PIONEERS IN PHOTOPHYSICS


(On the occasion of his 100th birthday anniversary)

The present review of Professor Aleksander Jabłoński's research work embraces his most important attainments that have had a strong impact on our knowledge of optical and spectroscopic properties of luminescent molecules in liquid and rigid media, as well as on the further development of the photoluminescence of solutions.

Due to the inaccuracy of the mostly subjective methods commonly used on the turn of the century most results reported in the literature were totally at variance. Lommel [1] was the first to express an opinion, opposing Stokes' concept [2], that the intensity distribution in the fluorescence spectrum is independent of the excitation light wavelength. The works of Nichols and Merritt [3] settled the problem of the inapplicability of Stokes' law in its primary form, thus confirming Lommel's idea. It was not until then that the independence of the intensity distribution in the fluorescence band was acknowledged as a characteristic feature upon which further investigations on the fluorescence quantum yields were based [4-7].

In 1926, Jabłoński carried out first objective investigations (using the photographic method) on the intensity distribution in the fluorescence band for fluorescein in water as a function of the excitation light wavelength (up to the far ultraviolet, 2537 Å) [8]. Even such a shift of the excitation light wavelength as 2063 Å towards short wavelengths from the shortest wave used by Nichols and Merritt and considerable improvement in the measurement accuracy did not reveal any changes in the intensity distribution in the fluorescence spectrum.

In the postwar years, further studies using the photoelectric method for many luminescent substances confirmed the results obtained by Jabłoński for solutions with only one type of luminescent centre [9-11]. By luminescent centre [12] Jabłoński meant a system consisting of a luminescent molecule with its closest surroundings of solvent molecules**.

As from 1930, when the mechanism of the fluorescence of solutions was poorly known, Jabłoński made efforts to explain fundamental phenomena of molecular luminescence. In one of his

* The personal data of A.J. were given by Z. R. Grabowski in his article on the occasion of the 80th birthday in EPA Newsletter September 1978, 27-30.

** Such a system was named a quasi-molecule by Bączyński et al. [13].
crucial works entitled *Über das Entstehen der breiten Absorptions und Fluoreszenzbanden in Farbstofflösungen* [12] Jabłonski considered the broadening of the absorption and fluorescence spectra, resulting from fluctuations in the solvent density in the immediate neighbourhood of the dye molecule. In addition, based on the configuration-energy diagram he explained the Stokes shift of the fluorescence band relative to the longwave absorption band and the independence of the intensity distribution in the fluorescence band from the excitation light frequency in liquid solvents. He noticed that Szczęsniowski's measurements [14] of the fluorescence quantum yield display marked deviations from the values reported by Vavilov [6], which could be due to the overlapping of different absorption bands. This problem was all the time disturbing for Jabłonski and many other research workers until several years later it was satisfactorily explained. We shall discuss this issue further on.

The papers by Jabłonski [12, 15, 16] were the basis to formulate the so-called Kasha's rule [17] according to which fluorescence almost always occurs from the lowest singlet state $S_1$, irrespective of which singlet state was primarily excited ($S_1, S_2$ etc.).

It could already be inferred from Jabłonski's theoretical considerations [12, 15], based on the configuration-energy diagram, that for a luminescent molecule in a low-viscosity solvent the energy levels for fluorescence are in general different from those attained directly upon absorption. This work of Jabłonski [12] suggested the introduction of a four-level system to explain absorption and fluorescence of polyatomic polar molecules in low-viscosity liquid solutions. It should be mentioned that already in 1936 Onsager's theory [18] was known. It concerned internal electric fields in liquids. Luminescent molecules with a permanent electric dipole moment in a polar solvent are in an electric reaction field of this very solute. In such a case, dipole moments of the solvent molecules become oriented around the luminescent molecule. Thus, the Onsager reaction field is capable of evoking different absorption and fluorescence band shifts if the electric dipole moment of the luminescent molecule changes from $\mu_0$ to $\mu_1$ following excitation.

It was not until 20 years later that the above-mentioned works of Jabłonski and Onsager became the basis for formulating the theory of the solvent effect upon the absorption and fluorescence spectra, as well as for working out the spectroscopic method to determine electric dipole moments of molecules in the lowest singlet excited state [19-23].

Another discovery that should also be mentioned is the fine shift of the fluorescence band with the change of the excitation light frequency in rigid and in some liquid solutions [24-29]. According to Jabłonski [30], an essential effect on fine fluorescence band shift is that from the local temperature of the luminescent centre.

Let us now revert to the already mentioned problem of fluorescence quantum yield of aqueous dye solutions at an excitation in the Stokes and anti-Stokes regions. At the beginning of the 20th century it was already known that the fluorescence light intensity is proportional to the excitation light intensity (the Knoblauch law). Thus, the fluorescence quantum yield is independent of the intensity of the excitation light. The dependence of the yield on the excitation light wavelength was studied first of all by Nichols and Merritt [31]. The result obtained by them for eosin and resorufin in alcohol solution indicates the growth of the energy yield when increasing the excitation light wavelength. Later, Vavilov [4] and Valentin and Rössiger [5] confirmed the result of Nichols and Merritt. Valentin and Rössiger [5] found in addition that upon excitation with wavelengths longer than that of the fluorescence maximum (the anti-Stokes region), the energy yield drops dramatically. This was confirmed by Vavilov [6] in 1927. The results obtained in that period were not quite reliable in view of the subjective methods applied. In 1927, along with Vavilov's report [6], a paper by Szczęsniowski was published [14] describing the employment of photoelectric photometry and monochromator instead of light filters. Szczęsniowski's measurements [14] for fluorescein in water and glycerin revealed essential deviations from the results obtained by Vavilov [6] in the Stokes region (4400–5100 Å).
In 1933, referring to Szcezeniowski's work [14] Jabłoński decided to determine the relative energy yield of water fluorescein solutions in the anti-Stokes region (5100 – 5500 Å) using the photographic method [7]. In this experiment he confirmed the drop in the energy yield observed previously[5, 6]. Attempts undertaken by Jabłoński [32] to explain the yield drop in the anti-Stokes region, caused by overlapping of different inactive absorption bands which appear in liquid solutions due to the disturbing fields of the surrounding molecules of the solvent (the probability of the forbidden \( N \rightarrow M \) transition increases), were not successful. It was not until 1954 that Jabłoński explained the drop in the relative yield in the anti-Stokes excitation region (independent of the explanation given by Förster [33]) assuming the occurrence of non-fluorescent dimers even in dilute dye solutions [34]. The maximum of the dimer absorption lies on the short-wave side of the monomer absorption maximum. Nonetheless, having in mind that the dimer absorption band is very broad, the long-wave limit of the dimer spectrum also lies on the long-wave side of the monomer spectrum. Such an interpretation is in accordance with Jabłoński's observations [7, 33] that in concentrated dye solutions the fluorescence yield drop is more distinct than that in dilute solutions.

Regardless of many experimental works devoted to the phenomenon of photoluminescence of solutions (see monographs [33, 35, 36]) the correct view on the mechanism of photoluminescence was not formulated for many years. Numerous attempts to explain this phenomenon, undertaken on the turn of the century and in 1918 by J. Perrin [37], failed. It was not until 1929 that F. Perrin [38] made a mention of a metastable level lying below the fluorescence level of a dye molecule.

The theoretical explanation of the coexistence of both phenomena, i.e. the delayed fluorescence and phosphorescence, was given by Jabłoński [32, 39] as a complete analogy to the energy level diagram of mercury atoms [35]*. The diagram of the electronic levels of luminescent molecules proposed by Jabłoński and showing the mechanisms of fluorescence, delayed fluorescence and phosphorescence has been generally accepted and called the Jabłoński diagram [33, 40, 41]. In this diagram a metastable level \( M \) was introduced, lying below the fluorescence level, \( F \), as an inner electronic state of the dye with a very low probability of the \( M \rightarrow N \) transition (\( N \) – the ground state). It was assumed that the distance between levels \( F \) and \( M \) was small enough for the thermal activation \( M \rightarrow F \) to occur, this being the second pathway to depopulate the state \( M \).

The emission resulting from transition \( M \rightarrow F \rightarrow N \) is today called the delayed fluorescence, and that due to transition \( M \rightarrow N \) is called phosphorescence. A short communication to Nature [32] announced the possibility of increasing the probability of transition \( N \rightarrow M \) in a luminescent molecule under the influence of disturbing fields originating from the surrounding solvent molecules. This fact may be treated as an image of the external heavy atom effect [42].

In 1935 Jabłoński [39] presented a quantitative analysis of the properties of dye molecules [39], developed from the energy levels diagram of a luminescent molecule. Based on a simple kinetic equation for the depopulation of molecules in state \( M \) and assuming intramolecular parameters only, he derived formulae for the lifetime in state \( M \) in the presence and absence of thermal activation to state \( F \), for the quantum yield of fluorescence, \( F \rightarrow N \), and phosphorescence, \( M \rightarrow N \), as well as for the exponential phosphorescence decay.

It should be emphasized that the papers of Jabłoński [32, 39] stand as giant steps in the interpretation of many qualitative results of studies on fluorescence and phosphorescence carried out in previous years, thus giving rise to a new exact discipline, molecular photophysics.

The nature of the metastable \( M \) state remained obscure for many years. As shown experimentally by Weissman and Lipkin [43] already in 1942, employing the phenomenon of Selenyi's wide-angle interference, the phosphorescence of dyes is due to the electric dipole transition. Many years later,

* It should be mentioned that Jabłoński also carried out investigations of the fluorescence of atoms and biatomic molecules.
using the same method only slightly modified in the detection section, Bissinger [44] confirmed the
electric dipole character of transitions $M \rightarrow N$.

In 1941, Lewis, Lipkin and Magel [45] advanced a hypothesis, that was next developed by Lewis
and Kasha [46] and independently by Tercin [47], that the metastable state has triplet character, i.e.
is a state with the spin quantum number $S = 1$, whereas the ground state, $N$, and excited state, $F$, are
singlet states with the quantum number $S = 0$. Further experimental works [48-52] showed
unequivocally the equivalence of the metastable state, $M$, and the triplet state, $T$. Experimental studies
on the nature of the metastable state were also carried out in Torun by Bauer, Bączyński, Czajkowski and
Bissinger [44, 53-57].

Another important Jabłoński contribution [15, 16, 59] to photoluminescence is the experimental
and theoretical investigation of the polarization of fluorescence, delayed fluorescence and phospho-
rescence of isotropic and anisotropic systems (Kautsky type phosphors). The problem of the funda-
mental polarization (when no depolarizing factors are present) was dealt with in the years 1923-1936
by Vavilov and Levshin [60], Fröhlich [61], F. Perrin [38] and Jabłoński [62]. The discovery of the
negative polarization, corresponding to the excitation of a molecule to higher energy levels ($S_0$, $S_1$, $S_2$, ...)
from which, according to Kasha's rule [17], the molecules undergo radiationless transition to the initial
fluorescence band, prompted Perrin [38] to assume different directions of transition moments (linear
oscillators) in absorption and emission. According to this theory, the value of the fundamental polar-
ization belongs to the interval $-\frac{1}{2} < P < +\frac{1}{2}$. The cases in which the limiting polarization ($P_{\text{lim}}$) strongly
differs from the fundamental polarization, $P_{\text{lim}}$, as is the case for the acetone-cellulose solution of
fluorocylene with $P_{\text{lim}} = 0.154$, prompted Jabłoński [62] into the development of the theory of the
fundamental polarization by replacing linear oscillators with spatial oscillators in which dipoles of the
same electronic transitions have different directions in the molecule. In special cases, the general
expression formulated by Jabłoński for the fundamental polarization gives a value of the fundamental
polarization resulting from the theory of Vavilov, Levshin and Perrin. Moreover, Jabłoński's theory
[62] predicted a case of a symmetric plane oscillator, which was later confirmed experimentally for
benzene and its derivatives [64-66].

In view of the fact that the measured values of $P_0$ are somewhat lower than the theoretical value,
$P_{\text{lim}}$, analyzing different possible depolarizing factors, Jabłoński formulated a hypothesis that the
fluorescence depolarization is due to torsional vibrations of the luminescent molecules [67]. This
theory was verified experimentally by Grzywacz [68] and Bauer [69] for anthracene in plexiglass and
glycerin, respectively, and by Marszałek for benzene in EPA (ether-isopentane-ethylalcohol) [66].

Before discussing further issues concerning the development of solution fluorescence polariza-
tion it is worth to mention a concept of the emission anisotropy proposed by Jabłoński [70-72]
instead of the commonly used definition of the degree of polarization $\gamma$. The emission anisotropy,
unlike the degree of polarization, is an additive quantity thus resulting in much simpler calculation
methods and formulae.

Encouraged by Jabłoński, in the 1930s Szymanowski in the Institute of Experimental Physics of
Warsaw University built a phase-modulation fluorometer enabling the direct measurement of fluores-
cence lifetimes. This was the second improved apparatus of this type in the world (the first one that
could be used in practice was constructed by Gaviola [76] in Pringsheim's laboratory in Berlin). The
theory of the principles of phase-modulation fluorometry was worked out by Duschinsky [77] and
Jabłoński [78]. The simple formula derived by Jabłoński [78] in 1935 is the basis for an elegant

* More information on the generalization of the Jabłoński diagram can be found in an article published by M.
Kasha [58].

** Although the idea of the emission anisotropy was already used by Perrin, he did not formulate its name and
definition [73, 74].
method of analyzing the decay curves. The theory of the phase-modulation fluorometer worked out in 1973 by Jabłoński [79] is fundamental for measuring the phase shift and relative modulation degree of the emitted light as a function of the excitation light modulation frequency [80].

Already in the thirties, making use of Perrin's theory [38] and based on the theoretical analysis of the effect of Brownian rotations of excited molecules, Jabłoński [78] found that the decay times of the fluorescence components polarized parallel and perpendicular to the excitation light direction are different. The effect of rotational diffusion on the above components was investigated experimentally by Szymanski [81] and Kessel [82] who found qualitative agreement only.

As already mentioned, the values of the limiting emission anisotropy, \( r_m \), determined from Perrin's equation [38] for an infinitely high viscosity coefficient, are always slightly lower than those of the fundamental emission anisotropy, \( r_f \). This very fact implies the necessity to modify Perrin's theory. In such a modification Jabłoński [83] assumed that torsional vibrations of luminescent molecules in liquids are usually about the equilibrium orientation and only from time to time, when the vibration energy and configuration of the environment are favourable, they change stepwise their equilibrium orientation. Thus, in addition to the depolarization of photoluminescence molecular rotation, depolarization due to torsional vibrations always occurs. The depolarization resulting from torsional vibrations was considered by Jabłoński to be an instantaneous process, reaching its maximum intensity practically at the moment of excitation.

When the luminescent molecule acquires the excess of vibrational energy directly following excitation (according to the Franck-Condon principle), part of this energy is dissipated in the environment in the form of elastic waves, and the rest causes local heating of the fluorescent centre, contributing as a result to the enhancement of fluorescence depolarization. Such a process, called an initial shock, was taken into account by Jabłoński in his theory [83, 84].

The experiments carried out by Bauer and Balter [85-87]. Heldt [88] and Grudziński [89] by means of a phase fluorometer and an apparatus for measuring light polarization, built by Bauer and Rozwadowski [90, 91], made possible the polarization degree and volume of the solvation shell to be determined and the average value of the torsion moment acting on the molecule in the solution studied to be evaluated based on Jabłoński's theory [73, 83, 84, 92]. The plots of the emission anisotropy versus excitation light frequency obtained from the measurements (for the excitation of the same electronic transition in the luminescent molecules) are in good agreement with Jabłoński's theoretical curves [72, 75, 79-81].

In addition to the effects mentioned above, another phenomenon discovered and confirmed experimentally in the Gdansk research centre is the time dependence of the initial course of the emission anisotropy, and the dependence of its stationary value upon the moment of inertia of the luminescent molecule [95-97].

The last papers of Jabłoński [98, 99] from the late seventies once more deal with the effect of torsional (irregular) vibrations upon fluorescence polarization in rigid media, as well as with the case of the superimposing effects originating from both torsional vibrations and Brownian rotations of molecules in liquid solutions, excited by a short pulse of linearly polarized light. It is unfortunate that equations derived by Jabłoński for the time dependence of the emission anisotropy have still to be verified experimentally and made use of.

Apart from investigations on photoluminescence polarization of isotropic solutions, in the thirties Jabłoński [59, 100-103] dealt with the polarization of ordered ensembles of molecules introduced into cellophane by Kautsky's method. As shown experimentally, the distribution of dye molecules in cellophane films is partly ordered. Jabłoński found the degree of polarization of photoluminescence of cellophane phosphors to depend on the azimuth of the excitation light polarization. He explained theoretically the run of the dependence of polarization degree upon the polarization azimuth for excitation with both polarized and natural light. The agreement of the theoretical curves
with experimental data is very good [59, 100].

Based on the previously formulated theory of fundamental polarization of fluorescence [61, 104], Jabłoński discussed some of the optical properties (such as dichroism and certain phenomena characteristic of fluorescence light emission) of sets of molecules partly or completely ordered in rigid media [103].

Although Jabłoński's pioneer works did not propose the determination of the electronic transition moment directions in a polyatomic molecule, they still became the fundamentals of electronic spectroscopy in polarized light. The method called Jabłoński's method was in the fifties used by Fraser [105], Beer [106] and Tanizaki [107] for determining the directions of the absorption electronic transition moments. The next steps in the investigations of the linear dichroism were made by Thulstrup, Eggers and Michl [108], as well as by other research workers [109, 110]. Today, polymer films are used as matrices (polyvinyl alcohol, polyethylene).

Jabłoński's expressions for the fundamental emission anisotropy of isotropic rigid solutions are helpful in determining the directions of transition dipoles in luminescent molecules by the method of photoselection [111-113]. This method consists in measuring the emission anisotropy of the same photoluminescence band upon excitation in different electronic absorption bands. The method of photoselection was transformed to be applicable also for linear luminescent molecules oriented in stretched polymer films at single- or two-photon excitation [114-116].

From among numerous Jabłoński papers [117-127] dealing with the theory of quenching and concentration depolarization of photoluminescence of solutions, worthy of attention is also the so-called multilayer shell model of the luminescent centre. The luminescent centre consists of an excited luminescent molecule surrounded by monomolecular layers of solvent molecules, including also some disturbing (e.g. quencher) molecules. Luminescent centres differ in the number of the quenching molecules embraced in the individual layers. All luminescent centres are divided into groups depending on the number of quenchers in the layer. The centre changes its group when the quencher passes from one layer to another. The quencher molecules continuously perform irregular oscillations about the instantaneous equilibrium position and can stepwise pass from layer to layer. The probability of such a transition depends on the viscosity and temperature of the solution. In the case of a high viscosity or rigid solution, the quencher molecules (or initially unexcited molecules, as is the case in the description of the concentration depolarization) stay indeterminably in respective layers. The probability of quenching depends on in which layer the quencher molecule stays. Fluorescence quenching is caused by the encounters between the quencher and the excited luminescent molecule. The general distribution of different configuration of the disturbing molecules (quenching or depolarizing) is given by the Smoluchowski distribution. Based on general assumption of the multilayer model, Jabłoński considered the simplest case of a liquid fluorescent solution [117, 119]. He assumed that the luminescent centre consists of an excited molecule surrounded by one layer, in which either one quencher molecule only or no molecule at all can be found. The expression obtained for the photoluminescence quantum yield in liquid solution in special cases transforms into Perrin's equation for self-quenching, or into the Stern-Volmer equation.

In the case of a rigid or high viscosity solution, the diffusion of quenchers can be neglected. In paper [122] Jabłoński considered the quenching of photoluminescence of solutions caused by the excitation energy transfer, by assuming the Förster law according to which the probability of quenching is inversely proportional to the 6th power of the distance between the quencher and the excited luminescent molecule. In the theory of concentration depolarization of photoluminescence (the so-called self-depolarization) Jabłoński employed a simplified model of the luminescent centre consisting of one initially excited luminescent molecule surrounded by the so-called active sphere, in which unexcited molecules of the same kind (acceptors) can be found [118]. In view of different numbers of initially unexcited luminescent molecules inside the active sphere, all luminescent centres
were divided into groups. Here, the excitation energy migration from the excited to the unexcited molecule is the depolarizing factor. The excitation energy can migrate only between the luminescent molecules belonging to a given centre, i.e. within the active sphere. Unlike other theories, this one of the concentration depolarization of photoluminescence of rigid solution takes into account fluctuations in the luminescent molecules concentration (given by the Poisson distribution) and the re-migration of the excitation energy. The simple equation obtained by Jabłoński, describing the phenomenon of self-depolarization, is in good accordance with the experimental results [128, 129].

In the simplified version of Jabłoński’s theory [118] the following assumptions were made:

1. The probability of radiationless excitation energy migration from the donor to the acceptor is the same for all acceptors (initially unexcited molecules) within the active sphere, irrespective of the donor-acceptor separation.

2. Mutual orientations of the acceptor and donor transition moments are disregarded.

Later Jabłoński made some attempts to refine the theory of self-depolarization by mitigating some of the drastic simplifying assumptions. Jabłoński suggested [122] that his theory could be improved by the employment of the multilayer model. Such theories were developed by Bojarski [130] and Kawasaki and Kamiński [131] for self-depolarization and for the quenching of photoluminescence by foreign fluorescent substances [132, 133]. The excitation energy migration between alike (homotransfer) and different (heterotransfer) molecules was finally described by a uniform theory within the framework of the multilayer model [134-136].

In paper [126] Jabłoński took into account the pre-relaxation excitation energy transfer in the self-depolarization theory. This effect was earlier detected experimentally by Guéron et al. [137] and Bauer [138].

The formulation of theoretical bases of the effect of the intedonor excitation energy migration upon the fluorescence anisotropy in binary systems [127] is Jabłoński’s equally valuable achievement. This paper inaugurated a series of experimental and theoretical works [139-143].

The author of the present monograph is aware that the selection of scientific attainments of Professor Jabłoński does not fully reflect his rich scientific output in the field of the photoluminescence of solutions. It is worth noting that in May 1936, in Warsaw, the International Conference on Photoluminescence took place for the first time in the world. In answer to the motion tabled by Professor S. Pieńkowski, the Chairman of the Organizing Committee, Peter Pringsheim, recognized as the most eminent expert in luminescence, was chosen as the Chairman, and Aleksander Jabłoński as the Secretary General of the Conference. Among the participants dealing with photoluminescence of solutions were F. Perrin, S.I. Vavilov, V.L. Levshin, F. Duschinsky, A. Terenin and P. Soleillet.

In 1963, Professor Jabłoński organized in Toruń the International Conference on Photoluminescence, which gathered the most respected specialists in this field. In the following year, Professor Jabłoński was granted the 1st degree State Award for his great achievements in the investigations of photoluminescence of solutions, in particular for the creation of the model of luminescence. Paying tribute to Professor Jabłoński for his contribution to the development of photoluminescence and his outstanding scientific attainments, on 9 October 1975 the University of Gdańsk conferred the honorary doctor’s degree on him. Professor Aleksander Jabłoński, Academican of the Polish Academy of Science, was one of the pioneers in the development of the field of molecular photophysics.
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received: 17 Sept. 1997

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