

PIONEERS IN PHOTOPHYSICS

From the Perrin Diagram to the Jabłoński Diagram.

Part 2.

1. Introduction

A year ago I published in this journal an article with the title "From the Perrin Diagram to the Jabłoński Diagram" [Ni96]. My aim in that article has been to let the reader see Jabłoński's Note in Nature [Ja33b] in the context of preceding work by F. Perrin, Vavilov and Pringsheim and by Jabłoński himself. Jabłoński's ideas on the metastable state and the delayed fluorescence of dye molecules [Ja33b] are virtually identical with F. Perrin's ideas on that subject [Pe29, Pe31], and his diagram looks like a completed Perrin diagram. Because of these facts I supposed that F. Perrin's ideas on metastable states were not completely unknown to Jabłoński in April 1933, when he submitted his Note to Nature [Ja33b]. My explanation of the missing reference to F. Perrin's work in [Ja33b] was that the main message of [Ja33b] refers to the efficiency of anti-Stokes fluorescence of dyes, as indicated by the title of [Ja33b], and not to the postulation of a metastable state.

This explanation was severely criticized by Jabłoński's daughter, Prof. Danuta Frąckowiak of Poznań Technical University, in a letter [Fr97] to H. J. Kuhn, the Managing Editor of EPA Newsletter. In particular she pointed out that Jabłoński writes in his habilitation thesis [Ja34] that he did not know Jean Perrin's work on phosphorescence when he wrote the Note for Nature. Because of that letter I decided to change my publication schedule: The originally planned Part 2, *From the Jabłoński diagram to the Lewis-Kasha diagram*, has been deferred to a later date. The objectives of the present article are as follows:

Section 2. As far as the controversy on Jabłoński's references to the work of J. Perrin and F. Perrin is concerned, the best I have been able to do is to offer in section 2 my translation of § 6 of Jabłoński's habilitation thesis. In this connection, relevant passages from the work of F. Perrin [Pe31] and J. Perrin [PeJ26] are quoted in the Appendices 1 and 2. Apart from that controversy, § 6 of Jabłoński's habilitation thesis is of interest, because it contains supplementary material to his Note in Nature [Ja33b]. At the end of section 2, two passages from another paper by Jabłoński [Ja35c] will be quoted, in which he cites F. Perrin in a completely satisfactory manner.

Section 3. The First International Congress on Photoluminescence in Warsaw in 1936 was a major event in the history of photoluminescence research. It will be shown that phosphorescence and metastable states of dye molecules were dealt with at that Congress in several lectures – in contrast to an assertion made by Kasha [Kas87]. Some details on the Congress will be given, including a list of all published lectures in Appendix 3.

Section 4. In Part 1 [Ni96] it has been shown that Jabłoński's Note in Nature [Ja33b] was an attempt to explain the drop of the quantum yield of anti-Stokes fluorescence (the second part of Vavilov's law). In the present section 4 my report on the history of Vavilov's law will be completed.

Finally I hope that the present article together with Part 1 may contribute to a more discriminate appreciation of Jabłoński's work at *The Jabłoński Centennial Conference on Luminescence and Photophysics* in Toruń in 1998.

Some overlap of Part 2 with Part 1 has been unavoidable. As far as possible I shall adhere to a chronological order. Furthermore, since most of the cited old literature is not easily accessible, I shall quote rather long passages from the cited literature. Most of the pre-war literature of interest here is written in French, German, and Polish. Quotations of original texts are marked by the quotation marks « ». Occasional errors in the originals have not been corrected. To my regret, in order to reduce this article to a reasonable length, I had again, as in Part 1, to omit most quotations of original texts. My English translations of quotations are enclosed in double brackets [[]. A question mark [?] will indicate either that I am not sure that my translation is correct or that I did not understand the meaning of a statement. In case of doubt about the original language, the list of references should be consulted. My own additions in a quotation are marked by single brackets [], and my own emphasis of a passage is indicated by underlining. My own inserted longer remarks or comments are in general indicated by separate paragraphs with the initial word *Comment*.

In most cases, quoted texts are labeled by two numbers in braces, $\{i,j\}$, where i is the page number of the original and j is the number of the paragraph (beginning with $j = 1$ on each page). Footnote signs like ¹⁾ or (¹) in the originals have been left unchanged in all quotations; the corresponding footnote is either inserted in brackets [] immediately after the footnote sign or given at the end of a translation. If a reference is identical with one of the references of the present article, it is replaced by the present reference.

In any work on the history of science, the author has to cope with the problem of changes in terminology. In particular the use of the word "phosphorescence" has changed completely. In the old literature, a phosphorescence is essentially an emission with a decay time long enough to be detectable with a phosphoroscope. Thus E-type delayed fluorescence and phosphorescence in the present sense, $T_1 \rightarrow S_0$, were both called "phosphorescence". In the table below the present terminology is compared with that in the cited literature. Whenever 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 [Lew41]	fluorescence, $F \rightarrow N$	alpha phosphorescence, $F \rightarrow N$	beta phosphorescence, $P \rightarrow N$
Lewis & Kasha [Lew44]	fluorescence, $S' \rightarrow S$	fluorescence, $S' \rightarrow S$	phosphorescence, $T \rightarrow S$

Finally a problem with the transcription of Russian names is to mention. For instance, the pre-war German transcription of "Вавилов" is "Wawilow", and the English transcription of "Вавилов" is "Vavilov". I have not yet found a completely satisfactory way to solve this problem.

2. Jabłoński's habilitation thesis and his references to the work of J. Perrin and F. Perrin

Jean Perrin writes in a footnote on page 337 of [PeJ26]: «On sait combien il est fréquent dans l'histoire de la Science, que dans le même temps (ici encore plus long à cause des cloisons produites par la guerre) une idée surgisse de façon indépendante en de nombreux esprits. » [[One knows how frequent it is in the history of science that in the same period of time (here still longer because of the barriers created by the war) an idea turns up independently in numerous minds.]] It should be clear that this quotation is made in Jabłoński's favor. – The following text is the complete § 6 of Jabłoński's habilitation thesis [Ja34] in my translation.

§ 6. [[Mechanism of the photoluminescence of dye molecules

{33,2} The phenomenon of phosphorescence in the true sense of the word is observed only in solids. We can distinguish two main types of phosphorescent solids, i.e. of phosphors. Representatives of the first type are the so-called Lenard phosphors.

{33,3} The phosphorescence centers in those phosphors are formed by activation with small additions, e.g. of heavy metals, to a chemical compound that is unable to phosphoresce without these additions. The structure of the phosphorescence centers in phosphors of this type is undoubtedly very complex. To the phosphors of the second type belong solid solutions as well as adsorbates of dyes (§ 3), in which the ability to phosphoresce is not due to the formation of molecular complexes of various kinds but exclusively due to the good isolation of the dye molecules from quenching acts. The ability to phosphoresce is a property of the dye molecule itself¹⁾ [Kau31, Kau32]. Here we will be concerned only with phosphors of this second type.

{33,4-34,1} Investigations of solid solutions of dye molecules²⁾ [Pr26] (e.g. in sugar) show that phosphorescent molecules are almost always able to fluoresce as well. Differences in the [spectral] excitation range of phosphorescence and fluorescence were not observed. At higher temperatures the spectra of phosphorescence and fluorescence are either identical or the phosphorescence spectrum is a little richer; that is, it possesses, apart from the bands common with the fluorescence spectrum, bands at the long-wavelength side of the spectrum, which are relatively weak at higher temperatures. At lower temperatures the relative intensity of these bands in the phosphorescence grows, and at the lowest temperatures (e.g. of liquid air) just these bands at the longest wavelengths remain the only bands in the spectrum – the color of the phosphorescence light exhibits a visible change. Simultaneously the lifetime of the phosphorescence always increases.

{34,2} H. Kautsky and coworkers¹⁾ [Kau31a, Kau31b, Kau32] made similar though only visual observations. He noticed that the fluorescence and the phosphorescence of adsorbates do not differ in their color at room temperature. At lower temperatures the color of the phosphorescence changes and its lifetime increases (similarly as in solid solutions). The experiments of the same authors on the quenching of the phosphorescence and the fluorescence from adsorbates by additives (e.g. by oxygen) led to the conclusion that dye molecules that are adsorbed at suitable places are in a state of good "energetic isolation". The luminescence is quenched only [at sites] where the molecules of the admixture (e.g. O₂) have access to the dye molecules.

{34,3} These interesting observations required supplementary [work], in particular the part concerning the identity of the spectra of phosphorescence and fluorescence at room temperature. That is, it seemed risky to me to draw the conclusion of the identity of the bands (resulting from the views developed below on the mechanism of luminescence [cf. {35.5-36.2}]) exclusively on the basis of the observed color of the light. Therefore I have performed special spectral investigations on the Cellophane adsorbates mentioned in § 3 (with the exception of isoquinoline red).

{34,4-35,1} The fluorescence was excited with the light of a Weule arc lamp (Zeiss), which had passed a Wood ultraviolet filter for the removal of the visible region of the spectrum; the spectrum [of the fluorescence] was photographed with a Fuess spectrograph (6.5 × 9 cm) with glass optics. The exposure time was about 1 min when a relatively wide slit of the spectrograph was used. After the superposition of a reference spectrum of a quartz mercury lamp of the Soltan type¹⁾ [A. Soltan,

Spr. i Pr. P. T. F. IV, 301, 129 [1929?]] on the fluorescence spectrum, the spectrograph was placed at a Becquerel phosphoroscope, to which the tested adsorbate was attached. The phosphorescence was excited with the total (nonfiltered) light of the Weule arc [lamp]. The use of a filter was now unnecessary, because there was no danger of a contamination of the phosphorescence by stray excitation light. The phosphorescence exposure time was about 1 hour.

{35,2} Fig. 13 (see plate on last page) is a reproduction of the printing block [?] with photographs of the spectra of fluorescence and phosphorescence from euchrysine.

{35,3} These photographs (made also for tryptaflavine and rhoduline yellow) show that indeed the same bands occur in the spectrum of the fluorescence and of the phosphorescence. Possibly they differ a little in the distribution of the intensity, but this distribution, as shown in § 3, depends on the spectral composition of the excitation light; the requirements of the experiments described here, however, demanded the use of different excitations for fluorescence and phosphorescence.]]

Comment. The next two paragraphs are those in which the preceding work of J. Perrin is mentioned and to which Prof. Frąckowiak refers in her letter [Fr97]. The pertinent text is quoted first in the Polish original and then in the translation. The important footnote ³⁾ on page 35 is given at the end, after {42,4}.

{35,4} «Opisane tu zjawiska fotoluminescencji nie znajdowały dotychczas teoretycznego wyjaśnienia. Pewne próby w tym kierunku były zrobione przez Jeana Perrina ³⁾. Nie obejmują one jednak całokształtu opisanych tu zjawisk. Niziej podam mechanizm, który, jak się zdaje nietylko się nasuwa, lecz wprost się narzuca ³⁾ [Ja33b].

{35,5} Częstoczka barwnika okazująca zdolność fosforyzowania posiadać musi, jak zakładam, conajmniej jeden poziom metatrwały (długożyciowy). (Założenie to zostało wprowadzone również przez J. Perrina). Poziom ten (*M*, rys. 4) musi być nieco niższy od poziomu nietrwałego (*F*), do którego prowadzi cząsteczkę akt absorpcji światła o jakiegokolwiek długości fali należącej do dziedziny widmowej pasma absorpcji.» (...)

{35,4} [[The photoluminescence phenomena described here have not yet found a theoretical explanation. Certain attempts in that direction were made by Jean Perrin ³⁾. They do not comprise, however, the whole of the phenomena described here. Below I will offer a mechanism which – as it seems – not only suggests itself but is simply obvious ³⁾ [Ja33b].

{35,5-36,1} A dye molecule that is able to phosphoresce has to possess, as I will demonstrate, at least one metastable (long-lived) level. (This assumption was also introduced by J. Perrin). This level (*M*, fig. 4) must be a little lower than the unstable level (*F*), to which a molecule is taken by the act of absorption of light of an arbitrary wavelength belonging to the visible region of the absorption band. As is known, the absorption act leading directly from the normal state (*N*) to the metastable state (*M*) has a very low probability, the absorption band corresponding to the direct transition *N*→*M* should have an unusually low intensity. To simplify matters, we assume that the energy levels of a molecule are completely "sharp" and, moreover, the same for the acts of absorption and emission. Hence we neglect the vibrational levels of molecules as well as the broadening of electronic levels by the action of intermolecular fields and the shifts of emission bands relative to absorption bands, discussed in § 3. We will consider only the electronic levels. A molecule, which has been excited by light absorption to the level *F*, can either return to the normal level by emitting the fluorescence band (the transition *F*→*N*) or alternatively reach the level *M* (transition *F*→*M*). The question, whether the transition *F*→*M* is a spontaneous transition or also a forced one must remain open for the time being.

{36,2} If the thermal energy of the surrounding medium is high enough, it may transfer to the dye molecule an energy sufficient for its renewed rise to the level *F*. The probability of such a transition will be therefore a function of the temperature of the medium. From the level *F* the molecule can pass to the normal level, emitting a band that is (nearly) identical with respect to its spectral composition with the fluorescence band. Therefore we have the emergence of phosphorescence at

higher temperatures, as for instance that observed in Cellophane phosphors at room temperature: the colors of fluorescence and phosphorescence are the same.

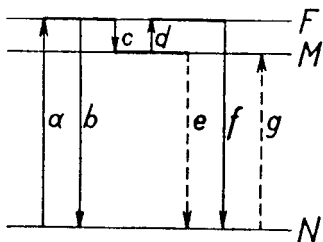


Figure 1. Fig. 1 is identical with Fig. 1 in [Ja33b], [Ja35a] and [Pr36b] and with Fig. 4 in [Ja34]. The following legend is almost identical with that of Fig. 1 of Ref. [Ja33b]:

[[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 weak intensity.]]

{36.3-37.1} If the probability of the direct transition (either spontaneous or forced, but with emission of light) from the metastable to the normal level, $M \rightarrow N$ is not negligibly small, then by sufficiently lowering the temperature of the phosphor, and hence by impeding the transition $M \rightarrow F$, we will be able to observe the light emitted at the direct transition from the metastable to the normal level ($M \rightarrow N$). The lower the temperature of the phosphor, the greater is the intensity of that band in the phosphorescence spectrum in comparison with the band $F \rightarrow N$. At the lowest temperatures only the band $M \rightarrow N$ will appear. Its emission corresponds to a phosphorescence with changed color and longer lifetime at low temperatures.

{37.2} If we took into account the vibrational energies of a molecule, we would get a more complex picture: several vibrational bands would be connected with each of the electronic transitions. The mechanism proposed here accounts for the observations by Pringsheim and Vavilov ¹⁾ [Pr26] on solid solutions and for the observations made by Kautsky and collaborators (loc. cit.) and by the present author on adsorbates of dyes. Unfortunately, the spectra of the adsorbates at low temperatures have not yet been investigated – the observations at those temperatures were made only visually; there seems to be no doubt that we have here phenomena completely analogous to those taking place in solid solutions.

{37.3} I note here that the mechanism proposed above does not comprise the problems connected with the polarization of photoluminescence. We will deal with the phenomenon of polarization in the next section [§ 7. Polarization of the photoluminescence light of dyes].

{37.4} The investigations by Kautsky showed enormous differences in the sensitivity of fluorescence and phosphorescence to quenching reagents.

{37.5} It is known that dyes, which fluoresce even intensely in some liquid solutions, never phosphoresce in such solutions – the phosphorescence occurs only in glassy solutions and possibly at lower temperatures. The explanation of these facts offers no difficulty.

{37.6-38.1} Stern and Volmer ²⁾ [O. Stern and M. Volmer, Phys. ZS. 20, 183, 1919] gave a formula for the intensity of the fluorescence light as a function of the number of quenching collisions per second (of the probability of quenching). To speak of collisions, and therefore also of quenching collisions, with the molecules of the solvent, in solids and liquids, is obviously meaningless; after all, the molecules are there always in the range of the fields of the adjacent molecules, that is, in the state of a collision. We will speak of quenching events instead of quenching collisions. And to this case the formula of Stern and Volmer can be applied.

{38.2} The intensity of the luminescence I depends on the number of quenching events per second (the probability of quenching) k and of the lifetime τ of the initial state for the luminescence according to the formula

$$I = I_0 / (1 + k\tau) \quad (17)$$

where I_0 is the intensity, which we would observe, if there were no quenching at all.

{38.3} For a molecule under definite external conditions (temperature, type of solvent, concentration of solution, etc.) k is usually different for different states of excitation, e.g. for the states F and M in fig. 4.

{38.4} However, the lifetimes in these levels differ considerably more. The lifetime in the level F is $\sim 10^{-10} - 10^{-9}$ sec., whereas for the levels M it approaches occasionally 10 to 20 seconds, i.e., it is $10^9 - 10^{11}$ times longer. In view of this it is clear that a molecule is able to phosphoresce only under conditions of an extremely good isolation of molecules from quenching acts. In connection with the rather short lifetime in the initial levels for the fluorescence bands, the latter can be found under conditions of considerably worse isolation than the phosphorescence. In liquids exclusively molecules with a sufficiently complex structure fluoresce, never simpler ones. In this connection the supposition is expressed that in those complex molecules the groups of atoms responsible for fluorescence are relatively well protected against quenching acts.

{38.5} In the light of these remarks it becomes clear why the photoluminescence, and in particular the photoluminescence of long duration – the phosphorescence, is a phenomenon so rarely encountered.

{38.6-39.1} In connection with the mechanism of the photoluminescence, a certain supposition suggests itself with respect to the cause of the sudden drop of the fluorescence yield curve for excitations in the long-wave part of the spectrum.

{39.2} The most natural explanation of the dependence of the fluorescence quantum yield on the exciting wavelength seems to be an interpretation in terms of the superposition of different absorption bands. For different absorption bands, i.e. different levels, the quantity k in the Stern-Volmer formula may be different; the fluorescence yield will be still the more different, in particular, with excitation of a molecule to an electronic level higher than the initial level for the fluorescence band (F); that level (F) can be reached only in an indirect way, whereby a large portion of the molecules can be just as well converted directly to the normal state, bypassing the level F . There may be entirely inactive absorption bands – the yield of fluorescence excitation is equal to zero in such bands.

{39.3} As classical theory as well as quantum theory teach, the probabilities of transitions between two states of a molecule at the act of absorption are proportional to the transition probabilities at emission. If there is a transition at all, although with very low probability, from the metastable level M (fig. 4) to the normal level N , then the opposite transition must take place, too.

{39.4} In the presence of perturbations, which occur for example in solutions through the fields of the surrounding molecules, the probability of a ("forbidden") transition may strongly increase. It seems absolutely possible that it reaches a value of the order of 1% of the probability of an allowed dipole transition. According to the above-mentioned, the absorption leading a molecule in liquid solution to the long-lived level will be totally inactive – the molecule at the long-lived level in liquid solution will be quenched undoubtedly.

{39.5-40.1} As the experiments by Pringsheim and Vavilov, by Kautsky and by the author ¹⁾ [description of sample preparation] show, the molecules of fluorescein phosphoresce [under suitable experimental conditions]. Therefore a metastable level M exists, and transitions $M \rightarrow N$ are possible. Hence there must be transitions $N \rightarrow M$, which cannot be discovered in the absorption spectrum – the main absorption band $N \rightarrow F$ completely covers its weak long-wavelength neighbor.

{40.2} In the region, where the absorption coefficients of the main band decrease to a value lower than 2% of the value in the maximum, the influence of that weak band on the fluorescence yield may appear, in particular in view of the perturbations by the surrounding molecules of the liquid, which increase the transition probability. Obviously the band $N \rightarrow M$ will be totally inactive, which explains in a completely satisfactory way the drop of the [fluorescence] yield curve at the long-wave side, observed in solutions of fluorescein (see § 5).

{40.3} In connection with this drop of the yield some observations were made on the scattering of the excitation light in concentrated solutions of fluorescein – since the suspicion had come up that scattering might be the cause of the drop of the yield. I quote them here although, as it seems, the effect is too small to explain the observed drop of the yield.

{40.4-41.1} The observations were made in the following way: two small plane-parallel cuvettes were placed side by side. One of them was filled with distilled water, the other, however, with an ammoniacal-aqueous solution of fluorescein of the concentration 1×10^{-2} gr./cm³. The fluorescein solution was filtered through a Schott sintered-glass filter [?] and stored in a Leybold bottle with a ground-glass stopper for half a year before performing the experiment. The light from a monochromator with glass optics (Leiss) entered the cell with distilled water and from there the cell with the solution. The light coming [from the cells] perpendicularly to the direction of the [incident light] beam was observed. By increasing the wavelength of the exciting light it was possible to notice the gradual transition from a surface fluorescence to a volume fluorescence; the color of the fluorescence light didn't change initially (the intensity distribution in the fluorescence spectrum of an aqueous solution of fluorescein does not change with the change of the excitation wavelength). Upon further increasing the wavelength, the color of the beam begins to change – it takes a reddish color (reabsorption has no influence on the change of the color, with the used arrangement). The intensity of the beam in the solution remains always stronger than in the pure solvent [this refers to the observed scattered light].

{41.2} This is, however not a pure fluorescence. The observed light is now polarized to a very high degree. This is testified by the photographs of the beams made through an Iceland spar crystal [= Nicol prism?] (figs. 14 and 15 on the last page). The "intensity" of one of the images is considerably higher than [that of] the other. It is known, however, that in aqueous solution of fluorescein the fluorescence light is completely depolarized. It seems, therefore, that we are dealing here indeed with scattering and, as the photographs show, with a considerably more intense scattering than in a pure solvent.

{41.3} We cannot say anything definite on the cause of the observed scattering. Perhaps it is brought about by more macroscopic causes; here an effort was made to eliminate at least some of them.

{41.4} Also the following causes are possible: as Weisskopf's theory ¹⁾ [V. Weisskopf, ZS. f. Phys. 85, 451, 1933] shows with respect to atoms – an atom that is irradiated with a wavelength longer than the wavelengths lying in the range of intense absorption can be excited to its eigen vibrations (anomalous scattering) or rather scatter light with unchanged wavelength (Raman scattering does not interest us here); both [processes] take place with a probability that is the higher the closer the frequency of the incident light is to the eigen frequency of the atoms.

{41.5} A necessary condition for the occurrence of anomalous scattering is the finite width of the initial state [?] of the scattering atoms.

{41.6-42.1} A similar phenomenon could take place in the case of molecules. The normal state of dye molecules in solution possesses a finite width due to the perturbation by the molecules of the solvent. In contrast to the case of monatomic vapors, the light emitted by molecules is not subject to a complete reabsorption, because the fluorescence band is shifted relative to the absorption band to the side of longer wavelengths. Thus, in addition to Rayleigh scattering also anomalous scattering may take place.

{42.2} Another cause could be the scattering by the "fluorescence center". The intensity of scattering depends on the size of the scattering particles as well as on the difference between the refractive indices of those particles and of the medium in which they are located.

{42.3} The refractive index of the "fluorescence center" must reach very considerable values for wavelengths close to the range of absorption bands. Hence, although the diameter of the "center" is probably relatively small in comparison to the wavelength of the scattered light, the intensity of the scattering may reach, in view of the magnitude of the refractive index, considerable values.

{42.4} Since it is premature, however, to draw final conclusions from these preliminary observations of scattering, their publication has not seemed advisable to me.]]

Footnote ²⁾ to {35.4}: «O próbach tych dowiedziałem się już po ogłoszeniu mojej notatki dotyczącej mechanizmu fotoluminescencji (Nature, 131, 839, 1933) pośrednio z broszury Francis'a Perrina. Odpowiednia publikacja Jean'a Perrina nie jest tam zacytowana.» [[About those attempts I learned indirectly from a brochure by Francis Perrin only after the publication of my note concerning the mechanism of the photoluminescence (Nature, 131, 839, 1933). A pertinent publication of Jean Perrin is not cited there.]]

Comments

Comment to {33,3}. Jabłoński's clear distinction between the two types of phosphorescence centers is essential. J. Perrin and Pringsheim were less clear in this respect, and this may be one reason why Pringsheim was unable to see the progress made by J. Perrin and F. Perrin in the interpretation of phosphorescence (cf. sections 3.4 and 3.5).

Comment to {35,3}. The slight dependence of the photoluminescence spectrum of a solid solution on the composition of the excitation light was correctly interpreted by Jabłoński. This dependence is the basis of spectral hole-burning.

Comment to {35,4}. The brochure by Francis Perrin, to which Jabłoński refers in footnote ²⁾ of page 35, is obviously identical with [Pe31], which is cited in his later paper [Ja35a]^{a1}. In Appendix 1 those passages from [Pe31] are quoted which refer to metastable states. Jabłoński's statement that no pertinent publication of J. Perrin is cited in [Pe31] is not entirely correct. It is true that the main text of [Pe31] contains no references at all. But at the end of [Pe31] a list of general references is given, the first of them being a long article by J. Perrin [PeJ26]. In Appendix 2 some passages from [PeJ26] are quoted. – For the last sentence of {35,4} I have not found an adequate English translation. In German one could say: "Weiter unten werde ich einen Mechanismus vorschlagen, der sich – wie es scheint – nicht nur anbietet, sondern geradezu aufdrängt." – This statement nicely expresses Jabłoński's amazement that nobody before him had found that simple explanation for the occurrence of two types of phosphorescence.

Comment to {36,3-37,1}. In this paragraph Jabłoński goes beyond the ideas of F. Perrin. The message of the last sentence of [Pe31] (cf. Appendix 1) is that the radiative transition $M \rightarrow N$ is not completely forbidden and that the radiative lifetime of M may be of the order of 1 second. Jabłoński seems to have come independently to the same conclusion, but in addition he was the first to assign the known low-temperature phosphorescence to the transition $M \rightarrow N$.

Comment to {37,5}. The statement that phosphorescence never occurs in liquid solutions has been wrong (cf. my comments to Pringsheim's lecture and the quotation from [Pe24] in section 3.5). The same wrong statement is repeated in {39,4}. Jabłoński shared this wrong view with most of his contemporaries working on photoluminescence of solutions.

Comment to {37,6-38,1}. Jabłoński's scientific background was in part his own work on collision-induced broadening of spectral lines and energy exchange at collisions [Ja31].

Comment to {38,6-40,3}. In these paragraphs Jabłoński develops in detail those ideas, which are the main message of his Note in Nature [Ja33b], i.e. his explanation of the alleged drop of fluorescence quantum yield in the range of anti-Stokes excitation.

Comment to {39,2}. Jabłoński's assumption of the existence of *inactive* absorption bands (above or below $N \rightarrow F$) that do not lead to fluorescence has been correct. An example of the direct internal conversion of a higher electronic state into the electronic ground state N , bypassing the lowest excited fluorescent state F , is reported by Vavilov (see Fig. 4 in [Vav36]), who also uses in this connection the term *inactive band*. The best known example for this kind of behavior is the anomalously low quantum yield of the fluorescence from benzene upon excitation at about 8000 cm^{-1} above $S_{1,0}$ [Bra63] (known as "channel 3" for benzene vapor). Finally, the "forbidden" transition $N \rightarrow M$ has been observed with many compounds, beginning with the early work by Lewis and Kasha in 1945 [Lew45].

Comment to {39,4-40,2}. The basic fallacy in Jabłoński's argumentation results in part from the missing clear distinction between radiative and nonradiative transitions. The increase of the rate constant for the nonradiative transition $M \rightarrow N$ by a quencher does not necessarily imply a proportional increase of the rate constant for the radiative transition $M \rightarrow N$ and the absorption coefficient

^{a1} The Polish language – like Russian or Latin – has no articles corresponding to the definite article "the" and the indefinite article "a" in English. Therefore, depending on the context, the translation of "pośrednio z broszury Francis'a Perrina" can be either "from *the* brochure by Francis Perrin" or "from *a* brochure by Francis Perrin". In the present case, the indefinite article "a" is appropriate, since Jabłoński doesn't cite this brochure at any other place in his habilitation thesis.

for the transition $N \rightarrow M$. Furthermore, even if such a proportionality existed, Jabłoński would be only partly right: He would be right as far as the lack of a phosphorescence is concerned, in the sense of a long-lived emission detectable with a phosphoroscope. But now the emission $M \rightarrow N$ should be observable as a *prompt* emission, whose distinction from the long-wavelength tail of the fluorescence band $F \rightarrow N$ would be difficult, admittedly, if the energy gap between the levels M and F is small (as with many dyes). – Jabłoński's explanation of the drop of fluorescence quantum yield with anti-Stokes excitation was later criticized by Vavilov [Vav45, Vav46] and Pringsheim [Pr46]; (cf. the quotations from the latter papers in section 4).

Comment to {40,3}. This paragraph shows that, despite his own "confirmation" [Ja33a] of Vavilov's results, Jabłoński was not yet completely convinced of the correctness of the experimental results.

Jabłoński's later citations of F. Perrin's work on metastable states. In my letter [Ni97] to Prof. Frąckowiak I wrote in item (4): «My criticism of Jabłoński's way of citing the scientific literature has been obviously restricted to the missing citation in [Ja33b] and the inadequate citation in [Ja35a] of F. Perrin's work on the metastable state. In his paper [Ja35c] on the negative polarization of the phosphorescence, Jabłoński cites F. Perrin [Pe29] in a satisfactory way: (a) [Pe29] is the first cited paper (page 313), and it is clear for the reader that F. Perrin was the first to explain the E-type delayed fluorescence by postulating the existence of a metastable state. (b) [Pe29] is a second time cited on page 321, and the name Perrin is even mentioned in the main text. Unfortunately, the unambiguous acknowledgment of F. Perrin's priority by Jabłoński in [Ja35c] was ignored by other scientists in this field of research.» In the following I quote the two mentioned passages of [Ja35c] in my translation:

§ 1. [[Introduction. If a piece of Cellophane foil is tinged by adsorption of a suitable dye, it becomes fluorescent and usually also phosphorescent. If the temperature of such a "Cellophane phosphor" is high enough, then the spectral position of the observed phosphorescence band [E-type DF] is identical with the spectral position of the fluorescence band. Obviously the initial level for both emission processes is the same. The ability to phosphoresce can be explained by the existence of a metastable level M in the molecule, which is below the initial level of the fluorescence (which we will call F). A molecule that is excited to the state F by light absorption may either emit the fluorescence band $F \rightarrow N$ (N – ground level), or pass to the metastable state M , and return from that state to the state F at the expense of thermal energy, and only then emit the fluorescence band $F \rightarrow N$].] (...)

¹⁾ F. Perrin, Ann. de phys. 12, 169, 1929. A. Jabłoński, Nature 131, 839, 1933 and ZS. f. Phys. 94, 38, 1929.

§ 3. [[Theoretical remarks. Attempts at a theoretical explanation of the occurrence of negative polarization of photoluminescence were made by Wawilow ¹⁾, Perrin ²⁾ and the author ³⁾.]] (...)

¹⁾ S. I. Wawilow, ZS. Phys. 55, 690, 1929.

²⁾ F. Perrin, Ann. de phys. 12, 169, 1929.

³⁾ A. Jabłoński, ZS. f. Phys. 96, 236, 1935.

3. The First International Congress on Photoluminescence in Warsaw, May 20 to 25, 1936

3.1. Kasha's report on the Congress in Warsaw. My first knowledge of the International Congress on Photoluminescence in Warsaw came from Kasha's article *Fifty Years of the Jabłoński Diagram* [Kas87], from which I quote the second and the third paragraph of the introduction:

«A comprehensive overview of Aleksander Jabłoński's work in molecular luminescence appears in his 1936 paper [6] [Ja36] presented at the International Conference on Photoluminescence in Warsaw. May 1936 (Pringsheim's introduction names it the World's first international conference on the subject). The names of the conferees cover the whole range of the World's most prominent scientists of the time, working on spectroscopic phenomena. Jabłoński's paper discusses vibrational structure of molecular transitions, the Stokes rule of fluorescence shifts, mirror symmetry of fluorescence and absorption, and especially, polarization of molecular electronic transitions. All of the discussion is oriented toward the properties of dyestuff molecules.

Inexplicably, Jabłoński's now classic and most influential papers [1, 2] [Ja33b, Ja35a] (1933-1935, on the "Jabłoński Diagram") are not cited in this *Acta Physica Polonica* paper (submitted March 15, 1936). This paper is a mathematical summary of Jabłoński's concepts, with quantum mechanical cognizance. His now famous diagram does not appear in this paper, nor any of his elegant analyses of the kinetics of excitation. Perhaps the spectroscopic uncertainties in the minds of physicists of the time on the nature of electronic states of molecules, uncertainties which persisted until a late date, cautioned Jabłoński against considering a quantum mechanical translation as being premature. These 1933 and 1935 papers on the "Jabłoński Diagram" therefore will be discussed in their full historical perspective in the last sections of the present paper.»

Having read this quoted text ten years ago I concluded that metastable states of dye molecules in general and the Jabłoński diagram in particular were not treated at the Congress in Warsaw. This conclusion has been wrong. Instead of directly commenting the quoted text, I prefer to communicate some details on the Congress in Warsaw and extracts from three articles that are directly or indirectly related to Jabłoński's work on metastable states of dye molecules.

3.2. Pringsheim's Foreword to Volume 5 of *Acta Physica Polonica*. The printed lectures of the Congress are contained in volume 5 (1936) of *Acta Physica Polonica*. From Pringsheim's Foreword to that volume one can learn a lot on the Congress:

(a) The original plan was to organize a small meeting of Polish and Russian physicists working on fluorescence. The correspondence with scientists from other nations revealed, however, the interest in an international conference on that subject, and it was agreed to organize such a conference in Warsaw.

(b) The aim of the organizers was to cover all aspects of photoluminescence. Hence each invited lecturer was asked to concentrate on a speciality in which he was particularly active and competent. As far as the phosphorescence of dyes was concerned, the first choice was Pringsheim – and not Jabłoński. As will be seen below, this was a clear advantage for Jabłoński, because his lasting achievements – the work connected with his diagram and with phosphorescence polarization – were treated in detail by Pringsheim, and on the other hand Jabłoński's wrong explanation of the drop of the fluorescence yield upon anti-Stokes excitation, was not mentioned by Pringsheim (Pringsheim strongly disagreed with Jabłoński on that explanation – cf. section 4.3).

(c) At the opening of the Congress, page proofs of most of the submitted articles of the invited lecturers were available to the participants; this greatly facilitated the later discussions. (Cf. the dates of receipt in the list of all printed articles in Appendix 3.)

(d) The Russian scientists were not able to come to Warsaw (in 1936 began the first great political purge of the Stalin era). Their names in the order of their printed lectures are: Kondratiev, Landsberg, Mandelstam, Terenin, Duschinsky, Levshin and Vavilov. In connection with a discussion of Jabłoński's work on metastable states and his (wrong) explanation of the second part of

Vavilov's law, in particular the absence of Terenin, Levshin and Vavilov was a great loss to the Congress.

(c) Apart from the Russian scientists, the following scientists were also unable to come to Warsaw: Kastler, Krishnan, J. Perrin, Przibram and Rosen. Kastler's lecture was presented by Soleillet and J. Perrin's lecture by F. Perrin. The total number of lectures was 19. The number of registered participants was 149.

(f) Pringsheim and Jabłoński were elected president and secretary general, respectively, of the Congress.

(g) The lectures were divided into two groups. In the first group the luminescence of gases and vapors was treated and in the second group the luminescence of condensed systems. In each group the lectures were given in the alphabetical order of the names of the lecturers.

(h) The allotted time for each lecture was half an hour, and most lecturers kept to that time. The discussions after the lectures were sometimes longer than the lectures themselves. Thus the printed discussion remarks can give only a weak impression of the discussions that really took place. One may get an idea of the intensity of some of the discussions from the discussion remarks after Mrozowski's lecture *Polarization of the fluorescence from diatomic vapors and the influence of collisions on it*. After the two and a half pages of discussion remarks, there are in addition three pages of supplementary remarks to the lectures of Finkelburg and Mrozowski; in eight items the agreement or disagreement on the electronic states of Hg, has been documented and signed by four scientists: W. Cram, W. Finkelburg, W. Kapuściński, and S. Mrozowski.

3.3. Levshin: Research on the decay of the luminescence and the emission mechanism of different substances [Lev36]. Since Levshin's manuscript was received only after the Congress (June 12, 1936), it did not influence the discussions at the Congress. Nevertheless it is of interest here, because it documents that the phenomenon of phosphorescence was one of the hot topics in photoluminescence research in 1936. The Introduction of [Lev36] is remarkable because of its distinct formulation of different positions. In the following the complete introduction of [Lev36] is quoted in my translation.

{301.1-303.5} [I. Introduction. Already the first quantitative investigations of the luminescence decay of phosphorescent substances (performed by E. Becquerel) have shown the great variety of laws that apply to it.

Thus, for example, for the description of the decay of the short-lived luminescence from uranyl salts, Becquerel¹⁾ found that it is possible to apply the exponential law

$$I = I_0 e^{-t/\tau}. \quad (1)$$

On the contrary, the decay of the phosphorescence from alkaline earth substances was expressed by the empirical formula¹⁾

$$I''(C+t) = C, \quad (2)$$

which has a hyperbolic character.

For the theoretical explanation of the phenomenon of phosphorescence, one usually applies one of the two following schemes: In the first scheme, the process of phosphorescence excitation is envisaged as a certain restructuring of the phosphorescence centers and the process of emission as the return of the centers to their normal state.

According to the second scheme, the excitation is accompanied by a complete detachment of a part of the phosphorescence center and the emission is produced during the recombination of the two parts.

The idea that one got of the parts that separate changed in the course of time. In the present interpretation these parts are electrons and ions.

The first scheme, which corresponds to an incomplete detachment of the electron from the phosphorescence center, leads to an exponential decay law.

If one has several species of centers, this formula is of course replaced by the formula

$$I = \sum I_{0i} e^{-t/\tau_i} \quad (3)$$

The second scheme, which corresponds to a complete detachment of the electron, leads to a hyperbolic law of the second degree in t :

$$I = a / (b + t)^2 \quad (4)$$

Thus, the processes of the two different schemes have a very different decay; for that reason the study of the decay laws can give valuable information on the luminescence mechanism.

The cases are rare, however, where the luminescence decay exactly conforms to the simple formulae (1) or (4).

Moreover, often a preconceived notion on the nature of the luminescence impeded the experimenters in getting an idea conform to reality, even in cases where the experiment gave sufficient results for that. In this connection, the example of the uranyl salts is very instructive. Despite the old works of E. Becquerel, cited before, E. Nichols, H. Howes and E. Merritt²⁾ tried at all costs to apply the bimolecular scheme in this case too, i.e. to subject the experimental data on the [luminescence] decay of the uranyl salts to a hyperbolic formula; since that attempt was not successful, they had to complicate the whole picture extremely by admitting the superposition of several different processes.

The more recent studies by S. I. Vavilov and the author have shown, however, that all data of Nichols and Merritt, as well as the new data obtained by us, agree perfectly with the simple exponential formula (1), i.e. they correspond to a strictly monomolecular [= first order] process.

In this report I intend to study two further cases of luminescence, whose course of decay, to all appearances, was explained in the wrong way: I want to speak on the one hand about phosphorescent zinc sulfide and on the other hand about phosphorescent substances on the basis of boric acid.

E. Nichols and E. Merritt considered the luminescence reaction scheme of zinc sulfide and of alkaline earth materials to be bimolecular⁴⁾, and P. Lenard, in his first studies of phosphorescent materials of the mentioned class, had initially the same view. Later, however, Lenard himself and the scientists of his school [e.g. Tomaschek] dissociated themselves from that opinion and allied with the party [of the supporters] of the monomolecular process.

P. Lenard's theory of phosphorescence centers that are clearly separated from the surrounding medium did not admit the detachment of the electron during excitation beyond the boundary of the center; this point of view has found its expression in the decay law (3) where the different I_{0i} and τ_i correspond to different groups of luminescence centers⁵⁾.]

Comment: Of the two remaining sections II and III of [Lev36], section III is of interest in connection with the decay of metastable states of dye molecules.

III. [[Investigations on the emission mechanism of phosphorescent substances on the basis of boric acid

{314,3-317,2} Completely different results were obtained in particular for another class of phosphorescent substances: for phosphorescent substances on the basis of boric acid (Tiede) and for the phosphorescent materials based on $Al_2(SO_4)_3 + 18 H_2O$ (Travnickč).

These substances are prepared by partially removing the water from the compounds serving as base and by introducing in its place certain organic compounds.

In 1922 R. Tomaschek¹²⁾ performed very careful experiments on the luminescence of phosphorescent boric-acid materials and arrived at the conclusion that the mechanism of their luminescence is similar to the mechanism of the luminescence of phosphorescent alkaline earth materials. For the phosphorescent materials that were activated by phenanthrene he found a complex decay law, which was expressed by the sum of four exponential functions. In our experiments, Vinokurov¹³⁾ and myself have taken dyes as activators: uranin, eosin, erythrosin, esculin and naphthionic acid. The luminescence spectrum consisted in all cases of an extremely broad luminescence band, which covers nearly the entire visible spectrum. The experiment was made at the two extreme parts of the spectrum. We have been able in this case to establish that the decay law is the same for the blue part and for the yellow part of the spectrum. The luminescence decay of that class of phosphorescent materi-

als strictly follows the exponential law (1) (in these experiments the intensity varied in a ratio of 1:100).

The study of the decay as a function of the intensity of the excitation light has shown no change of the decay for an increase of excitation by a factor of 50.

Fig. 10 represents the decay of phosphorescent boric-acid materials with different activators (I – uranin, II – eosin, III – erythrosin, IV – esculin, V – naphthionic acid). [Figs. 10, 11 and 12 are semilogarithmic plots of luminescence intensities as functions of time.]

In figs. 11a and 11b the decay of phosphorescent materials (uranin in boric acid) is given for different concentrations of the activator (uranin): I – 1×10^{-4} , II – 3×10^{-4} , III – 6×10^{-4} , IV – 3×10^{-3} g/g. These latter figures show the great change of the initial intensity of the luminescence and the relatively weak change of τ determined from the slope of these lines as a function of the activator concentration.

Table II.

Activator	C g/g	τ sec	I_0
Uranin	1×10^{-4}	1.00	—
"	3×10^{-4}	0.97	1.00
"	6×10^{-4}	0.95	—
"	3×10^{-3}	0.66	—
Eosin	3×10^{-4}	0.84	0.07
Erythrosin	3×10^{-4}	0.55	0.01
Esculin	3×10^{-4}	0.85	0.16
Naphthionic acid	3×10^{-4}	1.50	0.02

Fig. 12 represents the decay of the luminescence of phosphorescent materials based on $Al_2(SO_4)_3 + 18 H_2O$, activated by uranin: 1 – ($\lambda = 460 - 495 \mu\mu$), 2 – ($\lambda = 550 - 620 \mu\mu$).

In table II we give the values of τ for the phosphorescent materials of the mentioned type, corresponding to different activators with different concentrations. The strictly exponential character of the decay of the phosphorescent boric-acid materials testifies to an essential difference between the mechanism of their luminescence and the mechanism of the luminescence of phosphorescent materials based on zinc sulfide and alkaline earths; their excitation is not accompanied by a complete detachment of an electron.]]

¹⁾ E. Becquerel, *La lumière*, Tome 1, p. 278 et 295, Paris, 1867.

²⁾ E. L. Nichols and H. L. Howes, *Fluorescence of the uranyl salts*. Washington 1919. *Phys. Rev.* 9, 292, 1917.

³⁾ S. I. Wawilow und W. L. Lewschin, *ZS. f. Phys.* 48, 397, 1928.

⁴⁾ E. Nichols and E. Merritt, *Studies in luminescence*, Washington, 1912.

⁵⁾ V. p. ex. [[see for instance]] P. Lenard, R. Tomaschek u. F. Schmidt, *Handbuch d. Experimentalphysik*, 1928.

¹²⁾ R. Tomaschek, *Ann. d. Phys.*, 67, 612, 1922.

¹³⁾ W. L. Lewschin and L. A. Vinokurov, *Phys. ZS. d. Sowjetunion*, 10, 10, 1936.

Comment: The work by Levshin and coworkers on the decay law of the phosphorescence from dye phosphors was important for the later work of Lewis, Lipkin and Magel [Lew41] (that famous paper contains the first, tentative, identification of the phosphorescent state with the lowest triplet state). In the third paragraph of their introduction, these authors write:

«There has been some controversy as to the true law for the rate of phosphorescent decay, but the work of Schischlowski and Wawilow³ [*Physik. Z. Sowjetunion*, 5, 379 (1934)] and of Lewschin and Vinokurov⁴ [*Physik. Z. Sowjetunion*, 10, 10 (1936), identical with ref. 13 in Levshin's article] indicates that when the phosphorescence is due to a single substance the rate of decay is exponential. In other words, it is a reaction of the first order. If the reaction were due to some part of the molecule, which then returned slowly, owing to the high viscosity of the medium, the order of the reaction would depend upon the distance of ejection but would never be of the first order.»

3.4. J. Perrin: Molecular induction [PeJ36]. The title of J. Perrin's article refers to the ideas of J. Perrin and F. Perrin on the mechanism of fluorescence quenching. Two mechanisms were distinguished: (1) long-range energy transfer due to the overlap of the fluorescence spectrum of the excited molecule and of the absorption spectrum of the quencher (Förster energy transfer in the present terminology); (2) collision-induced energy transfer to an electron donor like an iodide anion followed by ionization of the latter; the electron acceptor is, however, the solvent – and not yet the excited molecule. Apart from "molecular induction" also the mechanism of phosphorescence is treated, which is of interest here.

The treatment of "phosphorescence" in the sections 1. *Activated molecules* and 5. *Phosphorescence* of [PeJ36] is essentially the same² as in [PeJ26] (cf. Appendix 2) – with one notable exception: In the first paragraph on page 326 J. Perrin admits the possibility of a direct radiative transition from a metastable state to the ground state:

«Il n'est pas exclu que certaines de ces phosphorescences soient des fluorescences à très longue vie moyenne, mais on doit classer à part celles qui sont sensibles aux variations de température.»

[[It cannot be excluded that some of these phosphorescences are fluorescences of very long lifetime, but one had to exclude those [phosphorescences], which are sensitive to variations of temperature.]]

Comment. "Fluorescences of very long lifetime" mean direct radiative transitions from metastable states to ground states, as postulated by Jabłoński. One misses a clear definition of the "metastable" state. – The lecture was given by F. Perrin, whose views in this matter were much more distinct, as can be seen from [Pe29] (cf. Part 1) and [Pe31] (cf. Appendix 1). One may assume that, in case of doubt, F. Perrin presented rather his own view than that of his father. Since the manuscript of J. Perrin's lecture was received in Warsaw only in the middle of the Congress (May 23), it is rather likely that the discussion remarks refer to F. Perrin's *oral* presentation – and not to [PeJ36]. The three printed discussion remarks refer exclusively (Pieńkowski) or in part (Pringsheim and Tomaschek) to the mechanism of phosphorescence:

Mr. S. Pieńkowski (in French):

[[How can one justify the necessity of the availability of additional energy in the moment when the activated center of the phosphor passes from the metastable state to the nonexcited state, i.e. in the moment of light emission? The influence of the temperature on the phosphorescence would become apparent in the same way, if the collisions played only the role of a perturbation leading to the liberation of the energy accumulated during the excitation; we know many normally forbidden spectral lines, whose emission is made possible by the action of collisions. Is it therefore absolutely necessary that the activated center receives energy?]]

Mr. F. Perrin (in French):

[[If the collisions intervened only to make possible the light emission, without transfer of energy, the influence of the temperature would be weak. One can understand a strong influence of the temperature only if energy has to be supplied to the metastable activated center (exponential Maxwell factor).]]

Comment: Pieńkowski was the director of the Institute for Experimental Physics, in which Jabłoński worked, and he should have been familiar with Jabłoński's work. His question indicates, however, that possibly he did not see the fundamental difference between the two kinds of "phosphorescence": delayed fluorescence $F \rightarrow N$ (E-type DF), to which Perrin referred, and low-temperature phosphorescence $M \rightarrow N$ ($T_1 \rightarrow S_0$) (cf. also section 2).

² Readers to whom the original of [PeJ36] is accessible should note that the assignment of the symbols a , A and α to electronic states in [PeJ36] differs from that in [PeJ26] (cf. Appendix 2) and [Pe29, Pe31] (cf. Appendix 1). The notation corresponding to the electronic states S_0 , S_1 , T_1 is a , α , A in [PeJ36], A , a , α in [PeJ26] and [Pe29, Pe31], and N , F , M in [Ja33b, Ja35a].

Mr. P. Pringsheim (in German):

1) [[I should like to point out that the interpretation of the phosphorescence given here only repeats Lenard's presentation, translated into a more modern language; the attachment of the detached electron to a new equilibrium position under simultaneous energy transfer to the heat motion, so that it can return to the initial position only by accepting energy from the heat motion, corresponds exactly to the transition to a metastable level that is energetically below the state directly reached by irradiation.

2) I really believe that all processes, in which a metastable state is interposed between excitation and light emission, and whose duration is therefore invariably temperature-dependent, should be called phosphorescence, in agreement with Mr. Perrin; in this connection it is not essential whether from the metastable level by heat supply the original excited level is reached or another level, from which then the emission of light takes place; i.e. the scheme is more general than given by Perrin, $\uparrow \text{---} \downarrow$.

3) There are still numerous organic substances that act as strong quenchers without having absorption bands close to the fluorescence band of the fluorescent dye; I am therefore somewhat skeptical, whether in other cases really this "induction moléculaire" through resonance action plays a role.]]

Mr. F. Perrin (in French):

[[I agree to the two first remarks of Prof. Pringsheim.]] (In French: «D'accord pour les deux premières remarques du Prof. Pringsheim.») [Then follows a detailed answer to the third remark.]

Comment: Pringsheim's first remark is typical for his attitude to J. Perrin's and F. Perrin's contributions to the elucidation of the phosphorescence mechanism (for a short description of Lenard's view cf. the introduction of Levshin's paper [Lev36] in the preceding section 3.3). Either he tries to belittle these contributions as in the first remark, or he does not even mention or cite them, as in all his papers, handbook articles and books that are known to me (cf. the list of references and in particular my comments to Pringsheim's lecture in section 3.5). F. Perrin's approval to Pringsheim's first remark was too generous; the progress made by J. Perrin and in particular by F. Perrin in the interpretation of phosphorescence was less trivial than suggested by Pringsheim. In Lenard's model the phosphorescence is due to geminate electron-cation recombination. The medium surrounding the central atom or molecule is essential for providing a trap for the incompletely detached electron. In F. Perrin's model the medium acts only as a heat bath, accepting or supplying energy; the transition from the fluorescent state to the metastable state is an intraatomic or intramolecular process. In contrast to Lenard's model, F. Perrin's model does not require a rigid medium for the explanation of phosphorescence. In this connection F. Perrin's discovery of phosphorescence (E-type DF) from liquid solutions of eosin and erythrosin was of fundamental importance (see also the quotation from [Pe24] in the next section).^{#1}

3.5. Pringsheim: Fluorescence and Phosphorescence of adsorbed dyestuffs [Pr36b]. Pringsheim begins his article [Pr36b] with a detailed description of Kautsky's work [Kau31a, Kau31b, Kau32, Kau33] on the fluorescence and phosphorescence (E-type delayed fluorescence and phosphorescence in the present sense) of adsorbed dyes (pp. 361-363). On page 364 he writes:

{364,1} [[Excited dye molecules can also react with oxygen, but it is not known whether this reaction is a direct one or if in the first step metastable oxygen is formed, which subsequently reacts with a second dye molecule. This fact has been known long since not only for adsorbed dyes but

^{#1} I did not have the time to study J. Perrin's publications preceding [PeJ26]. In [PeJ26] most of the references refer to his own work or that of his school (Lenard is not cited). In [PeJ36] there are no explicit references at all (names are cited, sometimes the year, but never the usual data as journal, volume, year, and page number). The omission of references in printed lectures was not unusual at that time; in volume 5 of *Acta Physica Polonica* also the lectures of Solcillet, Pohl, and Tijeica (cf. Appendix 3) contain no references. – If there was a kind of animosity of Pringsheim against J. Perrin, or at least a certain reluctance to cite J. Perrin, then perhaps this was caused by J. Perrin's lax citation practice in some of his papers.

also for liquid solutions of dyes: A bleaching or discoloration is the consequence of such photooxidation. In these processes too, metastable excited molecules seem to play the main role, as follows from an experiment of Miss Boudin ¹⁾ [Journ. Chim. Phys. 27, 285, 1930], an experiment perhaps worth to be repeated: she observes in a solution of eosin in waterfree glycerol apart from a fluorescence with $\tau = 3 \times 10^{-9}$ sec also a much weaker phosphorescence with $\tau \sim 10^{-3}$ sec; by addition of KI the phosphorescence is much more quenched than the fluorescence, but the rate of bleaching decreases in the same proportion as the phosphorescence intensity. From the relative intensities of the fluorescence and the initial value of the phosphorescence [= E-type DF] (ca. 400 : 1) Boudin calculates that in equilibrium [= in the steady state of continuous excitation?] the number of metastable molecules should be about 800 times larger than that of normal excited molecules. Now, in a solution [of eosin] in glycerol, the conditions for the metastable states are still much less favorable than for [eosin] adsorbed at silicagel in the vacuum, for which $\tau \sim 0.5$ sec was found ²⁾ [H. Vogels, Thèse, Brussels 1935, probably identical with [Vo35]; cf. also [Pr36c]]; quantitative measurements on the intensities are not yet available, but here the relative intensity of the phosphorescence [= E-type DF] should be also [i.e. in proportion to the longer lifetime of the metastable state] considerably higher than in glycerol. Thus it turns out that, in the undisturbed equilibrium [steady state?], the number of metastable molecules is by many orders of magnitude larger than the number of molecules in the fluorescent state.]]

Comment: Miss Boudin was a coworker of J. Perrin. The same qualitative result was already mentioned by F. Perrin in § 62 of his thesis [Pe29]. As already mentioned in connection with Pringsheim's first discussion remark after F. Perrin's presentation of J. Perrin's lecture, the observation of phosphorescence from a *liquid* solution cannot be explained in terms of Lenard's geminate-recombination model. Therefore the underlined phrase "an experiment perhaps worth to be repeated" (in German: «...wie aus einem vielleicht der Nachprüfung werten Versuch von Fräulein Boudin hervorgeht. ...») should not be understood in a positive sense: Pringsheim *doubts* the correctness of Boudin's results for an obvious reason: a phosphorescence from *liquid* solution can no longer be explained with Lenard's mechanism. In this connection F. Perrin's remarkable early paper [Pe24] on the role of viscosity in fluorescence phenomena is to be mentioned, from which the last paragraph is quoted:

«Ceci conduit à penser, en développant une idée déjà indiquée par Wiedemann [Wi1888], que la viscosité intervient seulement en gênant la diffusion : une molécule isolée peut subsister un temps très long dans l'état critique, mais elle retombe presque instantanément à l'état normal, lorsqu'une molécule de même espèce vient passer suffisamment près. Si la dilution n'est pas extrêmement grande et si la viscosité est faible, toute molécule se trouve approchée par une molécule semblable, même en un temps très court [...] et aucune molécule ne peut subsister longtemps dans l'état critique. Il me paraît probable que des solutions aqueuses très étendues (10^{-8} ou 10^{-9}) donneraient lieu à des phosphorescences observables, mais pour avoir une quantité de lumière suffisante il est nécessaire d'opérer avec des cuves très profondes.»

[[This makes one think, by developing an idea already indicated by Wiedemann [Wi1888], that the viscosity intervenes only by impeding the diffusion: an isolated molecule can exist a very long time in the critical state, but it returns almost instantaneously to the normal state, when a molecule of the same kind passes close enough. If the dilution is not extremely great and if the viscosity is low, every molecule is approached by a similar molecule, even during a very short time, and no molecule can remain for a long time in the critical state. It seems to me likely that very dilute aqueous solutions (10^{-8} or 10^{-9} [mol dm⁻³]) would lead to observable phosphorescences, but in order to have a sufficient quantity of light it is necessary to work with very deep cuvettes.]]

Comment. F. Perrin not yet uses the term "metastable state" in [Pe24], but it is clear that the critical state he refers to is the long-lived state responsible for phosphorescence [E-type DF]. Today many examples of genuine concentration quenching of triplet states are known (in the case of aromatic thiones, the concentration quenching of the lowest triplet state is diffusion-controlled even in fluid solvents [Brü78, Ma93]). F. Perrin's view of the metastable state in this early paper is

already more advanced than that of J. Perrin in [PeJ26]. For F. Perrin it seems to be already clear that the metastable state is a molecular property – and not the result of a particular interaction with the medium. – In the following the quotation from Pringsheim's lecture [Pr36b] is continued:

{365,2-366,1} [[The spectrum of the afterglow of the adsorbates in general does not differ from that of the fluorescence. This afterglow is a genuine phosphorescence [E-type DF] (in the sense of the nomenclature that after its proposal by Perrin now seems to be generally accepted), as has been recently demonstrated by quantitative measurements: Immediately after the end of excitation, the intensity of the light emission drops instantaneously to a [small] fraction of its previous value and then decays exponentially; the mean lifetime τ strongly increases with decreasing temperature, and at the same time the phosphorescence intensity becomes weaker and weaker. In the case of tryptophan adsorbed at silicagel, which has been studied in detail, the afterglow of the bands is virtually no longer observable at -70°C . This behavior corresponds exactly to the characteristic scheme in Fig. 1 [identical with the Jabłoński diagram in Fig. 1], which was given by Jabłoński for a typical phosphorescence. Part of the molecules primarily excited to the fluorescent state F pass to the metastable state M , from where they can return to F only by energy transfer from the heat bath. That the light sum [the total emitted E-type DF] does not remain constant, i.e. that the decrease of the brightness is not fully compensated by the increase of τ for each temperature, can be only explained by the fact that radiationless energy exchange with the medium ("collisions of the 2nd kind") becomes more probable with increasing τ . If a sample is excited at low temperatures, where the phosphorescence of the band $F \rightarrow N$ is absent, and then rapidly heated in the dark, a small fraction of the absorbed [excitation] energy is emitted as a flash of that band (in analogy to the behavior of the sulfide phosphors, but with much smaller yield); this phenomenon too was observed by Kautsky.

Comment: The preceding quoted paragraph is curious (but for me no longer surprising) by its giving credit exclusively to Jabłoński – and not to J. Perrin and F. Perrin. The reported explanation of E-type delayed fluorescence is virtually identical with that given by F. Perrin in [Pe29] and [Pe31] (cf. Appendix 1). An uninitiated reader might come to the conclusion that J. Perrin and F. Perrin introduced a new terminology – and nothing else. Jabłoński's own and undisputed contribution to our present understanding of phosphorescence is given in the subsequent paragraph:

{366,2} [[At low temperatures, in the afterglow of all hitherto investigated dyes a new band appears that is always shifted to longer wavelengths. As Jabłoński proposed as simplest possibility, one can tentatively interpret this band as "fluorescence of long duration" and assign it to the transition $M \rightarrow N$. That this emission is a very unlikely but nevertheless spontaneous transition – and not a genuine phosphorescence, has become very likely by quantitative measurements of the decay process ¹⁾ [Vo35]; the decay can be again represented by an exponential curve, but τ is virtually independent of temperature within wide limits (from -40° to -180°). That the simple scheme for the mechanism is nevertheless not sufficient, we believe to have demonstrated nearly with certainty, but I will not discuss in detail this question, which is not essential for the adsorbates. I have to come back to the just mentioned bands later.]]

Comment: The criticism expressed in the last but one sentence is fundamental. In the last sentence of [Pr35c] Pringsheim and Vogels write: «Ces deux luminescences ne peuvent donc pas provenir d'un même état métastable M .» [[Hence these two emissions cannot originate from the same metastable state M .]] The two luminescences are the E-type delayed fluorescence and the phosphorescence in the present sense. The quoted sentence means that the Jabłoński diagram was not really accepted by Pringsheim and Vogels. – Pringsheim comes back to phosphorescence in connection with polarization:

{373,3} [[The phosphorescence [E-type DF] from solid solutions and adsorbates shows in general a polarization of the same orientation and magnitude as the [prompt] fluorescence. Accordingly Jabłoński finds also for the phosphorescence of the cellophane phosphors the same behavior with respect to their polarization as described above for the fluorescence; only the absolute values of the degree of polarization are always a little lower, which of course is not surprising, since – with

longer duration of a luminescence – all secondary depolarizing effects (concentration effect, partial molecular reorientation) must become more important. The new, red-shifted bands that appear in the afterglow at low temperatures (and which, as already mentioned, should be considered to be not a phosphorescence [E-type DF] but a fluorescence of long duration [$T_1 \rightarrow S_0$]) are – also with polarized excitation – virtually unpolarized for many dyes.

{373,4-373,5} The corresponding bands of tryptaflavine and euchrysine, however, exhibit in isotropic [solid] media (sugar, glycerol, gelatin) a very pronounced "negative" polarization ³⁾ [Pr35 and a hint to Jabłoński's work], i.e. if the exciting light is polarized $\parallel Y$, and hence also the preferred vector of the normal fluorescence bands falls into the same direction, [on the contrary] the preferential direction of the polarization is now $\parallel X$; some other dyes like rhodamine and rhoduline orange display the same phenomenon to a much lower degree. Cellophane phosphors that are stained with these substances exhibit for the afterglow at -180° all [polarization] phenomena, which have just been described for the normal fluorescence bands, with negative sign ¹⁾ [Ja35c]: The maxima of the negative polarization occur at the same orientations, at which those of the positive polarization were found before, and for the orientations, in which the polarization became weakly negative, it is now weakly positive. The whole phenomenon can be interpreted as follows: For the electronic transitions characterizing the new band, the anisotropy of the emission oscillator is rotated by 90° relative to the other emission oscillators ²⁾ [= hint to analogous phenomena in atomic spectroscopy]. It is still completely open, why adsorbates of tryptaflavine at silicagel, whose fluorescence and phosphorescence [E-type DF] is polarized strongly positively at $+20^\circ$, exhibit at -180° a red-shifted afterglow without any trace of negative polarization, in contrast to Jabłoński's observations just described.]]

Comment: The possibility that a luminescence may have a negative degree of polarization was already shown by F. Perrin (§ 49 of [Pe29]), several years before Jabłoński (cf. the end of section 2). – In the discussion after Pringsheim's lecture, Tomaschek asked how sure it was that the short-lived fluorescence and the long-lived phosphorescence had the same excitation spectrum. Pringsheim first answered this question (no significant exception to the equality of both excitation spectra was known to him) and then made a critical remark on the often overestimated accuracy of polarization data. In comments to this remark, F. Perrin communicated the error limits of the methods applied by him, and Jabłoński mentioned that the results obtained with the Savart method and with the modified Cornu method agreed satisfactorily. Jabłoński continued his remark by asking Pringsheim for some details on the negative polarization of the [low-temperature] phosphorescence from isotropic materials. According to Pringsheim, the highest degree of negative polarization (13%) was found with tryptaflavine in glycerol at -185° ; with other dyes the degree of negative polarization was lower (acridine orange, 5%, and rhoduline orange, 7.5%) or not detectable (fluorescein, eosin, rhodamine 6G, acridine red, esculin, chinine sulfate).

4. Anti-Stokes fluorescence and Vavilov's law. Part 2.

4.1. **Vavilov's law.** Readers interested in the history of Vavilov's law should consult also Part 1 (section 4 in [Ni96]). Vavilov's law is based on an experimental result [Vav27] which is shown once more in Fig. 2. Jabłoński [Ja32] was one of the first who used the term *Vavilov's law*. The following formulation of Vavilov's law is taken from Levshin's memorial speech [Lev51b, p. 517]; it refers to the result in Fig. 2 and similar results obtained by Jabłoński [Ja33a] and other scientists:

«Эта закономерность, описывающая поведение энергетического выхода люминесценции при изменении длины волны возбуждающего света, может быть сформулирована следующим образом: при переходе от коротких волн возбуждающего света к более длинным энергетический выход свечения растет пропорционально длине волны возбуждающего света, в области первой полосы поглощения выход имеет почти постоянное значение, а затем быстро падает, как только частота возбуждения становится меньше средней частоты излучения. Это закономерность носит название закона Вавилова.»

[[This regularity, which describes the behavior of the energy yield of a luminescence upon a change of the wavelength of the exciting light, can be formulated as follows: at the transition from short wave[length]s of the exciting light to longer ones, the energy yield of the luminescence grows proportionally to the wavelength of the exciting light, in the range of the first absorption band the yield has a nearly constant value, but then falls rapidly, as soon as the excitation frequency becomes less than the mean frequency of the luminescence. This regularity bears the name Vavilov's law.]]

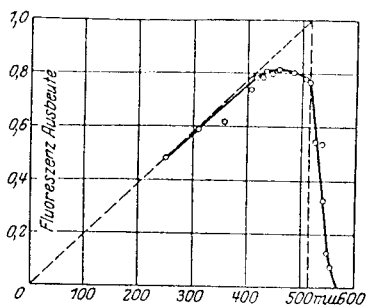


Figure 2. Energy yield κ of the fluorescence from an aqueous solution of fluorescein as a function of the excitation wavelength. Fig. 4 is identical with Fig. 3 of Ref. [Va27].

The first part of Vavilov's law is equivalent to the statement that the *quantum* yield ρ of a luminescence is independent of the excitation wavelength. The constancy of ρ has a remarkable corollary: If ρ is close to unity, then anti-Stokes excitation of a luminescence may lead to an *energy* yield κ greater than unity. Three different positions were adopted towards this corollary and the experimental result in Fig. 2:

(1) Vavilov [Vav45, Vav46] and still much later Ketskeméty and coworkers [Kc61-Kc70] believed that an *energy* yield κ greater than unity were in contradiction to the Second Law of thermodynamics. They considered the observed drop of κ in the range of anti-Stokes excitation to be a necessary consequence of a limit $\kappa \leq 1$ imposed by the Second Law (the second part of Vavilov's law) and sought a theoretical foundation of that limit.

(2) Pringsheim [Pr29] and Jabłoński [Ja33a, Ja33b] were convinced that there was no upper limit $\kappa \leq 1$ following from the Second Law. The correctness of the basic experimental result (drop of κ in the range of anti-Stokes excitation) was not disputed, but there was no agreement with respect to its explanation. The preferred explanation (which, however, was not shared by Pringsheim) was the

postulation of *inactive* absorption bands (first proposed by Vavilov [Vav27] – cf. section 4.10 in Part 1).

(3) The third position had no prominent supporters for many years. It is identical with Pringsheim's view, as far as the nonexistence of an upper limit $\kappa \leq 1$ is concerned. In addition, the drop of κ in the range of anti-Stokes excitation is considered to be an impurity effect (also first proposed by Vavilov [Vav25] – cf. section 4.6 in Part 1) or some other artifact.

In the following the post-war development of the interpretation of Vavilov's law is sketched. Five steps to our present understanding are noteworthy: (a) Vavilov's controversy with Pringsheim on the upper limit of the energy yield of a luminescence (cf. sect. 4.2 to 4.5); (b) the partial refutation of position (1) by Vavilov himself in his last paper [Vav52] (published after Vavilov's death in 1951) (cf. sect. 4.6); (c) the theoretical refutation [An55] of position (1) (cf. sect. 4.7); (d) the experimental refutation [Bor64] of position (2) (cf. sect. 4.8); (e) the experimental proof [Za95] of an energy yield $\kappa > 1$ (cf. sect. 4.9).

4.2. Vavilov (1945): Some remarks on the Stokes law. – In the present context, Vavilov's article [Vav45] is important in two respects: by his criticism of Pringsheim's view that the energy yield κ of a photoluminescence can be greater than unity, and by his attitude to Jabłoński's papers [Ja33a, Ja33b]. Confusion may arise from the nonuniform use of the Greek letters η , κ , and ρ for the two kinds of luminescence yield. In the following, in case of doubt the subscript "e" will be inserted to denote an *energy* yield.

{69,2} «Basing upon the second law Lenard ⁽⁸⁾ [Len28] (it seems at first) expressed without any special proof the statement that the yield of photoluminescence (the ratio of the emitted energy to the energy absorbed) can not exceed unity. This statement called forth, however, objections of thermodynamical character suggested by Pringsheim ⁽⁹⁾ [Pr29]. It is necessary to dwell upon these objections, as we consider Lenard's statement as quite true.»

Comment. In the following eq. (5) ρ_e is the *energy* yield of a luminescence, $\bar{\nu}$ is the average frequency of the luminescence, and ν' is the excitation frequency:

$$\{70,7\} \ll \rho_e = \bar{\nu} / \nu' \leq 1 \quad (5)$$

The inequality (5) is the generalization of Stokes's law sought for. To analyse it we choose as variable the ratio $\bar{\nu} / \nu'$, keeping in mind that, in general, $\bar{\nu}$ is a function of ν' .»

Comment. The following quotation contains Vavilov's remarks on Jabłoński's papers [Ja33a, Ja33b]:

{71,5} «4. To check the law deduced experimental data of sufficient extent are available in the old as well as in the new literature. Already in 1888, B. Walter ⁽¹⁰⁾ [Wied. Ann. **34**, 332 (1888); **36**, 522 (1889)] has found a sharp fall of intensity of luminescence in the region $\bar{\nu} > \nu'$, for the solutions of dyes. The same has been found later by S. Valentiner and M. Rössiger ⁽¹¹⁾ [Val24, Val26]. In a very broad spectral interval the dependence of the yield on ν' has been first determined by the author for a solution of fluorescein ⁽¹²⁾ [Vav27] (Fig. 3 [similar to the present Fig. 2 in section 4.1]), the results obtained wholly correspond to (5) and their graphical representation is given in Fig. 1 [schematic representation of Vavilov's law]. The results of the author have not been, however, confirmed by Szczeniowski ⁽¹³⁾ [Sz27], who did not obtain a fall of the yield and, besides, according to his measurements, in general the values of the yield exceeding unity were possible. But the work of Szczeniowski has been disproved in the same Warsaw Laboratory by Jabłoński ⁽¹⁴⁾ [Ja33a], who confirmed the results of the author. At the same time Jabłoński tried ⁽¹⁵⁾ [Ja33b] to explain the fact of a steep fall of the yield by a superposition of an inactive band corresponding to a quenched luminescence of greater duration. Such an explanation is inadmissible due to a number of reasons. First of all, the fall of the yield is a universal fact whereas the durable afterlighting is not always present. Furthermore, it is not seldom that an excitation spectrum for the durable afterlighting is the same as for the fluorescence and in that case the inactive absorption band must coincide with the

active one. With a temperature lowering, according to Jabłoński, we may expect a decrease of the steepness for the fall of the yield, actually - a contrary state of affairs, and so on.»

Comment. In the immediately following paragraph Vavilov mentions the work of Tumerman and Solomin, who observed the analogous fall of the fluorescence yield with many other dyes. Vavilov closes his paper with the statement: «At any rate, for all substance[s] studied the general law (5) has been confirmed without exceptions.» – Without doubt, Jabłoński [Ja35a] has done Vavilov a disservice by "confirming" Vavilov's results [Vav27].

4.3. Pringsheim's reply to Vavilov (1946): Some remarks concerning the difference between luminescence and temperature radiation. Anti-Stokes fluorescence. – In this reply [Pr46] to Vavilov, Pringsheim's comment to Jabłoński's interpretation of the low energy yield of anti-Stokes fluorescence is of particular interest:

{497.5-498.1} «**3. The drop of the fluorescence yield.** It seems to be a well proved fact that the curve representing the fluorescence yield as a function of the wave length of the exciting light shows a sharp drop at the wave length corresponding to the peak of the fluorescence band* [hint to refs. in [Vav45]]. Since this fact cannot be explained by Vavilov's theory, another interpretation must be found. An interpretation which has been proposed by Jabłoński (¹) [Ja33b] is definitely rejected by Vavilov, and this is the only point in his paper respecting which I agree with him although not for the same reason.»

Comment. Pringsheim, who was a master in the subtle formulation of doubt, reveals a trace of doubt in the correctness of the experimental results by the underlined "seems" in the preceding quotation.

{498.2} «Jabłoński assumes that the drop in the fluorescence yield is due to the superposition of another weak band on the long wave length tail of the normal absorption band and that absorption in this "forbidden" band raises the molecules to a metastable or quasistable state from which no normal fluorescence is emitted. It is well known that such states exist in many molecules and that when all competing processes are avoided by adequate experimental conditions a long lasting afterglow is emitted by the molecules in this state. This afterglow is a typical fluorescence of long duration, in F. Perrin's terminology, or a "slow fluorescence" as I proposed to call the phenomenon. Vavilov's first argument against Jabłoński's hypothesis is probably correct, since the drop in fluorescence yield has been observed in a few instances (rhodamine solutions) in which a slow fluorescence never could be obtained. Vavilov's second argument, on the other hand, need hardly be refuted; he states that the excitation spectrum of the afterglow "is not seldom the same" as that of the normal fluorescence and that then the forbidden absorption band must coincide with the normal absorption band. As a matter of fact, the slow fluorescence is excited *always* and exclusively by light absorption in the normal absorption band, and, in so far as dye solutions are concerned, the existence of the forbidden transition has never been observed in the absorption spectrum* [hint to different behavior of some other organic compounds [Lew45]]. Jabłoński was the first to explain this behaviour by assuming that some of the molecules which were raised by normal absorption to the excited state drop before the fluorescence emission takes place, to the quasi-stable state; and from there they are able under favourable conditions to emit the slow fluorescence band which always has a greater wave length than the normal fluorescence band.»

Comment. Note that the credit given by Pringsheim to Jabłoński in the underlined text should be given to F. Perrin and J. Perrin.

{498.3} «The average duration of the slow fluorescence, which is independent of temperature (¹) [Pr36c, Lew41], is of the order of a second, and thus the probability of the forbidden transition is about 10⁸ times lower than that of the normal fluorescence. Since, according to Jabłoński's own measurements, the drop in the fluorescence yield occurs at a wavelength at which the absorption is still about 1% of the peak absorption, it cannot be due to an appreciable degree to the forbidden transition.»

Comment. In the last paragraph {502.3} Pringsheim offers his own explanation of the drop of the fluorescence yield, which is rather vague (essentially an efficient internal conversion as a process competing with fluorescence).

4.4. Vavilov (1946): Photoluminescence and thermodynamics (Reply to Pringsheim's Reply). Although there is no doubt today that in this controversy Pringsheim was right and Vavilov was wrong, the behavior of Vavilov as a scientist was nevertheless essentially reasonable. At that time nobody seriously doubted the correctness of the experimental results on the decrease of the energy yield of the fluorescence from dyes with anti-Stokes excitation. In this respect the last paragraph of [Vav46] is of particular interest:

{502.3} «In any case, the present discussion draws attention to the necessity of studying further experimentally the photoluminescence yield, particularly as a function of the wave length of the exciting light and of the temperature. The conclusions drawn in the present paper are based on extensive experimental data on the photoluminescence of solutions. Up to the present the luminescence of gases and vapours, as likewise the photoluminescence of the crystallophosphors, has not been investigated in this respect.»

Comment. As long as Vavilov was firmly convinced of the correctness of the experimental data, he had to look for a theoretical explanation of them. Even if he had understood Pringsheim's argument in every detail, he wouldn't have been able to accept Pringsheim's conclusion, because it was at that time in contradiction to "experimental facts". In this respect it is important to distinguish a *real* experimental result from an *anticipated* one. Vavilov was right in writing:

{501.6} «This conclusion drawn by Pringsheim is of an *a priori* nature, as the anti-Stokes photoluminescence yield of Na, I, and the other simple vapours depending upon temperature has never yet, as far as I know, been measured. On the other hand, measurements for solutions confirm my point of view.»

Comment. At the end of his life, Vavilov was ready to change his mind in this question (see the end of section 4.6 below).

4.5. Landau (1946): Doubtful theoretical support for Vavilov from a theoretician. I have got the impression that Vavilov was entirely serious in his endeavor to understand theoretically the drop of the fluorescence energy yield with excitation in the anti-Stokes range. Otherwise it would be difficult to understand why he asked L. D. Landau, the eminent Soviet theoretical physicist, for support. I have made no serious attempt to understand the theoretical considerations of Pringsheim [Pr46], Vavilov [Vav46] and Landau [La46]. Nevertheless I have had difficulty in taking Landau's paper seriously. Vavilov was at that time the president of the Academy of Sciences of the Soviet Union. It would have been a very unpleasant (though not impossible) task to convince Vavilov that he was wrong. Thus Landau may have preferred to write a paper, which conceals his real opinion in that matter, a paper which most experimentalists will not understand anyhow, and from which one cannot easily draw a definite conclusion. To write a paper of that kind seems to be no problem for an experienced theoretician.

4.6. Vavilov's last paper (1951): On the causes of the decrease of the luminescence yield in the anti-Stokes range. Vavilov's last paper [Vav52] was published only after his death (January 16, 1951). Two short passages of that paper are of particular interest. The first quotation illustrates the long-lasting negative effect of authority in science (in this case of Jabłoński's authority):

{374.2} (...) «Единственная экспериментальная попытка [6] доказать, что в случае растворов красителей выход люминесценции может превышать единицу, оказалась экспериментальной ошибкой.»

{374.2} (...) [[The only experimental attempt [6] to prove that, in the case of dye solutions, the luminescence yield may exceed unity, turned out to be an experimental error.]]

Comment. Ref. [6] is identical with [Sz27]. Although Vavilov does not cite [Ja33a], it is obvious that he refers to that paper, in which Jabłoński writes that he had been able to reproduce Vavilov's results but not the results of his colleague Szczeniowski [Sz27]. By the way, it seems that in 1951 nobody doubted the correctness of the experimental results on the yield of anti-Stokes luminescence (cf. section 103 in Pringsheim's book [Pr49] and § 27 in Förster's book [Fö51]). – The following quotation is the last but one paragraph of Vavilov's paper, to which Antonov-Romanovski et al. refer in their paper [An55] (see section 4.7):

{387.5} «Вместе с тем ясно, что в случае разреженных газов, в которых за время возбужденного состояния молекулы вероятность тепловых столкновений мала, возможно ожидать антистоксову люминесценцию с выходом, превышающим единицу. Аналогичные явления могут наблюдаться при очень кратковременном возбуждении и непосредственно следующим за ним кратковременном наблюдении.»

{387.5} [[In this connection it is clear that in the case of rarefied gases, in which during the lifetime of an excited state of a molecule the probability of thermal [?] collisions is low, one may expect anti-Stokes luminescence with a yield exceeding unity. Analogous phenomena may be observed with very short excitation and immediately following short observation.]]

4.7. Pringsheim's rehabilitation: Antonov-Romanovski, Stepanov, Fok, and Khapalyuk (1955). Antonov-Romanovski et al. [An55] published in 1955 their article "Luminescence yield of a system with three energy levels". In this article it is shown for a three-level system that a fluorescence energy yield greater than unity is not in contradiction to thermodynamic laws. The authors had the thankless task to criticize a great Russian scientist who had left a large school. They met this delicate task in an admirable manner, by being in their argumentation as clear as possible and by choosing the simplest nontrivial system for their theoretical consideration. Since this excellent paper seems to be little known, I quote a large part of it in my translation.

{50.1} [[Together with the definition of luminescence given by S. I. Vavilov ⁽¹⁾ [Vav52], the law of the dependence of the fluorescence [energy] yield on the wavelength of the exciting light, formulated by him, is that principal fundament, on which the whole science of luminescence is based. Therefore the interest is completely understandable, which has been given to the theoretical proof of that law. In the literature there are a number of known attempts of a thermodynamic proof of the impossibility of an energy yield $\rho_e > 1$, however, none of them can be regarded as satisfactory.

{50.2} Sometimes it is believed (see for instance ⁽²⁾ [Lev51a]) that the existence of a process, whose only result is the production of quanta of high energy at the expense of quanta of low energy, is in contradiction to thermodynamics. But that is not the case. Without the help of luminescence, small quanta may unite in large quanta with an energy yield arbitrarily close to unity. For example in a high-frequency furnace a piece of metal can be made red-hot and its temperature can be maintained. In order to avoid thermal conduction and convection, this piece of metal can be suspended from a quartz filament in vacuum. Under these conditions the small quanta of radiowaves that are absorbed by the metal are practically completely transformed into the large quanta of visible and infrared light. In this case there are no compensating processes. Therefore, also for the luminescence one must not consider impossible the merging of small quanta into large ones without a compensating process.

{50.3} L. D. Landau ⁽³⁾ [La46] obtained from thermodynamic considerations an upper limit for the energy yield of a luminescence. But in fact it [= that upper limit] imposes nearly no limitations, because at sufficiently small density of the luminescence radiation the limit itself tends towards infinity.

{50.4} E. I. Adirovich ⁽⁴⁾ [E. I. Adirovich, [[Some questions concerning the theory of the luminescence of crystals]], Moscow, 1951, p. 24] proposed a thermodynamic cycle for the proof of $\rho_e < 1$. (...) [A detailed criticism follows.]

{50.5-51.1} The concrete model of Pringsheim ⁽⁵⁾ [Pr46], proposed by him for the proof of the possibility $\rho_e > 1$, has not been carefully examined up to now and no reason has been found why it should not work. This model consists in the following. Let us assume that there is a rarefied gas,

whose molecules in the electronic ground state possess some vibrational levels. If we irradiate it [= the gas] with light of a quantum energy corresponding to the distance between a vibrational level of the ground state and the lowest vibrational level of the excited state, then in the emission spectrum of the gas anti-Stokes lines appear, which correspond to transitions from that level to the lowest vibrational levels of the ground state. The quantum yield is equal to unity in this model and, therefore, the energy yield $\rho_e > 1$.

{51.2} The present paper is the attempt of a more careful consideration of Pringsheim's model by taking into account the background of heat radiation in the same way as it was done in the papers ⁽⁶⁾ [A155, St54] for systems with two levels. In this connection it is to be mentioned that it [= the model] is only the first step to solving the question about the yield. In it, for example, the opposite action of luminescence light on the luminescent substance (reabsorption and stimulated emission under the action of the light of the luminescence) is not taken into account. Physically this is equivalent to the consideration of an infinitely small volume of the substance, so that the density of the luminescence radiation produced by it be small relative to the density of the heat radiation.]]

Comment. After that the model is developed on two pages. The following quoted text corresponds to the last 20 lines of the original. The quantities d_{ij} below are rate constants for nonradiative transitions from the level i to the level j . Level 1 is lowest level and level 3 the highest.

{53.1} (...) [[Pringsheim's example corresponds to the case $d_{11} = d_{32} = 0$. Thus, also the more detailed calculation, with the background of heat radiation taken into account, leads to the conclusion of the possibility $\rho_e > 1$.

{53.2} It is obvious that a similar calculation can be repeated for an arbitrary system with a number of levels [= vibrational levels in the ground state] exceeding two.

{53.3} The question arises whether the obtained result contradicts the Second Law of thermodynamics. If this were the case, then from it [= the Second Law] [restrictive] conditions for the coefficients d_{11} , d_{12} and d_{21} would be obtained. Obviously, this is not at all the case. In fact, our system consists of three elements: apart from the luminescent body and the reservoir of the temperature T , from which it [= the body] draws heat energy, there is additionally the excitation source. This source can be a body heated to a temperature $T' > T$. The energy of the luminescent body together with the energy of the exciting radiation is transferred to the surrounding bodies, whose temperature is lower than the temperature of the exciting body. This is, as Pringsheim shows, analogous to the action of a refrigerator. Obviously, S. I. Vavilov arrived at similar conclusions, because in his last article ⁽⁷⁾ [Vav52], not yet published when he was still alive, he proposes that for rarefied gases $\rho_e > 1$ is possible.

4.8. Borisevich, Gruzinskii, and Tolkachev (1964): On the anti-Stokes fluorescence from molecules. – After the publication of [An55] it was probably clear to most experts that there was no chance to find a theoretical explanation of the second part of Vavilov's law. Hence only the positions (2) and (3) (cf. section 4.1) were left. The lasting (but nearly unknown) merit of Borisevich, Gruzinskii, and Tolkachev [Bor64] has been to have shown that also position (2) (the presence of "inactive" absorption bands) is no longer tenable. They demonstrated for a particular example (the fluorescence from 3,6-tetramethyldiamino- and 3-aminophthalimide in solution and in vapor phase) that the alleged drop of the fluorescence yield was an artifact resulting from impurities. Their important message is unambiguously stated in the first two short paragraphs of [Bor64]:

«В последнее время в печати появились работы ^[1-3] [Ke60, Al62, Ma62], в которых с помощью универсального соотношения ^[4,5] [St57, Al58] показано, что падение квантового выхода флуоресценции растворов при антистоксовом возбуждении связано с наличием невозбуждающего (неактивного) поглощения.

В настоящем сообщении показано, что для тщательно очищенных веществ не наблюдается антистоксово падение выхода флуоресценции паров и растворов.»

Comment: The following translation is taken from the English edition "Optics and Spectroscopy" of "Оптика и Спектроскопия". Note that – in contrast to the present situation – Western transla-

tions of Russian scientific journals were formerly rather poor (typographically as well as with respect to the quality of the translations).

«In recent years, articles have appeared in print ¹⁻³ [Ke60, Al62, Ma62] which, using a universal relation ^{4,5} [St57, Al58], have demonstrated that the decrease in the fluorescence quantum yield of solutions for anti-Stokes excitation is connected with the presence of unexcited [correctly: "unexciting" in the sense of "not leading to a fluorescent state"] (inactive) absorption.

This paper shows that, for carefully purified substances, no anti-Stokes decrease in the fluorescence yield of vapors and solutions is found.»

Comment. The attempts to find a thermodynamic explanation of the second part of Vavilov's law were continued by Ketskéméty and his coworkers in the sense of position (1) (cf. section 4.1). Inexplicably, neither the paper by Borisovich et al. [Bor64] nor the paper by Antonov-Romanovski et al. [An55] were cited by Ketskéméty et al. in their papers [Ke65, Ke70a, Ke70b, Ke82], although these two papers have probably been the most important contributions to our present understanding of Vavilov's law.

4.9. Zander and Drexhage (1995): Cooling of a dye solution by anti-Stokes fluorescence. With the paper by Zander and Drexhage [Za95] we make a leap of 30 years. Today it seems to be evident that in most cases the observed drop of the fluorescence yield upon anti-Stokes excitation was caused by unrecognized impurities with a lower S_1 state and a lower fluorescence quantum yield (relative to the main compound) [Dr96]. The post-war history of this problem is described in [Za95] and in more detail in [Za91]. Here I want to mention only one paper not cited in [Za91, Za95]. In their last article on the fluorescence yield in the range of anti-Stokes excitation, Ketskéméty and Farkas [Ke82] revise their view and write explicitly on page 20 of [Ke82]: «An analysis of this inequality [= Eq. (12) in [Ke82]] suggests that the entropy law does not exclude the possibility that the energy yield exceeds unity.»

In Fig. 3 the fundamental experimental result of Ref. [Za95] is shown: The energy yield Y_n of the fluorescence from a solution of Rhodamine 6G in deaerated monodeuterated ethanol may exceed unity. The cooling of the dye solution by fluorescence excitation can be directly observed by a thermal-lens technique.

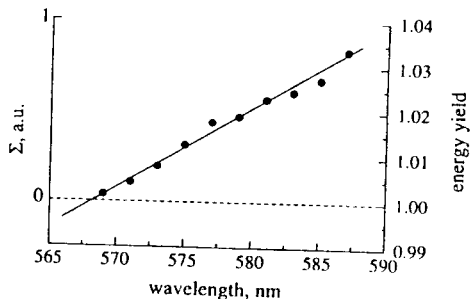


Figure 3. Figure 3 is identical with Fig. 14 of [Za95]. Energy yield Y_n versus excitation wavelength λ_0 . The quantity Σ is proportional to $(Y_n - 1)$. Experimental values of Σ : •. The solid line was calculated with Eq. (15), $Y_n = \eta_n (\lambda_0 / \lambda^*)$, where η_n is the fluorescence quantum yield and λ^* is the mean fluorescence wavelength. Parameter values: $\eta_n = 0.990$ and $\lambda^* = 563$ nm.

5. Conclusion

The Congress in Warsaw in 1936. The importance of a topic in photoluminescence research in 1936 can be measured by the invited lectures dealing with that topic at the First International Congress on Photoluminescence in Warsaw in 1936. With the exception of Kautsky, all leading experts for the phosphorescence of dye molecules were among the invited speakers (in alphabetical order): Jabłoński, Levshin, F. Perrin, J. Perrin, Pringsheim, Tomasczek, and Vavilov. J. Perrin, Levshin, Vavilov and the other invited Russian scientists were not able to take part in the Congress. The Perrin diagram was presented by F. Perrin himself, and the Jabłoński diagram was presented by Pringsheim.

Vavilov's law. In its traditional formulation Vavilov's law consists of two parts. The second part, the alleged decrease of the fluorescence energy yield with anti-Stokes excitation is no longer tenable. Positively formulated, the first part of Vavilov's law – the independence of the fluorescence quantum yield on the excitation wavelength – is valid also in the complete hot-band range of the lowest absorption band. Every identification of a compound by its fluorescence excitation spectrum is an application of Vavilov's law. By his work on fluorescence and phosphorescence Vavilov contributed much to our present understanding of radiative and nonradiative processes. In particular his determination of absolute fluorescence quantum yields has been of fundamental importance. Kasha's rule, as far as it concerns excited singlet states, is a corollary of Vavilov's law.

Pringsheim. Pringsheim has been right in considering a fluorescence energy yield greater than unity to be a physically possible process, not in contradiction to the laws of thermodynamics. As a critical scientist [Fr64] with an encyclopedic knowledge of luminescence phenomena and in part misled by his own experimental results, he became perhaps too skeptical towards Jabłoński's simple, but correct explanation of the two types of phosphorescence (i.e. of E-type delayed fluorescence and phosphorescence in the present sense). In his references to the work of Jean Perrin and Francis Perrin, Pringsheim was less generous than one might wish. In my view, Pringsheim – and not Jabłoński – has been mainly responsible for the fact that the pioneering work of Jean Perrin and Francis Perrin on the metastable state of dye molecules fell into oblivion outside France.

Authority in science and impurity effects. The history of Vavilov's law gives several examples of the negative role of authority in science: An unfounded statement of the Nobel laureate Lenard is taken more seriously than Pringsheim's well-founded view. Jabłoński's confirmation of Vavilov's results is taken more seriously than Szczeniowski's contradictory results. The second part of Vavilov's law survived Vavilov by more than 20 years. The other surprising fact is the gradual disappearance of a critical attitude towards the reliability of experimental results. Although the notorious impurity of commercial dyes was known and explicitly mentioned by Vavilov himself [Vav22], it was largely ignored in later research as a possible source of trouble.

Acknowledgment

In the present article, Jabłoński's habilitation thesis has been the most important scientific document. I am very grateful to Prof. Danuta Frąckowiak (Poznań) for drawing my attention to that thesis, and to Prof. Jan Jasny, Prof. Z. Grabowski, and Prof. Anna Grabowska (Warsaw) for making a copy of it available to me. I also thank Prof. K. N. Solovyov (Minsk) for drawing my attention to the very important papers [An55] and [Bor64], Prof. V. V. Gruzinskii (Minsk) for a reprint of [Bor64], Prof. V. L. Ermolaev (St.-Petersburg) for a copy of [Vav52], Prof. I. Ketskeméty (Szeged) for information on the second part of Vavilov's law and for reprints, and Dr. C. Zander (Siegen) for his thesis and copies of related recent publications. Several scientists have encouraged me to continue this historical review; among them was Dr. Berberan-Santos (Lisboa) who confirmed my assumption that F. Perrin's article [Pe29] is identical with his thesis. I am again very grateful to Dr. Christine P. Jaensch for her assistance in preparing the final manuscript. She checked all translations from German and French into English and suggested many improvements. Finally I thank Dr. H. J. Kuhn and my coworker Miriam Gehring for detecting a considerable number of errors in one of the last versions of this article.

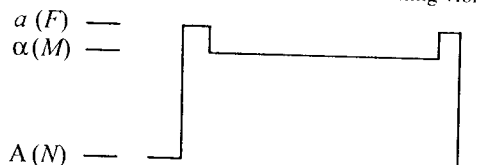
Appendix 1. F. Perrin's explanation of E-type delayed fluorescence [Pe31]

In 1931 F. Perrin gave a public lecture with the title *Fluorescence* and the subtitle *[[Elementary duration of light emission]]*. That lecture was published as a separate brochure [Pe31]. [Pe31] is a shortened version of F. Perrin's article [Pe29] (the contents of [Pe29] are identical with those of F. Perrin's thesis). Since the sections on metastable states in [Pe31] are almost identical with the corresponding sections in [Pe29] (cf. Part 1), the original French texts are not quoted in the following.

{23.2} § 19. **[[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, 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.]]

Comment. 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, but obviously [PeJ26] is implied, since this is the only reference to the work of J. Perrin in the list of general references at the end of the brochure.

{23.3} [[It may occur that a molecule that has passed to a first excited state a by light absorption, undergoes, either spontaneously or by reaction with other molecules, a transformation bringing it into a metastable state α , from which the return to the normal state is possible only by repassing the first excited state a or an analogous state with a higher internal energy 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 one and one delayed by the transition to the state α . The time, 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 typical phosphorescences, of which we thus obtain a theoretical interpretation (Jean Perrin), which can be represented by the scheme of figure 3, where for simplicity we have omitted intervening vibrational states.]]



Perrin diagram ([Pe31], Fig. 3) for the explanation of the delayed fluorescence $a \rightarrow A$ by the intermediate passage through a metastable state α . N , M and F are the state symbols used by Jabłoński [Ja33b]. The Perrin diagram is an energy histogram, the horizontal axis representing the time.

{24.1} [[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.

{24.2} Another type of phosphorescence could result from a light-induced dissociation or ionization, reemission taking place, when the recombination brings the substance back to its initial [excited] state. Here again the mean time separating the absorption and the emission would have no relation to the emission phenomenon itself, and it could be considerably modified, for instance by a change of the viscosity of the medium, without changing the luminescence yield.

{24.3} One sees that it is the proportionality of the mean duration of an emission and of the luminescence yield, which indicates the spontaneous character of a light reemission and which therefore constitutes the veritable criterion of fluorescences as compared to phosphorescences.]]

Comment. In the final section § 34. [[Interpretation through wave mechanics]], the underlined statement in {23.3} (i.e. the idea that the lifetime of a metastable state may become infinitely long) is revised. The last two sentences of § 34 are:

{41.3} [[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 one 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.]]

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Appendix 2. J. Perrin's explanation of E-type delayed fluorescence [PeJ26]

In the history of science, the Solvay Conferences in Brussels were perhaps the most exclusive international conferences and, as far as the development of quantum mechanics is concerned, also the most important ones. In April 1925 the Second Solvay Conference on Chemistry took place. The number of participants was limited to 25. J. Perrin was a member of the international scientific committee and gave himself a lecture with the title "Light and Chemical Reactions". The printed lecture [PeJ26] is 75 pages long, followed by 15 discussion remarks and Perrin's replies on 18 additional pages. Phosphorescence is treated in the sections 43, 44, and 45 of [PeJ26]. In section 43, *Phosphorescence*, J. Perrin states that the phosphorescent substances are in general solid solutions. The latter statement is revised in footnote (1) on p. 385:

[[Francis Perrin discovered, however, by means of Ed. Becquerel's phosphoroscope, in a liquid medium (mixtures of glycerol and water), phosphorescences whose persistence may attain one hundredth of a second, and which are the less persistent the weaker the viscosity (*Comptes rendus*, t. 178, 1924, p. 2252 [PeJ24])]].

Comment. A passage from [PeJ24] is quoted in section 3.5 in the context of Pringsheim's article [Pr36b]. – J. Perrin was probably the first who made a clear distinction between the measured lifetimes of luminescences from solid or liquid solutions and the radiative lifetimes of the emitting

excited states. The phosphorescences he refers to are either E-type delayed fluorescences or recombination fluorescences, but – as we know today – not phosphorescences in the present sense, i.e. direct emissions from a metastable state with a very long radiative lifetime (in J. Perrin's terminology: "fluorescence of long period"). J. Perrin continues as follows:

{385,2} [[The properties of these phosphorescences are in part those, which one would expect for a fluorescence of long [radiative] lifetime [i.e. for a phosphorescence $M \rightarrow N$ in the present sense]: Stokes' rule is observed; the brightness seems to be proportional to the intensity of the excitation light; finally, for a given thickness and with increasing concentration of the phosphorogen, this brightness first grows, goes through a maximum for an optimum concentration (Lecoq de Boisbaudran; G. Urbain), and then decreases tending to zero.

{385,3} But a difference of nature, which as I believe has not yet been noted, is revealed by the action of temperature, and separates in a fundamental manner fluorescences [here: $M \rightarrow N$] and phosphorescences [E-type DF and recombination fluorescence].

{385,4-386,3} **44. [[The phosphorescence is not a fluorescence of long period.]] (...)**

Comment. The title of section 44 resumes the statement of the immediately preceding paragraph {385,3}. J. Perrin mentions in section 44 some properties of thermoluminescence; his examples refer to inorganic substances.

{386,4} **45. [[Mechanism of phosphorescence.** – One takes into account these different properties [of phosphorescences] by imagining the succession of the following metamorphoses:

{386,5} First, the phosphorescent substance is fluorescent in the true sense of the word, i.e. that during the excitation itself a fluorescence is emitted, a fact observed by different authors ⁽¹⁾, a fluorescence which, due to molecular induction, will be weak in a concentrated medium.

{386,6-387,1} But one has to admit that, among the molecules brought into the critical [= excited] state, there are such molecules which, due to the diluting matter, transform into an intermediate complex α ; this is a proper chemical reaction ⁽¹⁾. For instance, each critical molecule may have a chance of 1 to 10 to escape in this way to direct regeneration [= return to the ground state]. Gradually, and as each regenerated molecule becomes soon [again] critical, all sensitive molecules would disappear by transforming into the addition complex α ⁽²⁾. In fact, since the inverse reaction must be possible, we will reach, for every given illumination, a steady state, where in every moment the same number of complexes α are formed and dissociate.

{387,2} Let us turn off the illumination; the inverse reaction continues to take place, i.e. the molecules α dissociate releasing critical molecules, which in their great majority become immediately ordinary molecules of the phosphorogen with emission of light (if the concentration of the phosphorogen is low enough so that the molecular induction does not much interfere). This light is the phosphorescence. The whole proceeds as if we had a *delayed fluorescence*.

{387,3} Finally it is obvious that, if we increase the temperature of the irradiated substance, we increase according to the Arrhenius law the dissociation rate of the complex α , hence, according to the same law, the brightness of the phosphorescence.]]

⁽¹⁾ [Footnote ⁽¹⁾ on page 386] [[In particular Guntz; this fluorescence is a little "sharper" than the phosphorescence that follows (F. Perrin).]]

⁽²⁾ [Footnote ⁽²⁾ on page 387] [[Chemical reaction depending on the diluent, to determine in each case (cf. Job, *Comptes rendus*, 1923, et Maurice Curie, *Thèse*, 1923).]]

⁽³⁾ [Footnote ⁽³⁾ on page 387] [[That is, I think, what takes place, when glass exposed to cathode rays progressively blackens and becomes less and less fluorescent. Such a "fatigued" glass regenerates, as one knows, with thermoluminescence, when one heats it to 200°.]

Comment. In J. Perrin's explanation of the phosphorescence as delayed fluorescence, the intermediate species α is not specified. In the present terminology, the species α was envisaged by him as a kind of exciplex or isomer. In most of the examples he had in mind, α was not a molecule in a metastable state. In the example in footnote ⁽²⁾ the delayed fluorescence is probably caused by ionization and subsequent thermally activated recombination. So far J. Perrin's ideas on the mechanism of phosphorescence do not significantly differ from those of Lenard (cf. also the

definition of a "Lenard phosphor" in Levshin's article in section 3.3 and Pringsheim's first discussion remark in section 3.5). Nevertheless it is rather likely that metastable states were included in his considerations. In this connection Lowry's discussion remark and J. Perrin's answer are of interest (p. 414-415):

Mr. Lowry. - (...) [[Mr. Perrin writes the reaction $A \rightarrow a \rightarrow A_1$ as if it represented a true chemical transformation, i.e. as if an isomerization could take place in the isolated molecule: in my opinion, this is simply an imaginary phenomenon, at least to consider the activation $A \rightarrow a$ to be an isomerization. The most facile isomerizations are those which include the migration of a proton, and one has proved repeatedly that they are not spontaneous. I think that the only changes that can take place in a simple molecule are radioactive changes.]]

Mr. J. Perrin. - (...) [[It is sufficient, for example, in the most simple case (an electron revolves round a proton), to recall that Bohr's theory has been able to link the possible discontinuities in a quantitative and perfect manner to the radiation emitted or absorbed by the hydrogen [atom].]] (...)

Comment: J. Perrin makes no fundamental distinction between a transition to a different electronic state and an isomerization. The same idea is expressed more clearly by Pringsheim two years later [Pr28, p. 194]:

[[Finally it is to emphasize that there is no longer a principal difference between a photoelectric and a photochemical theory of luminescence. For every optical excitation in Bohr's sense is simultaneously a chemical transformation: an excited Hg atom chemically differs completely from the normal Hg atom and the same must be true for a complex molecule.]]

Appendix 3. Table of contents of volume 5 of *Acta Physica Polonica* (1936)

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