence has to be a linear function of the reciprocal of the viscosity.]]

The practical application of the linear relation in Perrin's Eq. (1) is known as *Perrin plot* still today; as far as Perrin's nationality is concerned, the prevailing view seems to be that he was English.

In F. Perrin's work the investigation of the long-lived fluorescence of uranyl salts was very important because it yielded the definite proof that radiative lifetimes of excited states can be very long, of the order of a millisecond at least. § 59 gives a summary, whose translation is shortened:

§ 59. [[Properties of the photoluminescence from uranyl salts. - We have seen that certain fluorescent substances have mean emission durations close to the value foreseen by classical electromagnetism, [whereas] others, exhibiting no less typical fluorescences, have much greater emission durations. It seems that one has to prolong the range of fluorescence durations still far beyond the values we have given, and that in particular the brilliant green photoluminescence of the *uranyl salts* is a veritable simple fluorescence of very long duration.

The persistence of the emission of that photoluminescence is, as one knows, easily observable with mechanical phosphoroscopes and thus can be directly studied. Its essential properties are the following:

1° *The intensity of the luminescence decreases exponentially as function of the time after the end of an optical excitation.* - This law, roughly verified by E. Becquerel, has been established by S. I. Vavilov and V. L. Levshin [10] and by R. Delorme and myself [17].

2° *The mean duration of the emission is located, for the solid salts with brilliant luminescence, between one ten thousandth and one thousandth of a second.*

3° *The mean duration of the emission increases only little and tends to a limit when one much lowers the temperature* (qualitative observation by J. Becquerel, measurements by R. Delorme and F. Perrin [18]). The decrease of this duration when one raises the temperature always accompanies a decrease of the luminescence yield; there is never thermoluminescence.

4° *The solid state is in no way essential to the great duration of this luminescence.* In fact I have found [13] that the solutions of uranyl sulfate in pure sulfuric acid exhibit, although completely liquid, a brilliant luminescence whose persistence is easily observed with a conventional phosphoroscope of E. Becquerel, and [the luminescence] has a duration only about four times less than that of crystals of uranyl nitrate. Contrary to what was alleged by P. Pringsheim and E. Gaviola [5], it is here the main luminescence from these solutions, and not a weak phosphorescence following a nearly instantaneous fluorescence. By the way, S. I. Vavilov et V. L. Levschin have confirmed the existence of the fluorescence of long duration and the absence of a short-lived fluorescence [10]. Moreover they have determined the mean duration of the emission under different conditions of temperature and concentration and verified its proportionality to the luminescence yield. The same verification has been performed by R. Delorme in the case of the lowering of the luminescence yield by introducing into the solution of uranyl sulfate small amounts of hydrochloric acid acting as colorless quencher.

The whole of these properties seems to me to leave no doubt about the nature of the luminescence of the uranyl salts: this is a typical fluorescence, despite its more than ten thousand times longer duration than those of the short-lived fluorescences of dye stuffs. Its mean emission duration must be equal to the mean life of the radical UO_2 in an excited electronic state, capable to return to the normal state by spontaneous emission. Seen as a wave, it must represent the attenuation time of the wave trains associated with each elementary emission, which therefore in this case would have a length of the order of hundred kilometers. In the next chapter we will discuss the theoretical possibility of a such a weak attenuation.]]

In order to understand this careful argumentation one has to know Pringsheim's skepticism in this matter. In his book [Pr28] Pringsheim writes on p. 160: [... but – as long as the contrary has not been demonstrated – already decay times of the order of 10^{-3} sec should be regarded as too long for being assigned to the spontaneous transition probabilities in the interior of a molecule. For the time being one has to come to the conclusion that liquids always emit only fluorescence, whereas solids, if they are photoluminescent at all, always phosphoresce, but at the same time can often also fluoresce – possibly even with much higher intensity.]] Perrin has shown [De29,Pe24, § 62 in Pe29] that Pringsheim was wrong with respect to both underlined statements.

Chapter VII [[Discussion of results. Applications in chemical kinetics]] (§§ 61-63, pp. 269-274). In view of the aim of the present paper, § 61 is the climax of Perrin's treatise.

§ 61 **[[Values of the mean duration of emission. –** If one knows the luminescence yield ρ , one can deduce from the measured value τ of the mean duration of an emission that of the mean maximum life τ_0 of the excited molecules [$\tau = \rho\tau_0$], which represents the inverse of the probability of the spontaneous return to the normal state by light emission.]]

Perrin then summarizes the known facts about the enormous range of radiative lifetimes, from $\tau_0 \approx 0.5$ ns for the fluorescence from typical dyes (in accord with classical electromagnetic theory) up to $\tau_0 \approx 1$ ms for the fluorescence from uranyl salts (in strong disagreement with classical electromagnetic theory). Referring to the latter very long radiative lifetimes he continues:

»Des amortissements aussi faibles des trains d'ondes émis semblent tout à fait inexplicables par la théorie électromagnétique classique. Il est remarquable de constater qu'ils s'interprètent au contraire aisément en mécanique ondulatoire.

Dans les théories quantiques, la vie maximum τ_0 dans l'état excité est en effet déterminée par la condition

$$\varepsilon\tau_0 = h\nu,$$

ε représentant le pouvoir émissif, selon la théorie classique ⁽¹⁾ [= Ref. to work by Dirac and Fermi], d'un oscillateur de fréquence ν et d'amplitude q. Mais cette amplitude, reliée essentiellement à l'énergie d'oscillation disponible en théorie classique, en est indépendante en mécanique ondulatoire. Ses composantes doivent être calculées par des formules de la forme :

$$q_x = \int x \psi_1 \psi_2^* dx dy dz,$$

ψ_1 et ψ_2 représentant les fonctions de Schroedinger correspondant à l'état normal et à l'état excité considéré. Or on sait que l'amplitude ainsi associée à deux états quantiques peut être nulle, la transition entre ces états étant alors impossible par émission ou absorption de lumière (état excité métastable). Mais elle peut aussi être, dans certains cas, très petite sans être nulle, quelle que soit d'ailleurs la grandeur de l'énergie disponible ; l'émission sera alors possible, mais se produira en un temps très long, et les trains d'ondes associés auront un amortissement très faible.

Ainsi la durée très grande de la luminescence des sels d'uranyle n'a rien d'inadmissible pour une fluorescence véritable ; c'est la plus longue actuellement connue, mais des durées presque aussi grandes ont été observées même dans le domaine très simple des résonances optiques par P. Soleillet [27].

Des états d'abord considérés comme tout à fait métastables semblent même en réalité avoir une probabilité très petite mais non rigoureusement nulle de transformation par émission spontanée. C'est ainsi que I. S. Bowen [1] a pu interpréter les raies caractéristiques des nébuleuses, comme due au retour à l'état normal d'atomes d'azote et d'oxygène ionisés se trouvant dans des états presque métastables pour lesquels les vies moyennes maximum τ_0 seraient de l'ordre de une seconde.

[[Such weak attenuations of the emitted wave trains seem entirely inexplicable by classical electromagnetic theory. It is remarkable to see that they are on the contrary easily interpreted in wave mechanics. In the quantum theories [in contrast to wave mechanics], the mean maximum life τ_0 in the excited state is determined by the condition

$$\epsilon \tau_0 = h\nu,$$

ε representing the emissive power, according to the classical theory ⁽¹⁾ [= Ref. to work by Dirac and Fermi], of an oscillator of frequency ν and amplitude q. But this amplitude, which is fundamentally linked to the disposable oscillation energy in classical theory, is independent of it in wave mechanics. Its components have to be calculated by formulae of the form:

$$q_x = \int x \psi_1 \psi_2^* dx dy dz,$$

ψ_1 and ψ_2 representing the Schrödinger functions corresponding to the normal state and the considered excited state. Now one knows that the amplitude thus associated with two quantum states can be zero, the transition between these states therefore being impossible by emission or absorption of light (metastable excited state). But it can also be, in certain cases, very small without being zero, independently of the amount of disposable energy; the emission will therefore be possible, but will take place in a very long time, and the associated wave trains will have a very weak damping.

Thus the relatively very long duration of the luminescence of the uranyl salts has nothing inadmissible for a veritable fluorescence; this is the longest actually known, but nearly as long durations were observed by P. Soleillet [27] even in the very simple field of the optical resonances.

The states initially considered as completely metastable seem in reality to have a probability for the transformation by spontaneous emission, which is very small but not rigorously zero. In this way I. S. Bowen [1] has been able to interpret the characteristic rays of the nebulae, as due to the return to the normal state of ionized atoms of nitrogen and oxygen being in nearly metastable states, for which the maximum mean lives τ_0 would be of the order of one second.]

Since the cited short paper by Bowen [Bo28] is revealing in several respects, I quote the most important passages from it:

» It has recently been possible to explain most of the strong nebular lines as lines arising from electron jumps from metastable states in oxygen and nitrogen. ... This constitutes then the first direct

evidence that metastable states are not absolutely metastable but are states of long mean life, i.e., states from which the probability of a spontaneous jump in unit time is very small. ...

As was pointed out in the discussion of the nebular spectrum, this viewpoint makes it possible to explain the enormous variation in intensity of the nebular lines in going from terrestrial sources, where the lines are too weak to be observed, to the nebulae, where they are often the strongest lines in the spectrum. The intensity of the line depends directly on the ratio of the probability of the return from an atom from a higher state to a lower state with emission of that line to the sum of the probabilities of its return by all processes combined. ...

These same differences in lifetime can doubtless be used to explain various anomalous intensities found, to a lesser degree, in terrestrial sources. For example, calculations on the basis of the correspondence principle show that the intercombination jumps, i.e., jumps between a singlet and a triplet term, etc., in the simplest atoms are very improbable, or, interpreted on the above basis, have a very long life. In the case of the heavier atoms such as mercury the perturbations due to the other electrons are so great that the intercombination jumps have nearly the same probability per unit time as the regular jumps. ...

This indicates a whole gradation of mean lives extending from that of the regular lines whose mean life before emission is of the order of 10^8 seconds to that of the nebular lines whose mean life before emission must be of the order of a second or more.

Perrin's text and the quoted text from Bowen's paper leave no doubt that Perrin was very close to the correct interpretation of the phosphorescence [$T_1 \rightarrow S_0$] as radiative transition from the metastable state to the ground state and even to the triplet hypothesis. He only had to write that the low-temperature phosphorescence (observed by Pringsheim and Vavilov [Pr26] and discussed by him in § 38) might be the fluorescence of long duration $\alpha \rightarrow A$ (in his terminology). Why he did not take that last step, we do not know. A trivial reason might be that at that time he was not so much interested in the assignment of the low-temperature phosphorescence.

The following § 62 is of interest because of its clear description of the dominant role of the metastable state in photochemical reactions and the mention of a phosphorescence [= E-type delayed fluorescence] from eosin in liquid glycerol.

§ 62. **[[Negative catalysis in photochemistry.** – When a photochemical reaction is associated with a fluorescence, the reacting molecules are taken from those which are in the activated emitting state reached after absorption. *For a given substance*, the rate of the reaction must therefore be proportional to the mean life of the activated molecules, and consequently to the luminescence yield ρ of the fluorescence. This proportionality was verified in the case of the decrease of fluorescence yield by increase of concentration for the reaction of methylene blue with glycerol (Jean Perrin et Mlle Choucroun [22]).

The induced deactivation of molecules by colorless inhibitors must in the same way slow down the photochemical reactions. In fact I have found that for example potassium iodide negatively catalyzes [= inhibits] the decolorization by light [= photobleaching] of eosin dissolved in glycerol. But the measurements made by Mr. Privault have shown that this negative catalysis is much stronger than the decrease of the fluorescence strength. I have found the explication of this deviation in the existence of a weak phosphorescence of solutions of eosin in glycerol (τ of the order of 10^{-3} sec.), indicating that a small portion of the molecules activated by absorption fall back into an intermediate metastable state α , in which they store a great disposable energy for a relatively very long time [relative to the lifetime of the fluorescent state]. It is from this state that a molecule must react most frequently, and in fact one finds the proportionality between the negative catalysis and the decrease of the duration of the phosphorescence emission. The greater sensibility of molecules in the metastable excited state α (than in the emitting state) to deactivating substances [= quenchers] is explained by the long duration of that state, which permits the diffusion to intervene in an important way.

Many negative catalyses in photochemistry have to be explained by analogous mechanisms.]]

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4. Anti-Stokes fluorescence and Vavilov's law

4.1. Fundamentals. Let us consider the most simple example of **anti-Stokes fluorescence** from a four-level system in contact with a heat bath. In the case of a diatomic molecule, the four levels could for instance be the electronic and vibrational ground state $S_{0,0}$, the first vibrational level $S_{0,1}$ in the electronic ground state, and the corresponding levels $S_{1,0}$ and $S_{1,1}$ in the first excited singlet state S_1 - see Fig. 2. An anti-Stokes fluorescence may arise in two ways: First, molecules are excited in the 0-0 transition $S_{0,0} \rightarrow S_{1,0}$; in thermal equilibrium $S_{1,0} \rightleftharpoons S_{1,1}$, a small portion of the excited molecules will be in the vibronic state $S_{1,1}$, from which the anti-Stokes hot-band fluorescence $S_{1,1} \rightarrow S_{0,0}$ is emitted. Second, conversely, in the hot-band range of absorption, vibrationally excited ground-state molecules $S_{0,1}$ are excited, $S_{0,1} \rightarrow S_{1,0}$, and the anti-Stokes fluorescence $S_{1,0} \rightarrow S_{0,0}$ is observed.

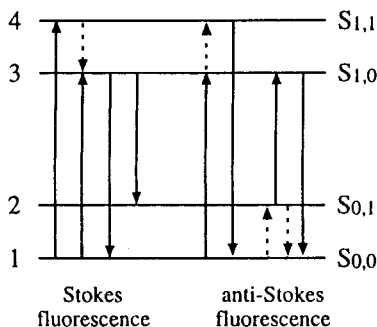


Figure 2. Illustration of Stokes fluorescence and anti-Stokes fluorescence in a four-level system.

The second type of anti-Stokes fluorescence is of interest here. The fluorescent molecules will be large dye molecules in liquid or solid solutions. From a naive point of view, the spectrum and the quantum yield ρ of the fluorescence are expected to be independent of the excitation wavelength (including the hot-band range of absorption) as long as vibrational relaxation and solvent relaxation are much faster than the radiative and nonradiative decay of S_1 to the ground state S_0 . This naive point of view has a remarkable consequence for the energy yield κ of a fluorescence relative to the energy absorbed by the fluorescent solute molecules. If the quantum yield of the fluorescence is close to unity, then, with extreme anti-Stokes excitation, the energy yield may be greater than unity. These implications of the naive point of view were regarded as contradiction to the Second Law of thermodynamics [Len28, Va45a, Va46]. It is the great merit of Pringsheim to have seen from the beginning that in this case the naive point of view is completely adequate, and moreover not in contradiction to the Second Law [Pr29, Pr46]. A clear formulation of the problem was given by Pringsheim in 1921 [Pr21]:

[According to the rule found by Stokes and named after him, the wavelength of fluorescence radiation has always to be greater than that of the exciting light. Einstein has shown that this regularity, which initially was deduced purely empirically, appears as a necessary corollary of the quantum theory, since at the emission act at most a quantum of the same magnitude can be emitted as that received before by the respective resonator. In reality there are numerous exceptions to Stokes' rule in its rigorous form. Although the fluorescence radiation can be always preferentially effected by light of shorter wavelength than its own wavelength, or in other words, the center of the excitation distribution is at smaller wavelengths than that of the fluorescence band, nevertheless these two spectral ranges frequently overlap, and by light, whose wavelength is beyond the short-wave limit of the emission band, the entire emission band can be brought to emission. Thus, in such cases the secondary radiation is partly of higher frequency than the primary – the emitted quanta are of higher energy than the absorbed ones. As Einstein was likewise the first to point out, this deficiency in the energy balance must be compensated by the internal heat energy of the luminescent molecules – at very low temperatures deviations from Stokes' rule should no longer occur. ...] [p. 206]

Most non-Russian readers of the EPA Newsletter are likely to know the first part of **Vavilov's law**, but little or nothing about the Russian physicist **Sergei I. Vavilov** (1891-1951). Let me first quote a short formulation of Vavilov's law by Vavilov himself [Va45b, p. 286]: [[The quantum yield of a fluorescence does not depend on the wavelength of the exciting light up to some limiting wavelength λ_0 , at which it begins to drop rapidly to zero.]] The importance of Vavilov's work in luminescence spectroscopy can be seen from the fact that he is the most often cited author in Förster's book "Fluoreszenz organischer Verbindungen" [Fö51] (33 papers are cited at 56 places). Vavilov's lecture "On the photoluminescence of solutions" [Va45b] gives an idea of his broad, critical and penetrating view of this field of research. Readers interested in Vavilov's achievements as a scientist and organizer of science in Russia should read a recent letter to Physics Today by Bolotowsky and Vavilov (a nephew of S.I. Vavilov) [Bol95].

In the present article the *second part of Vavilov's law* is of interest: the existence of a limiting wavelength λ_0 , at which the fluorescence quantum yield allegedly begins to drop rapidly. In this second part of his law Vavilov was not right. Nevertheless, his behavior as a scientist in this matter was on the whole reasonable. In the context of Jabłoński's Note [Ja33b], the second part of Vavilov's law is of interest in two respects: Jabłoński confirmed [Ja33a] Vavilov's experimental results [Va27], and he proposed an alternative interpretation [Ja33b] of the drop of fluorescence yield at excitation wavelengths $> \lambda_0$. In the following an outline will be given of the way from the early work of Nichols and Merritt to Jabłoński's Note [Ja33a].

4.2. Nichols and Merritt (1905, 1910): First fluorescence-excitation spectrum of a dye. The American physicists Edward L. Nichols and Ernest Merritt did fundamental work on the luminescence of organic and inorganic substances. Here three of their achievements are noteworthy: (a) First measurements of fluorescence spectra of dyes. (b) Experimental proof of the invalidity of Stokes' law for the fluorescence spectra of dyes (in the sense mentioned above). (c) First measurement of fluorescence excitation spectra. To illustrate the achievements (a) and (b), four of the nine items from the summary on p. 170 of the review [Ni05] are quoted in my translation:

[[
3. The position of the maximum of the fluorescence band is in all cases independent of the wavelength or composition of the exciting light.

4. The intensity distribution in the fluorescence spectrum is independent of the wavelength of the exciting light.

6. Stokes' law holds for none of the numerous substances which we have studied.

7. Fluorescent substances with absorption bands of shorter wavelength than that of the band, with which the fluorescence is connected, can be excited [to fluorescence] by the light absorbed in any band, whatever the wavelength may be.]]

The achievement (c) [Ni10] deserves particular appreciation in connection with Vavilov's rule. The fundamental results of Nichols and Merritt are shown in the figures 92 and 93 of Ref. [Ni10], of which the first one is reproduced here (note that Nichols and Merritt use a continuous numeration of their figures, not confined to a single paper). Nichols and Merritt comment these results as follows:

»In each of the two figures also we have plotted in the curves for the coefficient of absorption (A) and for the energy distribution in the fluorescence spectrum (F). It would seem reasonable to expect that the curve of the specific exciting power might show some peculiarities either in the region of maximum absorption or in that of most intense fluorescence. It appears, however, that nothing of this kind occurs.

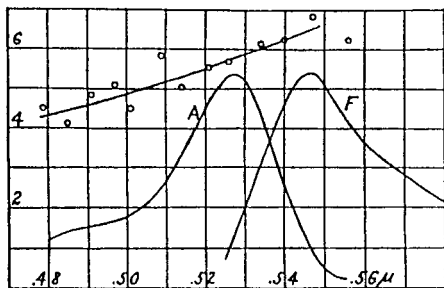


Figure 3. This figure is identical with Fig. 92. of Ref. [Ni10]. A is the absorption spectrum of a solution of eosin and F is the corrected fluorescence spectrum in energy per wavelength unit. The circles are the relative fluorescence energy yield referring to the absorbed energy. The wavelength is given in μm .

Before beginning these experiments we were of the opinion that either the specific exciting power would prove to be constant, so that the same quantity of absorbed energy would produce the same fluorescence regardless of its wave-length, or else that the effectiveness of the exciting light would prove to be greater for the shorter wave-lengths. The readiness with which fluorescence is excited in the ultra-violet spectrum made the latter view seem plausible. As it turns out neither of these views is in accord with the facts. We were unfortunately unable to extend the observations to the ultra-violet spectrum. It seems clear, however, that if we confine our attention to wave-lengths falling within the range of one absorption band, the light lying near the red side of the band is more effective in producing fluorescence than that lying on the violet side, and the change in the specific exciting power as we pass through the band is continuous, without any indication of anything selective in the neighborhood of the region of maximum absorption.« (p. 387)

This text was written, when Einstein's light quanta were still considered a bold idea, probably not yet generally known, and when Bohr had not yet published his theory. Nichols' and Merritt's result, the linear increase of the fluorescence energy yield, is qualitatively correct. The systematic error in the increase of the fluorescence energy yield is of the order of 10%. It took more than 50 years for this result to get generally accepted.

4.3. Vavilov (1922): Repetition of the experiments of Nichols and Merritt. Vavilov [Va22] started from the work of Nichols and Merritt [Ni10] and the therein reported increase of the fluorescence energy yield κ with increasing excitation wavelength. In his introduction he discusses different conceivable explanations of this observation. Two of them are particularly noteworthy:

»From our standpoint, the inconstancy of κ inside an absorption-band is an indication of its physical complexity. *Such a band is a result of a superposition of several bands belonging to resonators of different types: i.e., with a different κ .*« (p. 308)

»Einstein's theory of the simplest photochemical reactions leads to the result that the coefficient of the velocity of reaction must be inversely proportional to the frequency of the active light. Considering in accordance with modern theories the fluorescence as a production of light accompanying the simple reaction of dissociation [= photoionization?], we can hypothetically apply this

conclusion to fluorescence. Therefore we can expect the following dependence of κ upon λ inside a simple absorption band :

$$\kappa = a \cdot \lambda,$$

where a is constant. For a complex band, κ must be a totally different function of λ .

Thus we can interpret the experimental results of computation of κ on the following lines :—

(a) If $\kappa = \phi(\lambda)$, (3)

where ϕ is a more or less complicated function of λ , the absorption-band is a physically complex one.

(b) If $\kappa = a \cdot \lambda$, (4)

the band is a simple one and the theory of Einstein is true.

(c) If $\kappa = \text{const.}$, (5)

the band is a simple one and the theory of Einstein is not true.« { p. 309 }

Vavilov measured the excitation spectra of the fluorescence from three dyes: fluorescein, eosin, and rhodamin B. A serious problem in the investigation of dyes has been their often undefined degree of purity. Even today most commercially available dyes are rather impure substances. Vavilov writes: »The band of absorption of Eosin investigated by Nichols and Merritt differs considerably from that of Eosin studied by us (fig. 3). Unfortunately, among six Eosins at our disposal we did not find a dye very closely resembling the Eosin of Nichols and Merritt.« (p. 310)

Vavilov's results are best summarized by 4 of his own 5 conclusions:

»(1) Within the limits of errors of observation the specific fluorescence [κ] of our dyes is independent of λ within their band of absorption.

(2) According to all above-mentioned, this result is equivalent to the conclusion that the curves of absorption of our dyes are physically simple ones.

(3) The theory of Einstein is not confirmed, but the deviations required by this theory are so small that they exceed only a little the experimental errors, and we are unable to make a definite statement.

(5) The result of Nichols and Merritt shows probably only the physical complexity of bands of dyes studied by these authors.« (pp. 319-320)

Symbols: In the following the clear distinction between the quantum yield ρ and the energy yield κ of a photoluminescence will be important. In case of doubt, the implied kind of luminescence yield will be indicated by insertion of [ρ] or [κ].

4.4. Vavilov (1924): First absolute energy yield of a dye fluorescence. The completely new aspect of his work [Va24] is the *first determination of the absolute value κ of a fluorescence energy yield*. For example, with polychromatic excitation in the lowest absorption band of fluorescein in aqueous solution, Vavilov obtained $\kappa = 0.80$. The result that the fluorescence energy yield of a dye can be close to unity was unexpected at that time. Absolute values of fluorescence quantum yields have been of fundamental importance for the determination of radiative lifetimes of excited states (cf. section 3) and for our present understanding of radiationless processes.

4.5. Valentiner and Rössiger (1924): First report on steep drop of fluorescence energy yield with anti-Stokes excitation. Valentiner and Rössiger (in Clausthal in Germany) [Val24] started from the discrepancy between the results of Nichols and Merritt [Ni10] and those of Vavilov [Va22] on the dependence of the fluorescence energy yield κ ("Ökonomie der Fluoreszenzstrahlung" in [Val24]) on the excitation wavelength. They summarize their results as follows:

[1. The economy [= energy yield κ] of the fluorescence radiation depends on the wavelength of the exciting radiation; it is constant or increases a little with increasing wavelength up to that which approximately coincides with the wavelength of the maximum of the fluorescence emission; with further increasing wavelength it drops steeply.

2. In the range of concentrations from 10^{-7} to 10^{-5} g/ccm the economy $[k]$ increases with increasing concentration.]] (p. 215)

In their subsequent paragraph Valentiner and Rössiger criticize Nichols & Merritt [Ni10] and Vavilov [Va22, Va24] as follows:

[[Hence it is necessary, in the case of absolute measurements of the economy $[k]$, to take into account the concentration and the wavelength of the exciting radiation; observations with white exciting light of the kind recently performed by Vavilov [Va24] and also a longer time ago by us, yield only a rough average value. That our predecessors [Ni10, Va22] did not find the steep drop of the economy $[k]$ at longer wavelengths of the exciting radiation, may be attributed to the fact that the spectral ranges used by them were either too broad or did not reach far enough into the region of longer waves to make the drop of the energy yield at longer waves apparent.]] (p. 215)

Comment: The alleged decrease of the fluorescence energy yield with increasing excitation wavelength (the underlined text in the result 1) has been perhaps the most successful impurity effect in molecular photophysics. It gained high recognition as the second part of Vavilov's law, and it led Jabłoński to his diagram, as will be shown below. The second emphasized result, the increase of the energy yield with increasing concentration, was also an artifact, as was admitted by Valentiner and Rössiger in their subsequent paper [Val25].

4.6. Vavilov (1925): Reply to criticism by Valentiner and Rössiger. Vavilov [Va25] published a comment on the paper by Valentiner and Rössiger [Val24]. He first defends Nichols and Merritt by mentioning that their results refer to different dyes, whose fluorescence had not been studied by Valentiner and Rössiger. Referring to the reported strong drop of the fluorescence energy yield at long excitation wavelengths he writes:

[[Of course this sudden drop, no matter whether it is real or an artifact due to any unconsidered circumstances, does not contradict my experimental results, because it takes places outside the spectral region investigated by me. ... Sometimes one observes in aqueous dye solutions apart from the selective absorption additionally a very weak continuous background, which is superimposed on the absorption band. The origin of this background is not always clear, in some cases it is probably caused through the extinction of the light by scattering colloidal particles of the dye or even its large molecules. Various small impurities of the dye may as well lead to the superposition of such a different absorption spectrum. This background will increase the absorption constant at the long-wave end of the selective band apparently, and consequently k $[k]$ can turn out much smaller than it is in reality.]] (p. 237)

This last quoted text shows that Vavilov was aware of all conceivable errors resulting from insufficiently pure dyes and solvents. Further below Vavilov rightly rejects the classification of his absolute fluorescence energy yield [Va24] as a rough average value. He points out that, in the range of excitation wavelengths studied by himself, there is no significant discrepancy between his results and those obtained by Valentiner and Rössiger. Finally he points to fact that the alleged increase of energy yield with increasing dye concentration is in contradiction to earlier work by Mecklenburg and Valentiner [Physik. ZS. 15 (1914) 267]. The reply of Valentiner and Rössiger [Val25] to Vavilov's remarks [Va25] is written in a conciliatory tone, and the authors admit that the alleged increase of energy yield with increasing dye concentration reported by them was probably an artifact.

4.7. Valentiner und Rössiger (1926): Confirmation of strong drop of fluorescence energy yield with anti-Stokes excitation. In their paper [Val26] Valentiner and Rössiger confirm their previous experimental result [Val24]. The last part of [Val26] begins as follows (bold print also in the original !):

»Ergebnis. Das Ergebnis dieser Untersuchung ist die volle Bestätigung des früher gefundenen starken Abfalls der Energieausbeute, wenn Teile des erregten Fluoreszenzspektrums kurzwelliger sind als das erregende Licht.«

[[Result. The result of this investigation is the complete confirmation of the previously found strong drop of the energy yield, if part of the excited fluorescence spectrum is at shorter wavelengths than the exciting light.]] [p. 88]

In the subsequent paragraphs Valentiner and Rössiger first defend their result against conceivable objections (impurity absorption, vibrational overtone absorption) and then generalize it:

[[We now believe that this behavior of fluorescein is not merely a special property of this substance, but that in general, with the violation of Stokes' rule, any excitation is accompanied by a decrease of the yield. But with that, in place of the traditional, purely negative expression of this rule, a positive, more comprehensive formulation would have been found, which can be given as follows:

The energy yield of the fluorescence radiation of solutions decreases inside the emission band with increasing wavelength of the exciting light.

The experimental result of the present paper is in contradiction to the hypothesis, according to which the energy increment necessary for the emission of the anti-Stokes terms is taken from the available thermal [= vibrational] energy of the molecule. That view leads to the a priori improbable result that, with violation of Stokes' law, the excitation takes place with a particularly favorable energy yield ($\kappa > 1$!). According to the present results exactly the opposite is the case.]] [p. 88-89]

In connection with the last two quoted sentences it is noteworthy that the mentioned "a priori improbable result" of a dye fluorescence with an energy yield greater than unity was published by Zander and Drexhage [Za95] 69 years later. These authors found that, in the still more extreme case of negligible absorption of excitation light by the solvent, even cooling of a solution by extreme anti-Stokes excitation is expected and indeed observable (cf. Part II).

4.10. Vavilov (1927): Vavilov's rule, confirmation of results of Valentiner & Rössiger. Vavilov's paper [Va27] is remarkable in two respects: First, Vavilov's law in the present sense is communicated. Second, the results of Valentiner and Rössiger are confirmed! The basic result is represented in Fig. 3 of [Va27], which is reproduced below as Fig. 4 of the present paper. Vavilov writes in the discussion of his paper:

»Wenn die Ausbeute genau dem Einsteinschen Äquivalenzgesetz folgen würde, müßte sie nach der punktierten Linie in der Figur verlaufen. Die Abfallstelle müßte der Ausbeute 1 entsprechen. Wie man aus der Figur sieht, folgt die Fluoreszenzausbeute von Fluorescein im Ultravioletten dem Einsteinschen Gesetze nicht nur der Wellenlänge, sondern auch dem absoluten Werte nach. Im Sichtbaren aber, in der Nähe des kritischen Punktes, wo das Einsteinsche Gesetz seinen Sinn verliert, treten merkliche Abweichungen von diesem Gesetze auf.«

[[If the yield followed exactly Einstein's law of equivalence, it would have to proceed along the dashed line in the figure. The point of sudden drop would have to correspond to the yield 1. As one sees in the figure, the fluorescence yield of fluorescein follows Einstein's law in the ultraviolet not only with respect to the wavelength but also with respect to the absolute value. In the visible however, in the neighborhood of the critical point, where Einstein's law loses its meaning, appreciable deviations from this law occur.]] [pp. 316-317]

Without saying it explicitly, for Vavilov an energy yield greater than unity is unacceptable. Thus, also in this respect he adopts the position of Valentiner and Rössiger [Val26]. Vavilov continues in the next paragraph by proposing an explanation of the drop of the fluorescence yield in analogy to ideas in a paper by J. Franck. The following quotation reveals that Vavilov was still skeptical:

[[The proposed explanation is not the only possible. For instance, one might formally explain the course of the yield curve also by the superposition of several broad absorption bands with different activity constants. But the agreement of the absolute values of the yield in the ultraviolet makes this explanation little likely.]] {pp. 317-318}

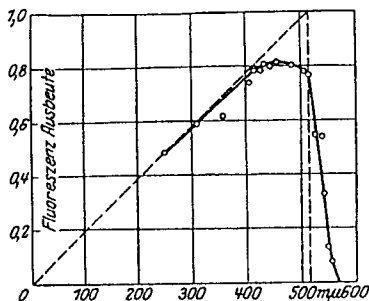


Figure 4. Energy yield κ of the fluorescence from an aqueous solution of fluorescein as a function of the excitation wavelength. Fig. 4 is identical with Fig. 3 of Ref. [Va27].

From the present point of view the underlined text is the correct explanation, if one refers "the other broad absorption bands" to impurities with a lower fluorescence quantum yield [Dr96]. It is not clear why Vavilov no longer discusses an impurity effect – in contrast to [Va25] (cf. 4.6). The superposition of two different absorption bands will be the explanation given by Jabłoński [Ja33b].

4.11. Lenard (1928): Luminescence energy yield and the Second Law. Philip Lenard (1862-1947, Nobel prize in physics 1906) was an eminent experimental physicist. His pioneering work on the photoluminescence from inorganic solids, which is of interest here, was highly appreciated by his contemporaries. The following quotation is taken from Lenard's article in vol. 23 of the "Handbuch der Experimentalphysik" [Len28]. Pringsheim will refer to the same quotation – see below.

[[The violations of STOKES' rule are of more fundamental importance in the resonance radiation, where the emission consists of lines, and in particular in line resonance, than in the emission of bands as for instance in the d-luminescence of the phosphors. For the emission of light of shorter wavelength than that of the exciting light, without the simultaneous emission of light of longer wavelength, would yield economy coefficients [κ] greater than unity, if light quantum after light quantum were processed, as was concluded for the phosphors (Ch. X, 659). The radiation transcending the economy unity would continually be taken from the heat energy; but this would contradict the Second Law of thermodynamics.]] (p. 946) [In the subsequent text Lenard questions the concept of light quanta that exist independently of the quantized transitions in atoms and molecules.]

4.12. Pringsheim (1929): Criticism of Lenard's assertion of an upper limit of the energy yield κ of fluorescence with anti-Stokes excitation. In the first sentence of the abstract of [Pr29] Pringsheim writes: [[It is shown that a continuous cooling of a fluorescent gas as a result of "anti-Stokes" fluorescence emission is not in contradiction to the Second Law.]] Pringsheim quotes Lenard's statement [Len28] (see quotation in 4.11) and then develops his argument. The main point in it is that a fluorescent body is not a closed system in the thermodynamic sense; hence the Second Law imposes no restriction corresponding to a fluorescence energy yield $\kappa \leq 1$. He then gives two very illustrative examples of open systems, where heat flows from a body of lower temperature to a body of higher temperature:

[[But that, when work is continually supplied from outside, one part of the system may cool down, the other one warm up, is absolutely in agreement with thermodynamics as everybody knows, every refrigerating machine is an example for it; the simplest analogy for it is perhaps offered by the Peltier effect: as soon as an externally maintained electric current flows through a wire consisting of

two metals, one soldered joint cools down and the other one warms up until also here again (by heat conduction) an equilibrium state [steady state?] develops.]] [p. 741]

The Peltier effect is a very good example. I am sure that if the Peltier effect had been predicted before its discovery, most physicists would have considered this prediction nonsense. Still today, for a simpleminded chemist like the author, the Peltier effect is a mysterious effect, whereas a fluorescence energy yield greater than unity is not mysterious at all. Pringsheim's argumentation was later criticized by Vavilov [Va45a], defended by Pringsheim [Pr46], again critically commented by Vavilov [Va46], and strongly supported by Antonov-Romanovski et al. [An55] (cf. Part II).

4.13. Jabłoński (1932): Superposition of different absorption bands. In his paper [Ja32], Jabłoński investigates the broadening of the absorption and fluorescence spectra of dyes due to density fluctuations of the solvent. The point of interest here is his discussion of Vavilov's law, to which the chosen subtitle "Superposition of different absorption bands" alludes. Jabłoński refers to Vavilov's results [Va27] as to "Wawilowsches Gesetz" ["Vavilov's law"] and writes:

[[The quantum yield of the fluorescence has to be always the same (when no other quantum jumps can take place), independently of the wavelength exciting the fluorescence. Hence the energy yield should increase linearly with the wavelength [Vavilov's law].

The sudden drop of the yield, when the exciting wavelength exceeds that of the intensity maximum in the fluorescence band [Va26, Va27], cannot be easily explained. It is very likely that in this region, where the absorption coefficient is merely 0.6 to 2 % [Sc27] of the maximum, the greatest fraction of the light attenuation does not at all result from the relevant band; for example there may be another band superimposed.

It is easy to understand that, with a superposition of different bands, among which may be also such bands that do not lead to fluorescence. Vavilov's law can be violated. The most accurate measurements of the fluorescence yield available up to now were performed by Szczeniowski [Sc27] for fluorescein in different solvents with a photoelectric photometry. These measurements show very considerable deviations from Vavilov's law; the deviations are just there particularly large, where new bands become apparent as humps on the main absorption band. It is rather surprising that the quantum equivalence law is well satisfied from 500 to 250 mμ in Vavilov's experiments. But that the law is not likely to be generally valid, can be concluded from Szczeniowski's measurements [Sc27].]] [p. 466-467]

Jabłoński then compares (in his figure 3) Szczeniowski's results [Sz27] with Vavilov's results (cf. 4.10 and Fig. 4). In the critical range between 440 and 520 nm, Szczeniowski's results agree qualitatively better with the results of Nichols and Merritt [Ni10] than with those of Vavilov [Va27]: His values of the fluorescence energy yield [κ] *increase* with increasing excitation wavelength!

The underlined text in the foregoing quotations from [Ja32] is of great interest in view of Jabłoński's later Note [Ja33b]. He develops the idea of *inactive* absorption bands not leading to fluorescence. The new feature in the Note will be the *assignment* of such inactive bands.

4.14. Jabłoński (1933): Experimental confirmation of Vavilov's results. In that golden age of science it was still customary to repeat the experiments of other scientists. Before embarking on the assignment of inactive absorption bands Jabłoński [Ja33a] decided to repeat Vavilov's experiments. Unfortunately for science and in some sense fortunately for himself, Jabłoński was able to reproduce Vavilov's results. His paper ends with a sentence referring to his Fig. 1 on p. 103: »Wie aus der Kurve ersichtlich ist, bestätigen unsere Messungen die Ergebnisse von Wawilow.« [[As evident from the curve, our measurements confirm Vavilov's results.]] This confirmation was later very important for Vavilov [Va45] (cf. Part II).

Jabłoński's manuscript [Ja33a] was received by the editor of Acta Phys. Pol. December 28, 1932. Three and a half months later, April 14, 1933, he submitted his Note [Ja33b] to Nature.

5. Jabłoński (1933): Radiative decay of the metastable state of dye molecules

With the title of this section I want to indicate Jabłoński's lasting great merit in luminescence research. In 1933 Jabłoński published his famous short Note [Ja33b], which is reprinted in the following. The only significant deviation from the original is the itemization [a], [b], ... which I have introduced to facilitate my subsequent comments to the Note.

» Efficiency of Anti-Stokes Fluorescence in Dyes

[a] ACCORDING to Kautsky and his collaborators¹, the majority of the molecules of dyes investigated by them, among which were also the molecules of fluoresceine, show an ability to phosphoresce when 'energetically isolated', for example, when adsorbed by convenient adsorbents. We can assume therefore that in such molecules there must be at least one metastable energy level M (Fig. 1), situated lower than the level F reached immediately after absorption. From the state F the molecules can pass either to a normal state N , emitting the band $F-N$ (fluorescence), or to the metastable state M . The probability of the transition $M-N$ is very small. Therefore when the temperature is sufficiently high, a great majority of molecules will be raised thermally from the level M to F and will be able to emit the band $F-N$ (phosphorescence at room temperature). At low temperatures, direct transitions $M-N$ take place. These transitions are accompanied by the emission of a phosphorescence band which is displaced towards the red relatively to band $F-N$; the duration of phosphorescence increases greatly (phosphorescence at low temperatures).

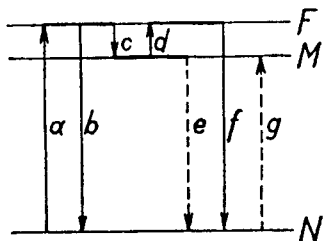


Figure 5. Fig. 5 and the following legend are identical with Fig. 1 of Ref. [Ja33b]:

Fig. 1 —Energy levels in a phosphorescent molecule. a —absorption, b —fluorescence, c —transition to metastable level, d —thermal excitation, e and f —phosphorescence, g —absorption of very small probability.

[b] As the mean life τ of the state M is much longer than that of the level F , the phosphorescence is quenched appreciably more than fluorescence. This follows from the formula² $I = I_0/(1 + k\tau)$, where k is the probability of a quenching act, I the observed intensity of photoluminescence.

[c] The absorption band $N-M$ (inverse transition) must also appear if the transition $M-N$ take place, notwithstanding its small probability. However, it will have a very small intensity as compared with band $N-F$.

[d] Under the influence of disturbing fields, for example of the surrounding molecules of the solvent, the probability of transition $N-M$ can become appreciably greater than that of the isolated molecule.

[e] In solutions, practically all the molecules which have reached the level M in any possible way will be quenched. Therefore the absorption band $N-M$ must be completely inactive.

[f] Such inactive bands, overlapping on the longer wave-length side the active absorption bands ($N-F$), can cause the falling off of efficiency as observed in fluoresceine solutions^{3,4,5}. It is to be noted in this connexion, that in the region of abrupt falling off of yield, the values of absorption coefficients of fluoresceine solutions reach only from 0.2 to 2 per cent of the maximal value.

[g] In the above considerations I have supposed for the sake of simplicity that the levels for absorption and emission acts are identical. I have dealt elsewhere with the relative displacements of emission and absorption bands.⁶

A. Jabłoński

¹ H Kautsky, "Energieumwandlungen an Grenzflächen", *Ber. Deutsch. Chem. Ges.*, **64**, 2053 and 2677; 1931; and **65**, 401; 1932.

² O. Stern and M. Volmer, *Phys. Z.*, **20**, 183; 1919.

³ S. Valentiner and M. Rössiger, *Z. Phys.*, **36**, 81; 1926.

⁴ S. I. Wawilow, *Z. Phys.*, **42**, 311; 1927.

⁵ A. Jabłoński, *Acta Phys. Pol.*, **2**, 97; 1933.

⁶ A. Jabłoński, *Z. Phys.*, **73**, 460; 1931. See also P. Pringsheim, "Handb. d. Phys.", **23**, Part 1, second edition, 244.«

For a reader of the subsequent discussion of Jabłoński's Note it will be advantageous to have in mind F. Perrin's ideas on radiative transitions in general on the metastable state of dye molecules in particular (§§ 7, 18, 19 (Fig. 1), 20, 38, 49, 59, 61 and 62 in section 3).

Jabłoński's selection of references has been puzzling for me. First of all, I have not been able to understand why he did not cite F. Perrin's treatise [Pe29]. There can be no doubt that Jabłoński knew [Pe29], on several grounds: First, Perrin's treatise was a major event in the literature on the luminescence of dyes. Second, the French journal "Annales de Physique", in which the treatise was published, was certainly available to Jabłoński. Third, Jabłoński amply uses Perrin's ideas: the term "metastable state" in connection with the phosphorescence (= E-type delayed fluorescence) of dyes had been introduced by F. Perrin, and the sequence *a-c-d-f* in Jabłoński's diagram in Fig. 5 is equivalent to Perrin's diagram in Fig. 1. (Jabłoński's diagram is a mixture of Perrin's pure energy histogram with an implied time axis and of an energy level diagram, in which processes are denoted by arrows.) In my view, the only acceptable and at the same time likely explanation of the missing citation of F. Perrin's work is that Jabłoński did not claim any priority for the assignment of low-temperature phosphorescence (the dashed arrow *e* in Fig. 5) – although this has been the lasting new idea of the Note. In the following the paragraphs [a] to [f] of Jabłoński's Note are discussed in turn.

[a] Jabłoński's new idea in paragraph [a] is the assignment of the red-shifted phosphorescence band to the transition *M-N* (postulated in a general way by F. Perrin in § 61 of [Pe29]). The new aspect of Kautsky's work was the photoluminescence from *adsorbed* dye molecules and its quenching by gaseous oxygen. The low-temperature phosphorescence [$T_1 \rightarrow S_0$] from dyes as well as from simple aromatic hydrocarbons had been known long before Kautsky's work (cf. pp. 230-238 in [Pr28] and section 2.3 of this paper). The clue to this biased citation may come from the fact that on the one hand Jabłoński was in 1932 a newcomer to the research on phosphorescence, and on the other hand his main source of information on phosphorescence seems to have been his Ref. 6, i.e. Pringsheim's handbook article [Pr33]. Pringsheim cites in [Pr33] essentially only the literature that had appeared after the middle of 1927. Thus Kautsky's work, which was published after 1927, is described in detail in [Pr33]. In many cases Pringsheim mentions scientists in the text without giving a reference (for example F. Perrin and his polarization formula – cf. the Summary of [Pe29] in section 3). But why Pringsheim did not cite Perrin's treatise [Pe29] is difficult to understand.

[b] This paragraph contains nothing new relative to §§ 16, 19, 20 and 62 of [Pe29]. The phosphorescence meant in [b] is mainly E-type delayed fluorescence.

[c] This is a paraphrase of Perrin's postulate in § 7 of [Pe29] (cf. also the quantitative relation between absorption and spontaneous emission in § 18 of [Pe29]).

[d] This is also in part a paraphrase of a statement in § 19 of [Pe29]. One might see in this item an anticipation of the heavy-atom effect [Ka87]. But Jabłoński refers to aqueous or alcoholic solutions of dyes, and in this respect his statement is wrong. In order to justify the assignment made in paragraph [f], the required enhancement of the transition $N \rightarrow M$ by solute-solvent interaction would have to be of the order of 10^6 .

[e] With *solutions* Jabłoński implies *liquid solutions*. By an *inactive band* Jabłoński means not an unobservable band but a band leading neither to prompt fluorescence nor to delayed fluorescence

or phosphorescence (Kasha [Ka87] misunderstood the meaning of *inactive bands* implied by Jabłoński). The second statement in [e] is certainly correct but not original.

[f] This paragraph contains Jabłoński's main message, to which the title of the Note refers. He offers an explanation for the drop of the energy yield of the fluorescence upon excitation in the hot-band range in the lowest absorption band. He explains this drop by assigning the weak absorption in the hot-band range to the transition $N-M$. It is not clear whether Jabłoński at that time knew the *quantitative* relation between the strength of an absorption band and the radiative lifetime of the excited state (cf. [Pe29], §§ 7, 18). If the radiative lifetime $\tau_r(N)$ of the fluorescent state N is of the order of 5 ns and the transition $N-M$ has still 0.2 to 2 % of the strength of the transition $N-F$, then the radiative lifetime $\tau_r(M)$ would be of the order 2.5 to 0.25 μ s, which is incompatible with the very long lifetimes of the low-temperature phosphorescence. This objection was advanced by Pringsheim [Pr46, Pr49, p. 308]. If Jabłoński indeed knew the quantitative relation between the strength of an absorption band and the radiative lifetime of the excited state, then he implied by the "appreciably greater" in [d] an extreme enhancement of the transition $N-M$ by solute-solvent interaction (as already mentioned in the comment to [d]).

If the title of Jabłoński's Note indeed indicates his main message, then – from the present point of view – his Note is essentially the wrong explanation of an impurity effect. A positive appreciation of the Note and of his later paper [Ja35a] will be given in section 7.

6. Jabłoński (1935): E-type delayed fluorescence and phosphorescence

Jabłoński's famous paper "On the mechanism of the photoluminescence of dye phosphors" [Ja35a] is an elaboration of the ideas in his Note [Ja33b]. The important original feature of this article is the quantitative treatment of the temperature dependence of the intensity ratio of the two types of "phosphorescence" (E-type delayed fluorescence and phosphorescence $T_1 \rightarrow S_0$, or in the terminology of [Le41], alpha and beta phosphorescence). From this temperature dependence an activation energy can be calculated that should be approximately equal to the energy difference between the states M and F . Lewis, Lipkin and Magel [Le41] later exploited and confirmed this idea. I quote the relevant passages from [Le41]:

»Jablonski [Ja35a] has interpreted some of these facts by assuming that a single excited state is responsible for both of these processes and that while the beta process [= phosphorescence $T_1 \rightarrow S_0$] is essentially spontaneous, the alpha process [= E-type delayed fluorescence] requires thermal activation up the fluorescent state. We shall find it possible to give a quantitative corroboration of this theory.« (p. 3005)

»In interpreting the two types of phosphorescence we shall adhere to an important theory of Jablonski. He considered three energy levels represented by the base lines N , F and P in Fig. 9. [Fig. 9 is Lewis own diagram taking into account also transient absorption leading to upper levels P' , P'' , ...] ... Some of the F molecules, however, instead of going directly to the ground state, pass into a state P , which Jablonski calls the metastable state [M], but which, to avoid any implications, we call the phosphorescent state. ...

This simple scheme of Jablonski has been criticized on several grounds by Pringsheim and Vogels [Pr36c]. ... It seems to us that the scheme of Jablonski is sufficiently flexible to take care of such complexities as they arise.

A second objection raised by Pringsheim and Vogels to Jablonski's scheme was that an inspection of the qualitative data existing in the literature made it seem doubtful whether the heat of activation of the P to the F molecules would at all coincide with the difference in energy between the alpha and beta bands. Our present experiments give the first opportunity of testing this question quantitatively.« (p. 3012)

Finally, the acknowledgment in [Le41] is noteworthy: »We wish to thank Professor Peter Pringsheim who has been kind enough to read our manuscript and to call our attention to several items in the literature which we had overlooked.« [p. 3017]

From the preceding quotations it is obvious that Lewis essentially accepted Jabłoński's ideas and not Pringsheim's objections against them. Jabłoński mentions his disagreement with Pringsheim in the footnote ²⁾ on p. 38 of [Ja35a]: »Herrn Prof. Dr. Peter Pringsheim sei auch an dieser Stelle für die Diskussion sowie für die Mitteilung einiger experimenteller, unter Mitwirkung von Herrn Vogels gewonnenen Daten herzlichst gedankt. Es sei jedoch bemerkt, daß die hier geäußerten Ansichten denen von Herrn Prof. Pringsheim (nach seinem letzten Brief) nicht vollkommen gleich sind.« [[I wish to say many thanks to Prof. Dr. Peter Pringsheim also at this place for the discussion and for the communication of experimental data obtained in collaboration with Mr. Vogels. It should be noted, however, that the views expressed here are not completely equal to those of Prof. Pringsheim (according to his last letter).]]

Apart from the disagreement alluded to by Lewis et al. [Le41], Jabłoński's explanation of the drop of the fluorescence yield with anti-Stokes excitation must have been a major point of Pringsheim's criticism (cf. [Pr46,Pr49] and Part II). In connection with F. Perrin's treatise [Pe29] the following sentence in [Ja35a] is of interest:

»Wir nehmen an: falls ein "energetisch isoliertes"²⁾ Farbstoffmolekül phosphoreszenzfähig ist, so muß in diesem Molekül mindestens ein metastabiles Niveau vorhanden sein³⁾.«

[[We assume: if an "energetically isolated" dye molecule²⁾ can phosphoresce, then there must be at least one metastable level in this molecule³⁾.]] [p. 39]

The two references are: »²⁾ Wie die energetische Isolation zu erzeugen ist, siehe [[On generating the energetic isolation see ...]] H. Kautsky, Chem. Ber. **64**, 2053, 2677, 1931; **65**, 401, 1932. –³⁾ A. Jabłoński, Nature **131**, 839, 1933; vgl. auch [compare also] F. Perrin, Fluorescence, Paris (Librerie Herman [Librairie Scientifique Hermann]) 1931, S. [page] 23.«

Jabłoński's way of citing F. Perrin's work may have caused at least in part the present lack of familiarity with F. Perrin's contribution to the "Jabłoński diagram". He did not cite the original article [Pe29] but the monograph [Pe31] which has been probably unavailable in most physics libraries in the world.

7. Conclusion

F. Perrin. In his paper "Fifty years of the Jabłoński diagram" [Ka87], Kasha writes on p. 667: »Nevertheless, overlooking these interesting but small pitfalls of his paper in the perspective of 50 years of hindsight (!), the Jabłoński 1933 Note and 1935 paper stand as giant steps in the transformation, of a long history of qualitative luminescence observation, into the beginnings of a quantitative science of molecular photophysics.« My comment to this eulogy: More than any other paper on the photophysics of solutions of that time, Francis Perrin's great treatise [Pe29] would deserve Kasha's words of praise. In my view, in the years from 1924 to 1929, Francis Perrin contributed more to our present understanding of the photophysics of solutions than anybody else in the field. The fact that part of his work has not found the deserved lasting recognition has two causes. First, Perrin's work on the metastable state of dye molecules was inadequately cited by Jabłoński and not at all cited by Pringsheim and Lewis. Second, and perhaps more importantly, Perrin changed his field of research completely in the mid-thirties. He found nuclear physics more interesting than molecular photophysics [Ch93]; in the last 20 years of his scientific career, from 1951 to 1970, Perrin was the head of the French Atomic Energy Organization (Commissariat à l'Énergie Atomique). Thus he did not have the opportunity to remind later generations of photochemists and photophysicists of his past scientific achievements by his presence at dozens of conferences on photochemistry and related subjects.

A. Jabłoński. His lasting merit is the assignment of the phosphorescence (in the present definition) to the direct radiative transition from a metastable state to the ground state. In this connection I should like to quote my favorite Göttingen physicist, Georg Christoph Lichtenberg [Li58]: »Es ist sonderbar, daß nur außerordentliche Menschen die Entdeckungen machen, die hernach so leicht und simpel scheinen.« [[It is curious that only extraordinary men make those discoveries that afterwards appear so easy and simple.]]

Although Jabłoński's interpretation of the alleged low quantum yield of anti-Stokes fluorescence was wrong, he was nevertheless right in his assumption that the radiative transition from the ground state to the metastable state should be observable, and he was moreover right in his implicit assumption that there is no upper limit of unity for the fluorescence energy yield. Thus his search for inactive absorption bands was reasonable.

By his second paper [Ja35a] on the temperature dependence of the intensity ratio of E-type delayed fluorescence and phosphorescence, Jabłoński had a great influence on the later work by Lewis, Lipkin, and Magel [Le41]. The fact that Lewis [Le44] called his own diagram "Jabłoński diagram" reflects Lewis' high appreciation of Jabłoński's work.

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