

## Pioneering Contributions of Jean and Francis Perrin to Molecular Luminescence

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Le but suprême que doit se donner tout homme de Science doit être  
de travailler pour la plus grande gloire de l'esprit humain.

(The supreme goal of a scientist must be to work for the greater  
glory of the human spirit.)

Francis Perrin, *Leçon terminale au Collège de France* (1972)

### 2.1 Introduction

... in science, what X misses today Y will surely hit upon tomorrow (or maybe the day after tomorrow) (...) Scientists are entitled to be proud of their accomplishments, and what accomplishments can they call "theirs" except the things they have done or thought of first?

P. Medawar (1964) [1]

*Timon of Athens* could not have been written,  
*Les demoiselles d'Avignon* not have been painted,  
Had Shakespeare and Picasso not existed.  
But of how many scientific achievements can this be claimed?  
One could almost say that, with very few exceptions,  
It is not the men that make science;  
It is science that makes the men.  
What A does today, B or C or D could surely do tomorrow.

E. Chargaff (1968) [2].

We know this to be very true. In science, priority is a key issue, and independent multiple discoveries are not uncommon. In art, the probability that two different creators will produce the same work is close to zero, and Pierre Menard's *Don Quixote* [3] stands as an isolated (and imaginary) exception.

On the other hand, the uniqueness of every scientist is undeniable. Remember Lagrange's famous comment about Lavoisier's death [4]:

Il ne leur a fallu qu'un moment  
Pour faire tomber cette tête.  
Cent années, peut-être, ne suffiront pas  
Pour en reproduire une semblable.  
(It took them only a brief moment to chop off this head. Yet, a hundred years  
will not be perhaps sufficient to produce a similar one.)

In the same vein, C.P. Snow wrote of Einstein's "prodigious year" (1905): It is pretty safe to say that, so long as physics lasts, no one will again hack out three major breakthroughs in one year [5].

How can these two apparently opposite views be reconciled?

A work of art is always the combined result of two distinct aspects: first, skills; and second, the artist's culture, imagination, and emotions. Furthermore, it relies weakly on previous works: progress does not exist in art.

To accomplish a scientific work, however remarkable, skills and creativity are also decisive, but the outcome is silent about the scientist's personality, and only the skills are apparent in it (even the reporting style is not free, following strict rules [6]). This is so because science refers to those parts of reality for which a general rational consensus can exist [7]. This essential difference between art and science was aptly summarized long ago: *l'Art, c'est moi; la Science, c'est nous* (Claude Bernard) [8]. Subjectivity, the very essence of Art, is not welcomed in science. Scientists (including mathematicians) believe in an independent and pre-existing reality that they progressively unravel (see Fig. 2.12). They are like the Renaissance navigators that discovered new worlds or established new routes across the oceans, connecting civilizations. Vasco da Gama or Magellan (had he survived) could claim no more (and no less!) than having been the first. Even the serendipitous voyage of Columbus finds many a parallel in science [9–11].

Of course, aesthetics is not foreign to science. The study of nature is a source of intellectual joy, *la joie de connaître*. After surmounting many difficulties, each newly found harmony, however small, is rewarding and beautiful. And a sense of enchantment comes from being the first and only one to know. The subsequent communication of the findings can convey and revive in the audience the same sense of harmony. But that is neither the ultimate purpose, nor the main quality of a scientific work.

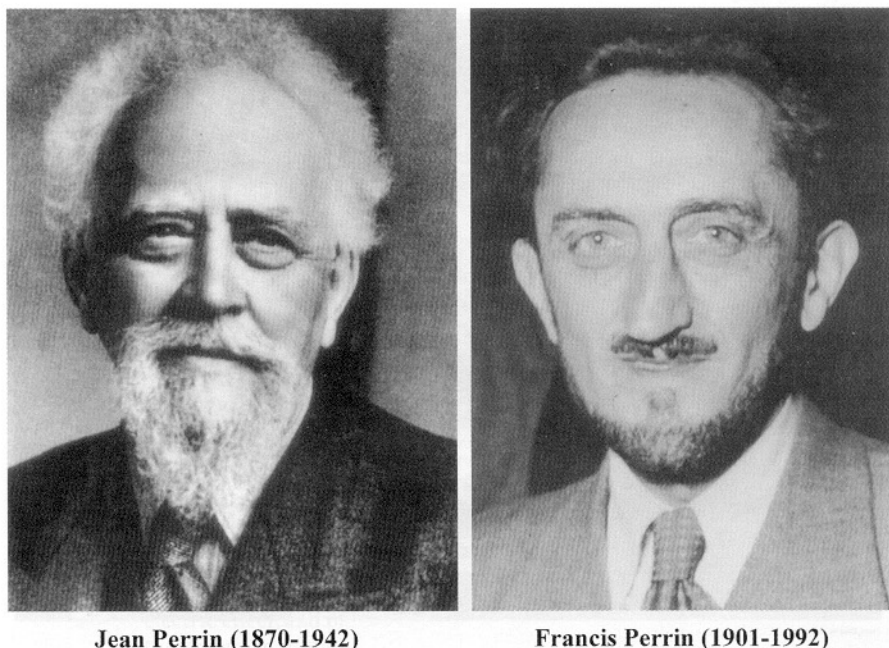
Another distinctive aspect of scientific works, as opposed to artistic ones, is the cooperative nature of the scientific endeavor:

1. In general, it builds upon previous contributions; given a common starting point, not all persons can accomplish the same, but a few always will.
2. It evolves within a given intellectual atmosphere and common view (the scientific community). The collective nature reaches extremes in some collaborative works, whose lists of authors extend for many lines. But papers with a few authors are very common.

Paradoxically, it is the collective nature of the scientific work that gives science its human dignity. While artistic expression is individual, and is mostly meaningful within a given culture, science cannot even be said to have a nationality: *La science n'a pas de patrie, ou plutôt la patrie de la science embrasse l'humanité tout entière* (Pasteur) (Science has no fatherland or rather, the fatherland of science is the whole mankind) [12].

The uniqueness of each scientist comes from the ensemble of his/her work, that reflects talents, tastes, motivations, and a personal evolution, and also results from a culture and an epoch.

It is with all these aspects in mind that the pioneering contributions of Jean and Francis Perrin to molecular luminescence will be discussed. In this chapter, after brief biographical sketches of Jean Perrin and Francis Perrin, their contributions to three different subjects will be described (Fig. 2.1).



**Fig. 2.1.** Jean Perrin and Francis Perrin (J. Perrin, Copyright Palais de la Découverte; F. Perrin, Copyright Robert Cohen, Reportages Photographiques, 3 rue Fontaine, Paris)

## 2.2 Biographical Sketches of Jean Perrin and Francis Perrin

The great French physicist Jean Perrin (1870–1942) is mostly remembered for the elegant experiments carried out before the First World War [13], that established the reality of atoms and molecules (Fig. 2.2), and for which he received the 1926 Nobel Prize in Physics. These studies are described in detail in his book (still in print) *Les Atomes* [14]. His earlier work on the nature of cathode rays (electrons) and X-rays [13], and his later work on molecular luminescence and photochemistry [15–32], are also remarkable. He was one of the first to apply the ideas of quantum theory to the absorption and emission of radiation by molecules. In particular, he was probably the first to have presented a molecular energy diagram with transitions between states [17, 18, 23]. In 1918 he proposed the mechanism of resonance energy transfer, refined in subsequent years (*induction moléculaire par résonance* [15, 23, 26, 27]). He also provided the correct model for thermally activated delayed fluorescence (E-type delayed fluorescence), based on the concept of metastable state, that he nevertheless supposed could also account for the phenomenon of phosphorescence [23].

Extensive biographical information on Jean Perrin is readily available, and here only a synoptic table (Table 2.1) and some selected topics are addressed. Relevant bibliography is discussed in Sect. 2.7.



**Fig. 2.2.** First Conseil de Physique Solvay (Brussels, 1911), where Jean Perrin presented his studies of the Brownian motion, finally demonstrating the existence of atoms and molecules. (Institut International de Physique Solvay, courtesy AIP Emilio Segrè Visual Archives)

Francis Perrin (1901–1992) was raised in a very rich cultural and scientific atmosphere. The inner circle of relations of his parents included Pierre Curie (deceased in 1906) and Marie Curie, the physicist Paul Langevin, the chemist and artist Georges Urbain, and the mathematician Émile Borel. It was only at the age of 11, already conversant with calculus, that Francis went to school. Before that age, he was taught by his parents and parents' friends. Following his father's footsteps, he became a *normalien* (graduate from the École Normale Supérieure). In the *post-scriptum* of a letter to Einstein (November 1919), Jean Perrin proudly announces the result of the admission examination: Francis a été reçu le premier (à seize ans et demi) à l'École Normale (Sciences). Il sera un meilleur physicien que son père (Francis was admitted to the École Normale (Sciences) in the top position. He will be a better physicist than his father) [33].

Working in his father's laboratory from 1924, Francis Perrin continued and extended the luminescence studies, with important personal contributions [30, 34–56]. His *Docteur ès Sciences physiques* thesis (1929) [46] deserves to be considered a classic for both style and scientific content. In the previous year he had already obtained the equivalent academic degree in mathematics, with a thesis on the mathematics of rotational Brownian motion [45], under the supervision of Borel.

**Table 2.1.** Jean-Baptiste Perrin (biographical synopsis)

Year	Major event	Biographical	Achievements
1870	Franco-Prussian war	Birth (Lille)	
1891–1894		Undergraduate studies at École Normale Supérieure (section sciences)	
1895–1898		ENS (agrégé préparateur)	
1897	Electron (Thomson)	Thèse de Doctorat: Rayons cathodiques et rayons de Roentgen. Marriage	Cathode rays are negatively charged particles (1895)
1898		Reader (chargé de cours) of the newly created physical chemistry course (Sorbonne)	
1900	Quantum (Planck)		
1901		Birth of Francis	First planetary model of the atom
1905	Theories of special relativity, of the photoelectric effect, and of the Brownian motion (Einstein)		
1908–1911		Chair of Physical Chemistry (Sorbonne, University of Paris, 1910)	Studies of the Brownian motion: first direct proofs of molecular reality
1911	Rutherford atomic model	First Solvay Council	
1913	Bohr atomic model	Book: Les Atomes	
1914		First studies of luminescence	
1914–1918	First World War	Military activities	Myriaphone (1916)
1916	Absorption and emission of radiation (Einstein)		
1918		Fluorescence studies	Radiative theory of chemical reactions. Induction par resonance
1919			Origin of stellar radiation
1922–1926		Laboratoire de Chimie Physique	
1923		Académicien	
1924	Matter waves (de Broglie)		

**Table 2.1** (continued)

Year	Major event	Biographical	Achievements
1925	Quantum Mechanics (Heisenberg, Born)		Delayed fluorescence. Induction par resonance
1926	Wave Mechanics (Schrödinger) Photon (Lewis)	Nobel Prize in Physics	
1927		Institut de Biologie Physico-Chimique	
1929		Last fluorescence studies	
1935	Jablonski's diagram		
1936–1938		Sous-secrétariat d'État à la Recherche	Creation of astronomical observatories, laboratories. Palais de la Découverte
1939			Creation of the CNRS
1939–1945	Second World War		
1941		Departure to the USA	
1942		Death (NY)	
1948		Funérailles nationales (Panthéon)	

**Fig. 2.3.** Francis Perrin, Jean Perrin, and Otto Stern (of Stern-Volmer and Stern-Gerlach fame) in 1928. (AIP Emilio Segrè Visual Archives, Segrè Collection)

The main experimental and theoretical achievements of F. Perrin in the field of molecular luminescence include the following:

1. The active sphere model for quenching (1924) [34].
2. The relation between quantum yield and lifetime (1926) [38, 39, 41].
3. The theory of fluorescence polarization, in relation to rotational Brownian motion (1926) [36, 38, 46, 55]. In particular, from the key (Perrin) equation, he was able to determine accurately, for the first time, the fluorescence lifetime of dyes in solution.
4. The first qualitative theory of depolarization by resonance energy transfer (*transfert d'activation*) (1929) [46].

From the 1930s onwards, F. Perrin's scientific and professional activity was mainly devoted to nuclear physics [57, 58]. In this field, he was again the author of several important contributions. For example, he introduced the concept of critical mass (*dimension critique*) for a nuclear chain reaction, and provided the first estimate of its value for uranium (1939).

The life and scientific achievements of Francis Perrin are summarized in Table 2.2.

It is interesting to note that Jean Perrin and Francis Perrin devoted their attention to luminescence for approximately the same amount of time: a decade (Jean Perrin started his studies shortly before the outbreak of the First World War, but he resumed them only after its end). As can be seen from the tables, the two contributed to it in more than one important way. Unlike another contemporary father-son combination (William Henry and William Lawrence Bragg),



**Fig. 2.4.** The team of the Laboratoire de Chimie Physique. First row, from left to right: Pierre Girard, Jean Perrin, Francis Perrin, Costa; second row, standing: Nine Choucroun, André Marcelin, Audubert, Hibben, Pierre Auger, and Platard. The bust of Jean Perrin, as Dionysos, sculpted by Urbain, can be seen at top right. (Copyright Palais de la Découverte)

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# THÈSES

PRÉSENTÉES

A LA FACULTÉ DES SCIENCES  
DE L'UNIVERSITÉ DE PARIS

POUR OBTENIR

LE GRADE DE DOCTEUR ÈS SCIENCES PHYSIQUES

PAR

**Francis PERRIN**

**1<sup>re</sup> THÈSE.** — LA FLUORESCENCE DES SOLUTIONS. — INDUCTION  
MOLÉCULAIRE. — POLARISATION ET DURÉE  
D'ÉMISSION. — PHOTOCHIMIE.

**2<sup>e</sup> THÈSE.** — PROPOSITIONS DONNÉES PAR LA FACULTÉ.

Soutenues le **juillet 1929** devant la **Commission d'examen.**

M<sup>me</sup> CURIE..... *Président.*  
MM. G. URBAIN..... } *Examinateurs.*  
A. COTTON..... }

PARIS

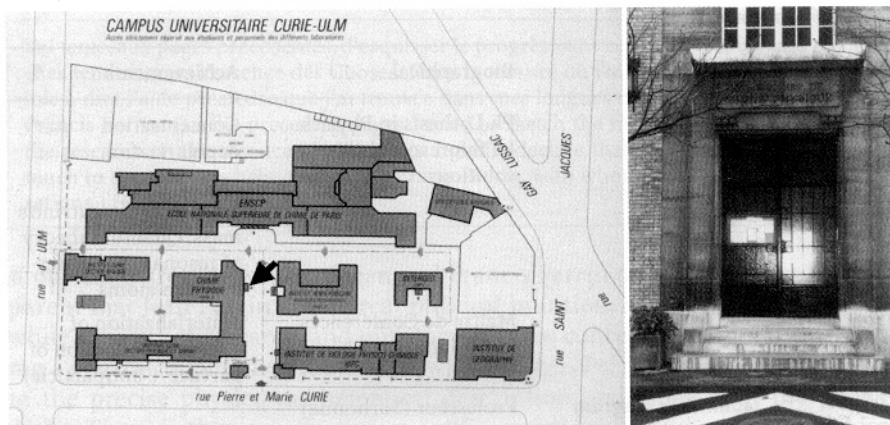
MASSON ET C<sup>ie</sup>, ÉDITEURS

LIBRAIRES DE L'ACADÉMIE DE MÉDECINE  
120, BOULEVARD SAINT-GERMAIN

1929

Fig. 2.5. Frontispiece of Francis Perrin Ph.D. thesis in physics. The first part of the thesis was published in the Annales de Physique [46]





**Fig. 2.6.** Location and façade of the Laboratoire de Chimie Physique (f. 1922–6; present situation of the campus), where the Perrins did most of their luminescence studies. Before, Jean Perrin's laboratory was located in the old buildings of the Sorbonne

**Table 2.2.** Francis-Henri-Jean-Siegfried Perrin (biographical synopsis)

Year	Major event	Biographical	Achievements
1901		Birth (Paris)	
1918–1922		Studies at École Normale Supérieure (section sciences)	
1919	Stern-Volmer relation		
1920	Polarization of solutions (Weigert) Bohr-Grotrian diagram	Licencié	
1922	Sensitized fluorescence (Cario and Franck)	Agrégé	
1923	Polarization (Vavilov and Levshin)	Military service	
1924		Assistant (lab. de chimie physique, Sorbonne)	Active sphere model
1925	Approximate theory of polarization (Levshin)		Approximate theory of polarization
1926	Direct determination of nanosecond lifetimes (Gaviola)		Quantum yield and lifetime theory of fluorescence polarization (sphere) Experimental determination of lifetimes in solution. Comparison with radiative lifetimes.
1928	Quantum theory of molecular interaction (Kallmann and London)	Ph.D. thesis in Mathematics: Étude mathématique du mouvement brownien de rotation	

Table 2.2 (continued)

Year	Major event	Biographical	Achievements
1929		Ph.D. thesis in Physics: La fluorescence des solutions	Concentration depolarization
1932			Smallness of neutrino's mass. Quantum theory of resonance transfer between atoms
1933		Maître de Conférences (Sorbonne)	Materialization of energy (production of particle + antiparticle)
1935	Jablonski's diagram	Professeur (Sorbonne)	
1936			Theory of fluorescence polarization (ellipsoid)
1936–1938		Political activity	
1939		Book: Mécanique statistique quantique	Critical mass of natural uranium nuclear chain reaction
1939–1945	Second World War Triplet state (Lewis and Kasha, 1944)	Military mobilisation (1939–40). Stay in the USA (Columbia University: 1941–43) France Forever movement	
1946		Commissariat à l'Energie Atomique. Collège de France	
1948	Quantum theory of RET (Förster)		
1950–1972	Additivity of anisotropies (Weber, 1952)	Haut Commissaire du CEA	French nuclear programme
1953		Académicien	Co-foundation of CERN
1957	Anisotropy (Jablonski)		
1972		Retirement	
1973			Proposal of a new periodic table
1992		Death	

most of the work was carried out in relative independence – only one publication [30] is co-signed. This, in spite of great affection and frequent scientific discussions, as is evident from the following two extracts, written by Francis Perrin and Jean Perrin, respectively:

J'ai eu le très rare bonheur de faire ce travail au côté de mon père dans son laboratoire; en tant que disciple je tiens à exprimer ici ma profonde reconnaissance pour tout ce que je lui dois. (I had the very rare pleasure of doing this work beside my father, in his laboratory; As his pupil, I must express here my deep gratitude for all that I owe him.) [46]

J'ai tenté, aux pages précédentes, d'esquisser le progrès, sans cesse plus rapide, des recherches tendues vers l'essence des Choses. Dans la mesure où j'ai pu réussir, j'ai une grande joie à dire l'aide précieuse que j'ai trouvée dans mes longues conversations avec mon fils Francis Perrin. (In the preceding pages I tried to sketch the increasingly fast progress of the research on the essence of all Things. I gladly declare that my possible success owes much to the precious help of my son Francis Perrin, with whom I had many long conversations.) [59]

If one compares the works of Jean and Francis Perrin on luminescence, it is apparent that Jean Perrin has a great physical intuition, chooses new and worthwhile subjects of research, and puts forward new concepts and views, establishing a general, qualitative framework, while Francis Perrin is particularly skilled in the precise physico-mathematical description and analysis of the phenomena. There is thus an effective scientific complementarity, even if it did not materialize in joint papers.

Jean and Francis Perrin held similar political and philosophical ideas. Both were socialists and atheists. Like many nineteenth century French men of science, Jean Perrin viewed science almost as a religion. In the words of Raspail, inscribed in the surviving pedestal of his statue, located near Francis Perrin's residence: ...la Science, l'unique religion de l'avenir (Science, the only Religion of the future). Francis Perrin publicly denied all religions and gods, and was the President of Honour of the *Union des Athées*. He donated his body to science.



**Fig. 2.7.** Francis Perrin in the US, during the Second World War. (Copyright Fred Stein, 11525–25 Metropolitan Ave., Kew Gardens, NY 11418)



**Fig. 2.8.** Louis de Broglie, Maurice de Broglie, and Francis Perrin in 1951. (AIP Emilio Segrè Visual Archives)

Jean and Francis Perrin were, in their own ways and in the best French spirit, defenders of the *Droits de l'Homme*, and rejected all totalitarianisms. In the difficult period between wars, both actively opposed the rising fascism in Europe. The post-war positions of Francis Perrin on communism, at a time where it was fashionable among intellectuals, are worthy of mention.

Both actively labored in favor of science. Jean Perrin, in particular, was the founder of the CNRS, and of several important scientific institutions. He was also greatly concerned with the dissemination of scientific culture. One of his permanent concerns was the motivation for science of the greatest number of young people. For these purposes, he founded in Paris the Palais de la Découverte (1937), and wrote several books of popularization (e.g., [14, 59]), among other activities.

### 2.3

#### The Perrin-Jablonski Diagram

The history of the “Jablonski diagram” has been the subject of a recent and thorough investigation [60–62]. The views and reminiscences of the only living direct participant Michael Kasha, are presented in [63–65]. The name “scheme

of Jablonski” was used for the first time by Lewis, Lipkin, and Magel (1941), in a paper on the phosphorescent state [66]. In a following paper by Lewis and Kasha (1944), where the phosphorescence state was identified with the lowest triplet state, the designation “Jablonski diagram” makes its first appearance [67]. Interestingly, in later papers by the same authors [68, 69], the diagram is simply referred to as “energy diagram.” This usage remained common up to the 1970s. The name “Jablonski diagram” nevertheless made its way into the recent photochemical vocabulary. It is defined by the IUPAC as detailed below.

### 2.3.1

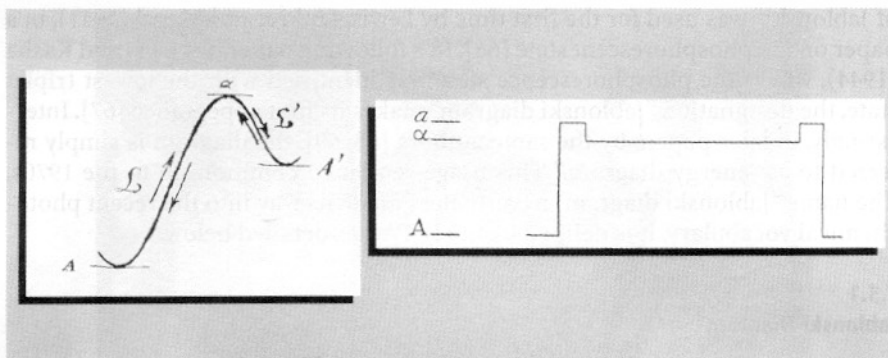
#### Jablonski Diagram

Originally, a diagram showing that the fluorescent state of a molecular entity is the lowest excited state from which the transition to the ground state is allowed, whereas the phosphorescent state is a metastable state below the fluorescent state, which is reached by radiationless transition. In the most typical cases the fluorescent state is the lowest singlet excited state and the phosphorescent state the lowest triplet state, the ground state being a singlet. Presently, modified Jablonski diagrams are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines displaced vertically to indicate relative energies, are grouped according to multiplicity into horizontally displaced columns. Excitation and relaxation processes that interconvert states are indicated in the diagrams by arrows. Radiative transitions are generally indicated with straight arrows, while radiationless transitions are generally indicated with wavy arrows [70].

As pointed out by B. Nickel [62], G.N. Lewis created a misnomer when he decided to refer to his own diagram (the original form of the diagram, according to the IUPAC definition above) as the “Jablonski diagram”. In fact, most of the characteristics of the diagram, as presently perceived, are not due to A. Jablonski. This point is clearly recognized by Kasha: later use of the “Jablonski diagram” fails to recognize the limitations of his interpretations [63]. However, like Lewis, he fails to give appropriate credit to the contributions of Jean and Francis Perrin to the early stages of this diagram [62, 65].

Schematically, it may be said that:

1. The type of diagram, with electronic states represented by horizontal segments, arranged vertically according to relative energies, and arranged in columns according to the spin multiplicities, and including lines connecting states corresponding to electronic transitions, turns out to be an extension of the Bohr-Grotrian diagram for atoms (1920) [71–73]. This diagram, originally due to Bohr [71], and used at length by Grotrian (but not introduced by him, as stated in [64]), replaced the Fowler representation, where the energies plotted were those of the atomic lines, and not those of the terms.
2. The first use of an energy level diagram for molecules in connection with the absorption and emission of light is probably due to Jean Perrin [17, 18, 23].
3. Using his diagram, that contains a metastable state (Fig. 2.9), Jean Perrin correctly explains, long before Jablonski, the phenomenon of thermally activated delayed fluorescence (presently sometimes called E-type delayed fluores-



**Fig. 2.9.** Two forms of the diagram of Jean Perrin: *left* 1920 [17, 18], *right*, since 1922 [18, 23, 32]. In both diagrams, energy is the ordinate. In the second representation, time is the abscissa

cence), including its temperature dependence. Jean Perrin even uses the words “delayed fluorescence” (*fluorescence retardée*) [23, 32]. The model of Jean Perrin is discussed in detail by Francis Perrin in his Ph.D. thesis [46]. For unknown reasons, Lewis et al. [66] attributed the interpretation of thermally activated delayed fluorescence (called by him alpha process) to Jablonski and not to Perrin.

4. It was recently argued that the metastable state implied by Jean and Francis Perrin was a trap state (only possible in a solid matrix), generated by photoinduced charge separation [65]. In this way, the actual resemblance of their diagram to the “Jablonski diagram” would be superficial. Jean Perrin indeed consistently explained thermoluminescence on the basis of this diagram [14 (1936 edn.), 23]. However, in several publications [30, 41, 46], including the one invoked in [65] (see the excerpt given below, in point 5, and also [60–62]), both Perrins explicitly distinguish between the two cases: charge separation and metastable states analogous to those of atoms. The above argument is therefore invalid [62].
5. The diagram of Jean and Francis Perrin is, of course, still incomplete: the metastable state cannot revert radiatively or otherwise to the ground state, and has therefore an essentially infinite lifetime at low temperature. This is the only (and crucial) point where a difference exists between the scheme of Perrin and the scheme of Jablonski. By allowing such a transition, a second emission at longer wavelengths becomes possible (true phosphorescence), as well as a weak absorption. That is the merit of Jablonski’s work [74]. It is, nevertheless, interesting to quote the two passages of the Perrins given below.

### 2.3.2

#### États Métastables – Phosphorescence

Lorsqu’un état activé peut être atteint directement, à partir de l’état normal, par absorption de lumière, réciproquement le retour à l’état normal est possible par émission spontanée de lumière. Mais il existe des états activés, dit *métastables*,

pour lesquels aucune transformation de ce genre n'est possible; le retour à l'état normal ne peut alors se produire que par interaction avec d'autres molécules (désactivation induite) ou par passage intermédiaire par un autre état activé d'énergie interne plus grande. L'existence de ces états métastables, prévues théoriquement par Bohr, comme conséquence du principe de correspondance, a été démontrée expérimentalement dans plusieurs cas (hélium, mercure,...). Tous les principes de sélection en spectroscopie expriment d'ailleurs l'impossibilité de certaines transformations quantiques par rayonnement [46].

(Whenever an activated state can be attained directly from the ground state, by light absorption, then the return to the ground state by spontaneous emission of light is also possible. Nevertheless, there are some activated states, called *metastable*, for which this kind of transition is not possible. The return to the ground state can only occur by interaction with other molecules (induced deactivation) or via a further intermediate state of higher energy. The existence of metastable states, theoretically predicted by Bohr, as a consequence of the correspondence principle, has been experimentally demonstrated in several cases (helium, mercury, etc.). Furthermore, certain quantum transitions with the emission of radiation are not allowed by spectroscopic selection rules).

Il semble bien d'ailleurs que cette probabilité de désactivation par émission lumineuse spontanée ne soit jamais rigoureusement nulle, c'est-à-dire qu'il n'existe pas d'état activé absolument métastable. C'est ainsi que certains états activés des atomes d'azote et d'oxygène ionisés, considérés comme tout à fait métastables, donnent pourtant lieu à des émissions lumineuses lorsqu'ils sont soustraits à toute cause de désactivation induite pendant un temps suffisamment long, de l'ordre de la seconde (...) [30].

(It also appears that this probability of radiative decay is never strictly zero, that is, the absolutely metastable activated state does not exist. It is for this reason that certain activated states of ionized nitrogen and oxygen atoms, long considered as strictly metastable, are now known to slowly deactivate with the emission of light, if they are isolated from all causes of induced deactivation for sufficiently long times, of the order of one second (...)).

Other relevant citations are given by Nickel [60–62], which also discusses at length several shortcomings in Jablonski's 1935 paper [74]. In particular, the kinetic model and analysis are incorrect. Also, the proposed mechanism by which the weak long wavelength emission is possible is solvent perturbation (forced dipole) or quadrupole emission [62], and not spin-orbit coupling.

Following namely Mulliken's results, and Kasha's experiments, the role of the triplet state was finally advanced (and demonstrated) by Lewis and Kasha in 1944 [65, 67], and in subsequent works. Only then did a close parallel with the Bohr-Grottrian diagram become possible.

It is interesting to note that Pringsheim, in his 1943 book with Vogel [75], still uses the model of Perrin (the authors make a clear distinction between Perrin's monomolecular delayed fluorescence, then called phosphorescence, and bimolecular recombination afterglow), not mentioning Jablonski's 1933 and 1935 works, of which he was nevertheless aware. Only in his 1949 book, *Fluorescence and Phosphorescence* [76], after Lewis' studies, does he write the following (repeated in [77]): A theoretical explanation of the coexistence of the two pheno-

mena [*in modern terminology: fluorescence and phosphorescence*] has been given by Jablonski in complete analogy to the energy-level scheme of the mercury atom (...) (p. 435).

What is meant by Pringsheim is best understood if another extract of his book [76] is also quoted: An instance in which all possible luminescence processes [*in modern terminology: prompt and delayed fluorescence, phosphorescence; these terms do not strictly apply to the mercury transitions mentioned by Pringsheim*] can be observed (...) is provided by mercury vapor (...) (p. 290).

A (modern) reader of the first statement above could be led to believe that Jablonski had already reasoned as if something analogous to the Bohr-Grottrian scheme should exist for molecules, while Pringsheim only implies that an energy level scheme accounting for the three types of processes was already known.

In fact, Jablonski (as the Perrins before him) does not discuss his diagram nor the nature of the metastable state in terms of spin multiplicity [62]. He even opposed until very late the triplet hypothesis [62].

The contribution of Jean and Francis Perrin to the formation of the “Jablonski diagram” was important. A better name, correct from the photokinetic point of view, would therefore be “Perrin-Jablonski diagram,” although it would still leave aside the final contribution of Lewis and co-workers.

It should be remembered at this point that incorrect attributions are legion in science. In a very interesting article, Laidler [78] gives several examples pertaining to physical chemistry: Boyle’s law, Le Chatelier principle, Arrhenius equation, etc.

It is appropriate to close this section with a quotation of G. N. Lewis, that he wrote in 1906: Perfection is rare in the science of chemistry. Our theories do not spring full-armed from the brow of the creator. They are subject of gradual growth ... [78].

## 2.4 Resonance Energy Transfer

The pioneering role of Jean and Francis Perrin in the field of molecular resonance energy transfer is generally acknowledged [79]. In the paper by Theodor Förster that laid down the standard quantitative theory of molecular resonance energy transfer [80], it is written that: J. Perrin was the first to note [23, 26] that in addition to radiation and reabsorption, a transfer of energy (*transfert d’activation*) could also take place through direct electrodynamic interaction between the primarily excited molecule and its neighbors. He presented a theory of such processes based on classical physics, and F. Perrin [52] later gave a corresponding quantum mechanical theory, the latter leaning on Kallmann and London’s theory [81] of excitation energy transfer between various atoms in the gas phase [82].

In order to understand fully the early stage of molecular resonance energy transfer, which is not without its twists and turns, mention must be made of the studies of atoms in the gas phase.

In a famous experiment (1913), Franck and Hertz [83] showed that the collision of fast electrons with slow-moving atoms could result in the production of



excited atoms and slow electrons. These collisions, where a transfer of energy takes place, with the conversion of translational energy into electronic energy, were called *collisions of the first kind*.

The reverse process, collision of slow electrons with excited atoms, resulting in the production of ground state atoms and fast electrons, was postulated by Klein and Rosseland [84] in 1921. These collisions, where a radiationless transfer of energy again takes place, with the conversion of electronic energy into translational energy, were called *collisions of the second kind*.

In 1922, Franck [85] extended this last mechanism to include collisions between atoms or molecules. In this case, the collision of an excited atom  $A^*$  with an unexcited atom B can produce an unexcited atom A and an excited atom  $B^*$ . Cario [86] and Cario and Franck [87] experimentally demonstrated in 1922 the existence of collisions of the second kind between atoms. A mixture of mercury and thallium atomic vapors, in conditions of selective photoexcitation of mercury (mercury resonance line at 254 nm), also displayed thallium (sensitized) green emission (535 nm). A more familiar situation where this process also occurs is the helium-neon laser.

It was later demonstrated by Beutler and Josephy [88] that the transfer occurs with high probability only when there is a near match of electronic transition energies between A and B. One thus speaks of *resonance energy transfer*. The need for near resonance is classically explained by the Franck principle [76], more familiar in its application to molecular spectroscopic transitions [89–91]. Kallmann and London developed the quantum theory of resonance energy transfer between atoms in 1928 [81]. The dipole-dipole interaction and the parameter  $R_0$  are used for the first time in this work.

Jean Perrin's concept of molecular transfer of energy (*transfert d'activation*) evolved in the context of his first studies of fluorescence [15] and of his theory of unimolecular chemical reactions [16–18, 23]. In [15], based on the observation of photobleaching of several dyes and other organic compounds (and of the corresponding fluorescence recovery by molecular diffusion, also noted by him), he (incorrectly) concludes that the fluorescence emission implies the destruction of the emitting molecule. The (complex) effect of concentration on the photobleaching rate led Perrin to propose that the neighboring molecules had a protecting role on the molecule directly excited. He advanced the following explanation.

D'autres molécules, même très voisines, ne seraient pas directement absorbantes. Mais la masse mise en vibration dans la molécule sensible exercerait sur les masses semblables des molécules voisines une "induction" qui les ferait à leur tour, par une résonance secondaire, entrer en vibration, induction d'autant plus active que les molécules sont proches, et qui, en définitive, aurait encore pour effet de partager entre plusieurs molécules qui resteraient intactes, l'énergie qui aurait été nécessaire pour en remanier irréversiblement une. [15]

(The other molecules, even if very close to the excited one, would not absorb the exciting radiation. But the vibrating part of the excited molecule would exert over similar parts of the neighboring molecules an "induction" that would put them in vibration by means of a secondary resonance. This induction would be the stronger the closer the molecules, and would result in the sharing of the

energy absorbed. This sharing would render harmless the absorbed energy, only destructive if concentrated in a single molecule.)

This induction was supposed to be of electromagnetic origin. The model used by Jean Perrin was that of a common transformer, with two synchronous circuits [22, 23, 26, 29–32]. Since these circuits, when in phase, repel each other, this provided him with the explanation for the conversion of electronic excitation energy into heat: the repulsion between the two molecules results in the production of kinetic energy [18, 22, 23]. This also accounted for the mechanism of heating by the absorption of radiation, a question that had been raised by Pierre Curie [18].

The proposal that fluorescence emission implies the destruction of the emitting molecule was afterwards withdrawn, on the basis of new experimental evidence (namely the effect of oxygen) [20]. Notwithstanding, Jean Perrin had measured in the meanwhile a continuous decrease of the intrinsic fluorescence yield of dyes in solution with an increase in concentration [19]. He explained it on the basis of the same mechanism of induction. The neighboring molecules, instead of helping to preserve the excited one, were acting as quenchers! [20].

It is interesting to note that the well-known exponential dependence on quencher concentration, for active-sphere quenching in rigid medium, known as the Perrin equation [92], was derived by Francis Perrin [34] precisely to account for the hypothetical self-quenching by resonance energy transfer previously postulated by Jean Perrin [20]. Only much later was it demonstrated that the true cause of self-quenching of dyes is the formation of nonfluorescent aggregates that, apart from reducing the number of luminescent molecules, may also act as traps by means of nonradiative and radiative transfer [93]. Additionally, in some experimental conditions, radiative transport also decreases the macroscopic fluorescence yield [94].

It is not known when Jean Perrin became aware of the results for energy transfer between atoms in the gas phase. He cites them in 1929 [29, 30], the year of Francis Perrin's Ph.D. thesis [46], where the subject is also raised, and where the 3rd edition of Pringsheim's book *Fluorescenz und Phosphorescenz* (1928) is indicated as a comprehensive bibliographical source. In the same year, in a work with Nine Choucroun, probably motivated by Cario and Franck's experiments, it is conceded that: Si, par suite de l'induction, il peut se produire à distance une transformation intégrale du quantum d'activation en énergie cinétique, il doit également pouvoir se produire, sans répulsion (et plus particulièrement en milieu visqueux ou rigide), un passage intégral de ce quantum du premier circuit au second. Ce sera le *transfert d'activation* qui substitue, à distance, sans changer les vitesses, une molécule activée à une autre molécule activée [29]. (If, by induction, the quantum of activation can be totally converted in kinetic energy at distance, then it must also be possible to produce, in the absence of repulsion (particularly in a viscous or rigid medium) the total transfer of this quantum from the first to the second circuit. This would be a *transfer of activation* at a distance, replacing one activated molecule for another one, without any change of speeds.)

They then give experimental evidence for sensitized fluorescence of molecules in solution, and establish a parallel with the Cario and Franck studies

cited above. A similar discussion appears in [30]. It was suggested [95] that the experimental results of Choucroun and Perrin could be at least in part due to radiative transfer.

Jean Perrin did not altogether abandon his original view of deactivation by direct electronic-to-translation transfer, as is clearly stated in [30, 32]. The same explanation is found in Francis Perrin's thesis [46].

There, when discussing the case of identical molecules, Francis Perrin makes the important remark that the transfer of energy is observable by the depolarization of fluorescence. In fact, it had been previously reported by several researchers that an increase in the concentration of dyes in viscous solvents was accompanied by a progressive depolarization [96–98], even for concentrations where quenching was still negligible, but no explanation had been given. To Francis Perrin, the cause can only be energy transfer: *Il suffit qu'un transfert d'activation puisse se produire entre deux molécules voisines d'orientations différentes, c'est-à-dire portant des oscillateurs non parallèles, pour qu'il en résulte en moyenne une diminution de l'anisotropie de distribution des oscillateurs excités et par suite de la polarisation de la lumière émise* [46]. (It suffices that a transfer of activation can occur between two neighboring molecules with different orientations, that is, with non-parallel oscillators, in order to have, on the average, a decrease in the anisotropy of the distribution of excited oscillators, and therefore a decrease of the polarization of the emitted light.)

Francis Perrin does not develop in his thesis the theory of the corresponding kinetics, that he considers quite difficult. He nevertheless estimated the distance at which the transfer may take place. From the concentration at which the depolarization becomes important for fluorescein in glycerol ( $10^{-3}$  g/cm<sup>3</sup>), the average distance is found to be 80 Å (the calculation presupposes a cubic lattice; the value for a random distribution is 45 Å). It is thus concluded that the probability for transfer at this distance is reasonable within the excited state lifetime, that is, transfer takes place at distances much larger than molecular dimensions [46].

Francis Perrin later developed a quantum theory of resonance energy transfer between atoms [52, 53], based on Kallman and London results [81]. He concluded that the transfer would be probable for distances of the order of one-quarter of the wavelength, in agreement with his previous estimates for molecules. He also qualitatively discussed the effect of the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, on the efficiency of transfer [52, 53], an effect that Jean Perrin had already recognized [26]. The development of the first quantitative theory of molecular resonance energy transfer, and corresponding kinetics were left to Theodor Förster [80, 99, 100].

## 2.5 Fluorescence Polarization

We saw in the previous section that Francis Perrin provided the correct interpretation of concentration depolarization in solution. He was particularly well placed to understand the problem, as he had been studying for some time the effect of molecular rotational motion on fluorescence polarization. This sub-

ject forms the core of his Ph.D. thesis in physics [46], while the mathematics of rotational Brownian motion was the subject of his Ph.D. thesis in mathematics [45].

Weigert discovered the polarization of the fluorescence of solutions in 1920, and already noted the effect of molecular size, solvent viscosity and temperature [101]. As a result of their own experiments, Vavilov and Levshin proposed in 1923 that the origin of depolarization was molecular rotation [102]. A first quantitative treatment was attempted by Levshin [98, 103], but the approximations made were too unrealistic. Francis Perrin published in 1925 his first results [36], not entirely correct because he supposed a circular oscillator and used a wrong definition of polarization. These two errors compensated in part, so that a good agreement with Levshin's experimental results [98] was obtained. In the following year, Francis Perrin publishes one of his best works on luminescence [41], where he corrects the problems mentioned and gives the equation that bears his name:

$$p = p_0 \frac{1}{1 + \left(1 - \frac{1}{3} p_0\right) \frac{RT}{V\eta} \tau} \quad (2.1)$$

where  $p$  is the polarization,  $p_0$  is the polarization in the absence of rotation (limiting polarization),  $R$  is the gas constant,  $T$  is the temperature,  $V$  is the solute's effective molar volume,  $\eta$  is the viscosity of the solvent and  $\tau$  is the lifetime of fluorescence. The modern, but equivalent form of the equation is deceptively simple:

$$\frac{r_0}{r} = 1 + \frac{\tau}{\tau_r} \quad (2.2)$$

where  $r$  is the anisotropy,  $r_0$  is the fundamental anisotropy,  $\tau_r$  is the rotational correlation time,  $\tau_r = \eta V / (RT)$ , and  $\tau$  is the lifetime of fluorescence. This equation, valid for spheres, was later generalized to ellipsoids [55].

Francis Perrin applied the equation to experimental polarizations obtained by him for fluorescein in water-glycerol mixtures at 20 °C. A plot of  $1/p$  vs  $RT/(V\eta)$  gave a straight line, as predicted, and yielded  $p_0 = 0.44$  and  $\tau = 4.3$  ns [41]. This last value is in good agreement with the presently accepted value, 4.1 ns [104]. The Perrin equation thus allowed the determination of fluorescence lifetimes [38, 39]. This was particularly important, since no other reliable method was then known. More experimental lifetimes are given in Francis Perrin's thesis [46]. One, particularly interesting, refers to erythrosin (tetraiodofluorescein) in water, for which a lifetime of ca. 80 ps was found. Again, this value is in very good agreement with more recent determinations,  $\tau = 75 \pm 5$  ps [105].

In 1926, Enrique Gaviola, working in Pringsheim's laboratory in Berlin, built the first phase-shift fluorimeter (based on the Kerr effect), for the direct measurement of short lifetimes [106, 107]. The values reported for uranin (fluorescein sodium salt) in water and in glycerol (4.4–4.5 ns) [107] agree with those of Perrin. But the value measured for erythrosin (1–2 ns) [107] is much higher than the correct one, showing the limitations of the apparatus for the measurement

of picosecond lifetimes. Curiously, this last value still appears in a 1967 compilation of lifetimes [108], although it had been previously criticized by Förster [109]. The use of Perrin's equation for the determination of lifetimes is also of course subject to limitations [76].

In the cited 1926 paper of Francis Perrin [41], he also obtains for the first time the relation between lifetime and quantum yield. Computing the radiative lifetime of fluorescein from its absorption spectrum by means of a relation that was already known, he could show that the estimated quantum yield was close to unity, in good agreement with direct determinations by Vavilov (Fig. 2.10).

Francis Perrin also obtained the relation between  $p_0$  and the angle made by the absorption and emission dipoles [46], predicting a variation between  $-1/3$  and  $1/2$  (the same result, in a less clear context [62], had been obtained before by Levshin [103]). The existence of negative values of polarization, experimentally established by Vavilov in 1929 [110], but incorrectly interpreted (attributed to an interaction with the magnetic field of the radiation), was also discussed by F. Perrin [51].

The last published work of Francis Perrin on molecular luminescence [56], results from his lecture in the first international luminescence conference, held in 1936 in Warsaw, where Jablonski and Pringsheim played major roles [61]. In

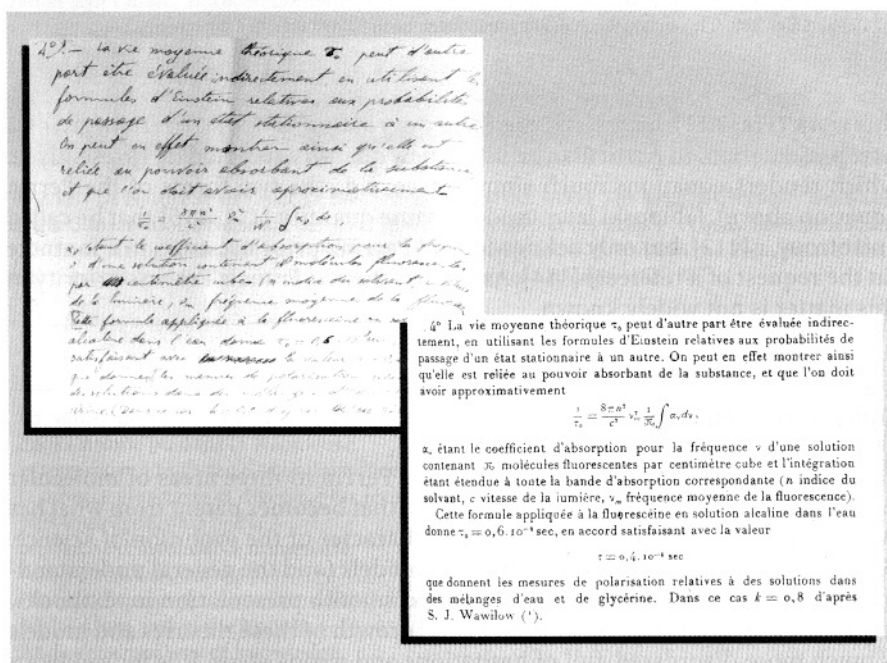
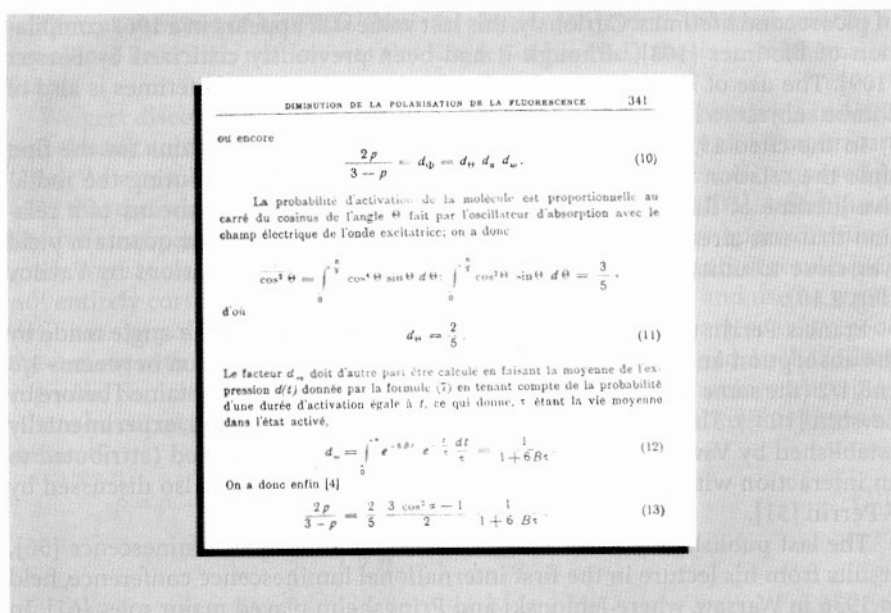


Fig. 2.10. Original manuscript and corresponding printed text of part of the article of Francis Perrin “Détermination de la vie moyenne dans l'état activé des molécules fluorescentes”, Comptes Rendus 182 (1926) 219–221. (Archives de l'Académie des Sciences, Paris)

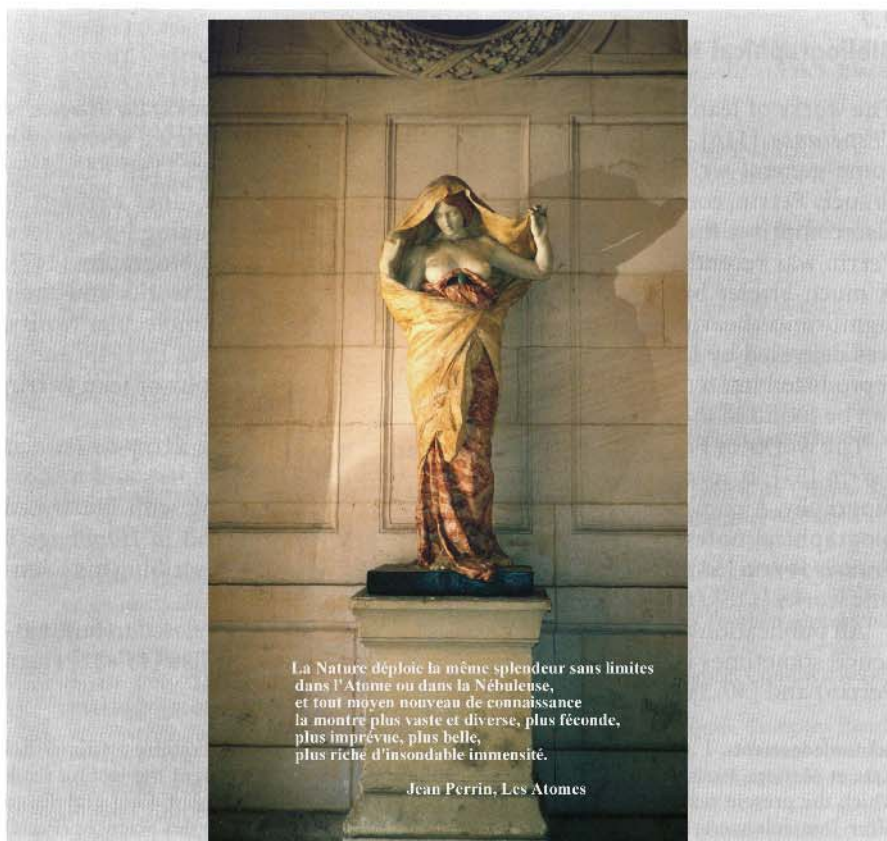


**Fig. 2.11.** Facsimile of part of the article of Francis Perrin “Diminution de la polarisation de la fluorescence des solutions résultant du mouvement brownien de rotation”, *Acta Phys. Polon.* 5 (1936) 335–347. The quantity  $2p/(3-p)$  was later named anisotropy by Jablonski

this work (Fig. 2.11), he reviews the theory of rotational depolarization, giving a new presentation. In particular, he uses a new quantity, denoted  $d_{\phi}$  (presently  $r$ ), which renders equations much simpler (see, e.g., the two forms of the Perrin equation above). Jablonski later used the same quantity [111–115] that he called anisotropy,  $r$  [112], but only acknowledged Perrin’s prior use once, in a footnote (at the request of a referee?) [114]. As a consequence, Francis Perrin’s priority in this matter is not widely known.

## 2.6 Concluding Remarks

The main contributions of Jean and Francis Perrin to three areas of molecular luminescence have been reviewed. An aspect that becomes patent from what has been presented is the complex, nonlinear character of the evolution of science. To a student acquainted with theories and models (and the general understanding of a subject), only from their logical and smooth presentation in textbooks, it may come as a surprise that the birth and growth of these theories and models is much more disordered, full of hesitations and wrong steps. It is indeed like a succession of multi-authored drafts converging to the final, collective text. Yet that is the true way of science, in an ever-greater understanding of nature (Fig. 2.12):



**Fig. 2.12.** La Nature se dévoilant à la Science (E. Barrias, 1899). The original, initially intended for the Conservatoire National des Arts et Métiers, is now at the Musée d'Orsay. Similar statues by Barrias can be found in the Ancienne Faculté de Médecine in Paris, in the Pena palace (Sintra, Portugal), and in the Smart Museum (University of Chicago, USA)

La Nature déploie la même splendeur sans limites  
dans l'Atome ou dans la Nébuleuse,  
et tout moyen nouveau de connaissance  
la montre plus vaste et diverse, plus féconde,  
plus imprévue, plus belle,  
plus riche d'insondable immensité.

Jean Perrin, Les Atomes [14]

(Nature displays the same boundless splendor  
In the Atom and in the Nebula,  
And every new way of knowledge  
Shows her more vast and diverse, more fecund,  
More unpredictable, more beautiful,  
And more full of inscrutable immensity.)

## 2.7 Bibliographical Notes

The works of Jean Perrin are collected in two posthumous books, *La Science et l'Espérance* [116], containing his philosophical and social views, along with some general writings on science, and *Oeuvres Scientifiques* [13], edited by Francis Perrin, containing a selection of scientific papers and other writings. It also comprises the full list of Jean Perrin's publications, including books. Jean Perrin was recently the subject of a very readable but biased biography [117]. A much briefer but more balanced account of his scientific works and their significance, bearing especially on the experimental proofs of molecular reality, was delivered by Louis de Broglie at the Académie des Sciences in 1945, and is reproduced in *La Science et l'Espérance* [116]. A short biography of Jean Perrin can be found in the Nobel Foundation web page.

The works of Francis Perrin are collected in a recent book, *Écrits de Francis Perrin* [57]. It specifically contains a selection of scientific papers and a short biography. A complete list of his scientific publications, along with illustrated biographical notes and interesting recollections, can be found in *Hommage à Francis Perrin* [58]. Francis Perrin wrote in 1951 a brochure describing his scientific works [118] (reproduced in part in [57]).

All publications of Jean Perrin and Francis Perrin directly related to luminescence, sometimes incorrectly cited, are given in the reference list: [15–32] (Jean Perrin) and [30, 34–56] (Francis Perrin).

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