JOURNAL OF CHEMICAL EDUCATION

ARTICLE

pubs.acs.org/jchemeduc

A Brief History of Fluorescence and Phosphorescence before the Emergence of Quantum Theory

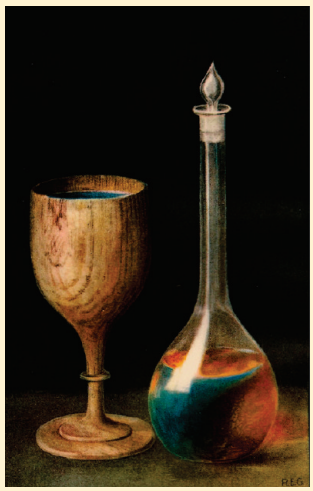
Bernard Valeur*,† and Mário N. Berberan-Santos*,‡

†Conservatoire National des Arts et Métiers, 292 rue Saint-Martin, F-75003 Paris, and Institut d'Alembert, Laboratoire PPSM, ENS-Cachan, 61 Avenue du Président Wilson, F-94235 Cachan Cedex, France

‡Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

ABSTRACT: Fluorescence and phosphorescence are two forms of photoluminescence used in modern research and in practical applications. The early observations of these phenomena, before the emergence of quantum theory, highlight the investigation into the mechanism of light emission. In contrast to incandescence, photoluminescence does not require high temperatures and does not usually produce noticeable heat. Such a "cold light" was the object of an interesting controversy in the 19th century: does it fit into thermodynamics? The early applications, such as the fluorescent tube, fluorescence analysis, and fluorescent tracers, are described.

KEYWORDS: General Public, Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, History/Philosophy, Textbooks/Reference Books, Fluorescence Spectroscopy, Quantitative Analysis



Photoluminescence, the emission of light arising from excited electronic states following absorption of light, is important in many scientific and technological fields, namely, physics, chemistry, materials science, biology, and medicine.[1] Many important applications based on photoluminescence have been developed, such as fluorescence microscopy, fluorescent tubes and lamps, optical brighteners, plasma screens, forensics, tracers in hydrogeology, fluorescent and phosphorescent paints, phosphorescent labels, safety signs, and counterfeit detection (security documents, bank notes, art works).[2]

The aim of this paper is to briefly describe some of the early milestones in the study of photoluminescence. The explanation of how light can be emitted by atomic or molecular excited states following absorption of light can include a historical introduction or be intermingled with historical remarks. Generally speaking, luminescence can be distinguished from incandescence, which is light emitted by bodies heated at high temperatures. The question as to whether photoluminescence, often considered as cold light, fits into thermodynamics was the object of a controversy in the 19th century. This could lead to an interesting discussion in a thermodynamics course. Information provided here might also be useful for instrumental analysis and quantum mechanics courses.

WHAT IS PHOTOLUMINESCENCE

The term *luminescence* comes from a Latin root (*lumen* = light). It was first introduced as *luminescenz* by the German physicist and science historian Eilhard Wiedemann in 1888 for all phenomena of light that are not solely conditioned by the rise in temperature, that is, incandescence. Before considering the historical evolution of the understanding of luminescence, it should be noted that the present definition of luminescence is "a spontaneous emission of radiation from an electronically excited species (or from a vibrationally excited species) not in thermal equilibrium with its environment".[3]

The various types of luminescence are classified according to the mode of excitation. In particular, photoluminescence is the emission of light arising "from direct photoexcitation of the emitting species".[3] Fluorescence, phosphorescence, and delayed fluorescence are well-known forms of photoluminescence. There are other types of luminescence that differ by the mode of excitation (chemiluminescence, bioluminescence, electroluminescence, cathodoluminescence, radioluminescence, sonoluminescence, thermoluminescence, triboluminescence).

Published: March 18, 2011

ACS Publications Copyright © 2011 American Chemical Society and Division of Chemical Education, Inc.

Milwaukee Electric Tool Corporation
Ex-1019
Page 1 of 8

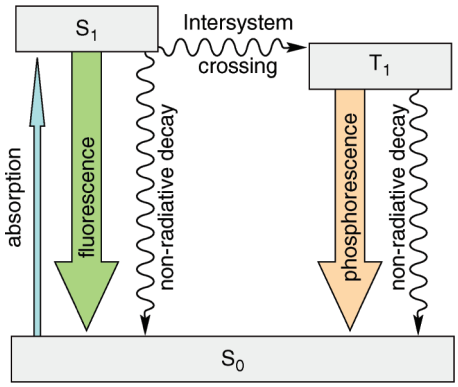


Figure 1. Simplified Perrin–Jablonski diagram showing the difference between fluorescence and phosphorescence. Fluorescence occurs when radiation is emitted from the first excited singlet state S_1 that is reached by previous absorption of a photon.[a] Phosphorescence occurs when radiation is emitted from the triplet state T_1 after intersystem crossing from S_1.

For a long time after the introduction of the term *fluorescence* by G. G. Stokes[4] in the middle of the 19th century, the distinction between fluorescence and phosphorescence was based on the duration of emission after the end of excitation: fluorescence was considered as an emission of light that disappears simultaneously with the end of excitation, whereas in phosphorescence, the emitted light persists after the end of excitation. But such a criterion is insufficient because there are long-lived fluorescences (e.g., divalent europium salts) and short-lived phosphorescences (e.g., violet luminescence of zinc sulfide) whose durations are comparable (several hundreds of nanoseconds). The usual condition for observing phosphorescence is that the excited species passes through an intermediate state before emission, as stated for the first time by Francis Perrin in 1929.[5] More precisely, in the frame of molecular photochemistry, we now say that the *spin multiplicity*[a] is retained in the case of fluorescence, whereas phosphorescence involves a change in spin multiplicity, typically from *triplet* to *singlet* or vice versa (Figure 1).[3]

■ EARLY OBSERVATIONS OF PHOTOLUMINESCENCE[6–8]

Phosphorus was the ancient Greek name given to planet Venus when appearing as the morning star and thus announcing the imminent sunrise. The term means *the light bearer*: $\phi\omega\varsigma$ = light; $\phi\varepsilon\rho\varepsilon\iota\nu$ = to bear.[b] The term *phosphor* has been used since the Middle Ages to designate materials that glow in the dark after exposure to light. There are many ancient reports of glow-in-the-dark minerals, and the most famous of them was the *Bolognian phosphor* (impure barium sulfide) discovered by a cobbler from Bologna in 1602, Vincenzo Cascariolo. Later, the same name *phosphor* was assigned to the element phosphorus isolated by Brandt in 1677 because, when exposed to air, it burns and releases glowing vapors. But emission of light is in this case *chemiluminescence*, not photoluminescence; the species that emit light are excited by the energy provided by the combustion reaction and not by the absorption of a photon.

In 1565, a Spanish physician and botanist, Nicolás Monardes (Figure 2), reported the peculiar blue color (under certain conditions of observation) from an infusion of a wood from Mexico and used to treat kidney and urinary diseases (Figure 3).[9–12] This wood (later called *Lignum nephriticum*), whose peculiar color effect and diuretic properties were already known to the Aztecs, was a scarce and expensive medicine. Therefore, it was of interest to detect counterfeited wood. Monardes wrote on this respect,[12]

> *Make sure that the wood renders water bluish, otherwise it is a falsification. Indeed, they now bring another kind of wood that renders the water yellow, but it is not good, only the kind that renders the water bluish is genuine. (in Spanish in the original).*

This method for the detection of a counterfeited object can be considered as the first application of the phenomenon that would be later called *fluorescence*. Extracts of the wood were further investigated by Boyle, Newton, and others,[6] but the phenomenon was not understood at the time.

Figure 2. Portrait of Nicolás Monardes. From the front page of the book *Dos Libros, el Vno Qve Trata de Todas las Cosas que traen de nuestras Indias Occidentales, que siruen al vso de la Medicina, y el otro qve trata de la Piedra Bezaar, y de la Yerva Escuerçonera*, Seville, Spain, 1569.

The chemical species responsible for the intense blue fluorescence was recently identified in an infusion of *L. nephriticum* (*E. polystachya*): it is called *matlaline* (from *Matlali*, the Aztec word for blue) (Figure 4).[12c] This compound is not present in the plant but results from an unusual spontaneous oxidation of at least one of the tree's flavonoids.

In 1819, a peculiar property of some crystals of fluorite (calcium fluoride, then called fluated lime, spath fluor, or fluor spar) from Weardale, Durham, England, was reported by Edward D. Clarke, Professor of Mineralogy at the University of Cambridge.[13] These crystals of the "Durham Fluor" surpassed in magnificence and beauty any other mineral substance he had ever seen. The finer crystals, perfectly transparent, had a dichroic nature: the color by reflected light was a deep sapphire blue, whereas the color by transmitted light was an intense emerald green (Figure 5). Clarke offered no explanation for the observations reported.

In the second edition of his famous treatise on mineralogy, published in 1822,[16] the French mineralogist René-Just Haüy mentions the double color of some crystals of fluorite (reported to be from Derbyshire County, England) The color by reflected light was described as violet, whereas the color by transmitted light was again green. Haüy explained the phenomenon as a type of opalescence (which is observed with opal, a naturally occurring hydrated silica glass, and results from light scattering): the two colors were complementary, violet being the dominant hue of the scattered light and green the dominant hue of transmitted (i.e., unscattered) light. Although the explanation was incorrect

Milwaukee Electric Tool Corporation
Ex-1019
Page 2 of 8

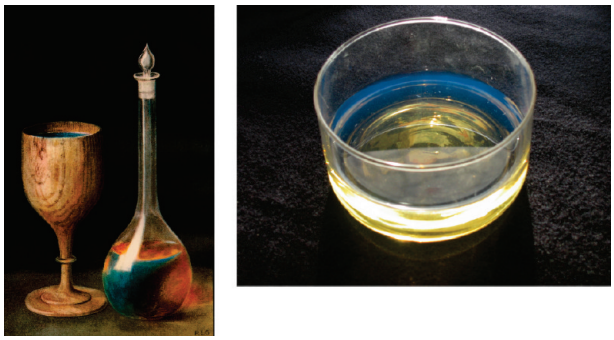


Figure 3. Absorption and fluorescence colors of infusions of *L. nephriticum* in daylight: (left) image taken from ref 9 and (right) mildly alkaline aqueous solution to which chips of *Eysenhardtia polystachia* (kindly provided by Dr. A. U. Acuña) were added.

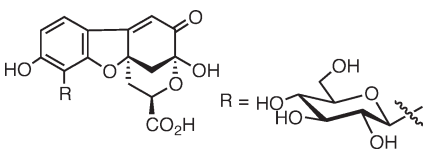


Figure 4. Structure of tetrahydromethanobenzofuro[2,3-*d*]oxacine, which is responsible for the fluorescence of *L. nephriticum*.

(see the caption of Figure 5) and a correct one was still a long way off, Hauy's view and the two minerals mentioned, fluorite and opal, were going to play a central role in the understanding and naming of fluorescence.

In 1833, Sir David Brewster, the well-known Scottish physicist, described the beautiful red fluorescence of chlorophyll in the article "On the Colour of Natural Bodies",[17] where it is reported that a beam of sunlight passing through a green alcoholic extract of leaves (mainly a chlorophyll solution) appears to be red when observed from the side. He pointed out the similarity with the blue light coming from a light beam when entering some fluorite crystals. Again, similar to Haüy, Brewster interpreted these phenomena as manifestations of opalescence (light scattering).

In 1845, the polymath Sir John Herschel, son of the famous astronomer and the originator of the word photography (where light is again involved), prepared an acid solution of quinine sulfate and stated,[18]

> *Though perfectly transparent and colorless when held between the eye and the light, it yet exhibits in certain aspects, and under certain incidences of the light, an extremely vivid and beautiful celestial blue color.*

As the color was always superficial, he believed it to be a hitherto unidentified phenomenon, "a case of superficial colour presented by a homogeneous liquid, internally colourless".[18] Herschel called this phenomenon *epipolic dispersion*, from the Greek: *επιπολη* = surface. In fact, the solutions observed by Herschel were very concentrated so that the majority of the incident light was absorbed near the surface and all the blue fluorescence originated from there. Herschel used a prism to show that the epipolic dispersion could be observed only upon illumination by the blue end of the spectrum and not the red end. The crude spectral analysis of the emitted light with the prism revealed blue, green, and a small quantity of yellow light, but Herschel did not realize that the superficial light was of longer wavelength than the incident light. Herschel also discussed the superficial blue color

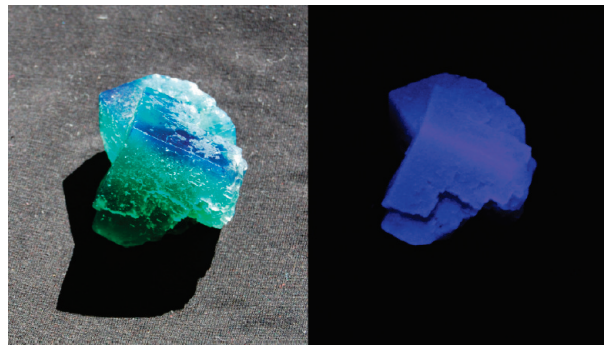


Figure 5. Twinned crystals of green fluorite (from Rogerley, Weardale, Durham County, England) illuminated with sunlight (left) and a UV lamp (right). The double color is apparent. Pure fluorite is colorless and nonfluorescent; however, natural fluorites usually contain many elements from the rare-earth family. The green color is due to Sm^{2+} absorption (in the blue and in the red),[14] whereas the deep blue color is due to Eu^{2+} fluorescence. The states involved in the emission have 7 unpaired electrons; hence, their spin multiplicity[a] is 8.[15] Both elements are present as substitutional impurities in the range 10−100 ppm.

of some green fluorite crystals, noting the similarity with the observations made with quinine solutions, and considered that it was also a case of epipolic dispersion. On the other hand, he attributed the blue color of *L. nephriticum* extracts to ordinary dispersion by tiny particles in suspension.

When the epipolic theory, which contradicted Brewster's earlier views, became known to Brewster, he carried out further experiments showing that the phenomenon was not superficial, as assumed by Herschel. On the basis of polarization measurements, Brewster proposed instead[19] that "...unless this [...] is a new property of light, produced by a peculiar action of certain solid and fluid bodies..." all the media studied contain minute crystals randomly oriented, with the consequence that unpolarized light is dispersed in all directions. He coined the term *internal dispersion* for this explanation. However, Brewster had made the wrong choice.

INVENTION OF THE TERM FLUORESCENCE[4,6,8]

A major event in the history of photoluminescence was the publication by Sir George Gabriel Stokes (Figure 6), physicist and professor of mathematics at Cambridge, of his famous paper entitled "On the Refrangibility of Light" in 1852.[4] In it, and in detailed experimental studies on several samples, both organic (including quinine) and inorganic (including a fluorite crystal similar to that shown in Figure 4, reported to be from Alston Moor, England[c]), he clearly identified a common phenomenon he called *dispersive reflection*: the wavelengths of the dispersed light are always longer than the wavelength of the original light. One of Stokes's experiments that is spectacular and remarkable by its simplicity deserves attention. Stokes formed the solar spectrum by means of a prism. When he moved a test tube filled with a solution of quinine through the visible part of the spectrum, nothing happened: the solution remained transparent.[20] But beyond the violet portion of the spectrum, that is, in the invisible zone corresponding to ultraviolet radiation, the solution glowed with a blue light (Figure 7). Stokes wrote,[4]

> *It was certainly a curious sight to see the tube instantaneously light up when plunged into the invisible rays: it was literally*

Milwaukee Electric Tool Corporation
Ex-1019
Page 3 of 8

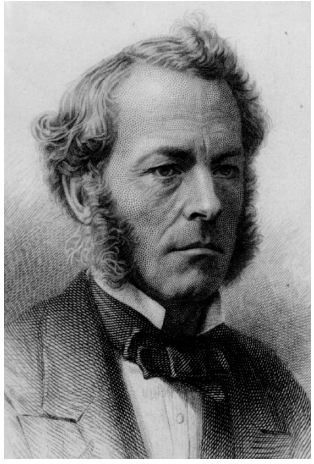


Figure 6. Portrait of Sir George Gabriel Stokes (permission obtained from AIP Emilio Segre Visual Archives, E. Scott Barr Collection).

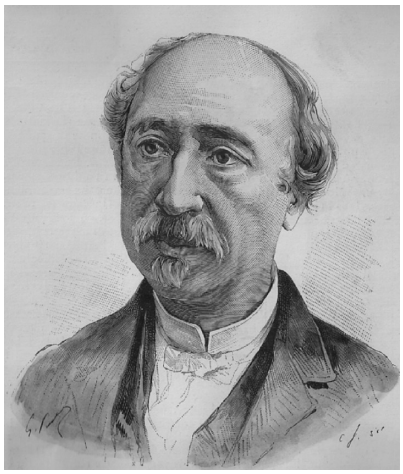


Figure 8. Portrait of Edmond Becquerel (author's collection).

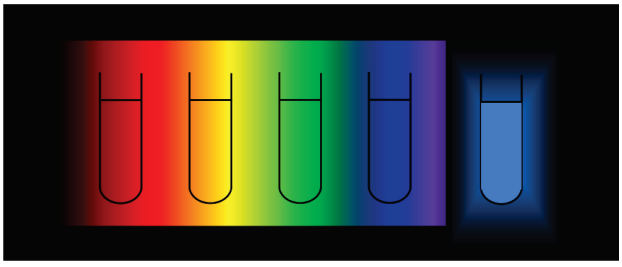


Figure 7. Principle of Stokes's experiment showing that a solution of quinine irradiated with UV emits blue light, whereas no effect is observed when it is placed in the visible part of the solar spectrum.[20].

> *darkness visible. Altogether the phenomenon had something of an unearthly appearance.*

From his experiments with a wide range of substances, Stokes concluded that the dispersed light was always of longer wavelengths than the incident light. Later this statement became the *Stokes law*.

Stokes also noted that the dispersion of light took place in all directions, hence, the fluid behaved as if it were self-luminous. In his paper, Stokes called the observed phenomenon *true internal dispersion* or *dispersive reflection* but in a footnote,[4] he wrote,

> *I confess I do not like this term. I am almost inclined to coin a word, and call the appearance fluorescence, from fluorspar, as the analogous term opalescence is derived from the name of a mineral.*

In his second paper,[21] Stokes definitely resolved to use the word *fluorescence*.

It is often ignored that, 10 years before Stokes's first paper, the French physicist Edmond Becquerel (Figure 8) (discoverer of the photovoltaic effect and father of Henri Becquerel, the discoverer of radioactivity) published an original paper[22] in which he described the emission of light by calcium sulfide deposited on paper when exposed to solar light beyond the violet part of the spectrum. Therefore, he was the first to state that the emitted light is of longer wavelength than the incident light. Stokes's paper led Becquerel to a priority claim for this result.[23] The difference between the Stokes and Becquerel experiments is that, according to the definitions given in the preceding section, quinine is fluorescent whereas calcium sulfide is phosphorescent, but both species are relevant to photoluminescence.

All modern accounts of Stokes's contributions to the understanding of fluorescence fail to mention that he viewed it as an instantaneous scattering process that ceases immediately after the exciting light is cut off. In his own words,[4]

> *...in the phenomenon of internal dispersion, the sensitive body, so long as it is under the influence of the active light, behaves as if it were self-luminous. Nothing then seems more natural to suppose that the incident vibrations of the luminiferous ether produce vibratory movements among the ultimate molecules of sensitive substances, and that the molecules in turn, swinging on their own account, produce vibrations in the luminiferous ether, and thus cause the sensation of light.*

The change of refrangibility (i.e., the wavelength or the Stokes shift) could be explained in the same way: "The periodic times of these vibrations depend upon the periods in which the molecules are disposed to swing, not upon the periodic time of the incident vibrations".[4] Thus, internal dispersion would correspond in this respect to what is now known as inelastic scattering, for example, vibrational Raman scattering, and not to the postquantum description of fluorescence as a two-step process with a finite waiting time between absorption and emission. Interestingly, such a connection can be found in the well-known terminology of Raman lines as either Stokes or anti-Stokes. Nevertheless, in vibrational Raman scattering, a characteristic and fixed emission spectrum does not exist, and it is only the shift in energy that is constant and specific of the molecular vibrations.

Becquerel, on the other hand, considered that phosphorescence and Stokes's fluorescence were one and the same emission phenomenon, always with a finite duration that was simply shorter in the case of fluorescence and longer in the case of phosphorescence. He even advocated the term fluorescence to be abandoned, which according to his view was a short-lived phosphorescence (ref 24, p 321).

From our present vantage point, it can be seen that both Stokes's and Becquerel's views of fluorescence and phosphorescence contain important elements of truth derived from carefully designed experiments, but none is completely correct in its theoretical aspects. As is often the case, theories are subject of gradual growth and progressive improvement.

Milwaukee Electric Tool Corporation
Ex-1019
Page 4 of 8

COLD LIGHT VERSUS INCANDESCENCE[25]

In contrast to incandescence, fluorescence and phosphorescence do not require high temperatures and do not usually produce noticeable heat. Such emissions were named *cold light* for this reason.

In the late 19th century, the laws of radiation were thoroughly studied. In particular, Kirchhoff's law of radiation stated that the ratio of the absorptive and emissive powers of any material was a universal function of temperature and wavelength. Fluorescence and phosphorescence were in apparent contradiction with this law because they were highly dependent on the chemical nature of the substance and did not show a strong temperature dependence.

The mechanism of cold-light emission invoked by Wiedemann was based on the kinetic theory stating that matter is composed of molecules in motion and postulating that each molecule (or atom) is surrounded by an ether shell. At that time, ether was assumed to be necessary for explaining the propagation of light that should require, similar to sound, a supporting medium. Collisions cause vibrations that are transmitted to the ether shells, which produce light whose intensity depends on the strength of vibrations. These considerations led Wiedemann to reject the term cold light and to propose instead the term *luminescence* to designate any emission of light more intense than expected from the source's temperature.[26]

DOES COLD LIGHT FIT INTO THERMODYNAMICS?[25,27]

In the late 19th century, the question arose whether cold light violates the second law of thermodynamics, in that heat cannot flow from a colder body to a warmer body. In 1889, Wiedemann envisioned a case where the second law seems to be violated: a luminescent material could transfer radiant energy to an object having a higher temperature if this object absorbed the luminescence. To rescue the second law, Wiedemann introduced the concept of *luminescence temperature*, that is, the temperature required for the incandescent emission from a body to match the intensity of the body's luminescence. But this concept was found to be unnecessary because a fundamental distinction should be made between energy transferred from a body with a well-defined temperature (i.e., in internal thermal equilibrium) and energy transferred from a body not in internal thermal equilibrium, in the same way as Kirchoff's law applies to thermal radiation but not to nonthermal radiation (cold light).

At the end of the 19th century, the Berlin physicist Wilhelm Wien[25] considered that the Stokes law was simply a special case of the second law. But several cases of violation of the Stokes law were reported. The first of them is due to Eugen Lommel in 1871: upon excitation of a solution of a dye (naphthalene red) with the yellow lines from a sodium flame, he was able to detect a weak green fluorescence, that is, of shorter wavelength.[28] The contamination of the light source was suspected by other researchers. In 1886, after checking carefully that no extraneous light contaminated his experiments, Franz Stenger studied not only naphthalene red, but also fluorescein and eosin: he found that all samples showed fluorescence at shorter wavelengths than excitation.[29] Wien and also Karl von Wesendonck[30] considered that in the cases where the Stokes law failed, there must be an increased absorption of energy by the fluorescent species.

Additional evidence for the Stokes law violation was provided in 1904 by Edward Nichols and Ernest Merritt, physicists at Cornell University, who were able to record the fluorescence spectra of naphthalene red, fluorescein, and eosin.[31] The spectra extended beyond the short-wave limits of the exciting light (Figure 9). The Stokes law violation happens only in the region where the absorption and fluorescence curves overlap, as first noted by Lommel.[32]

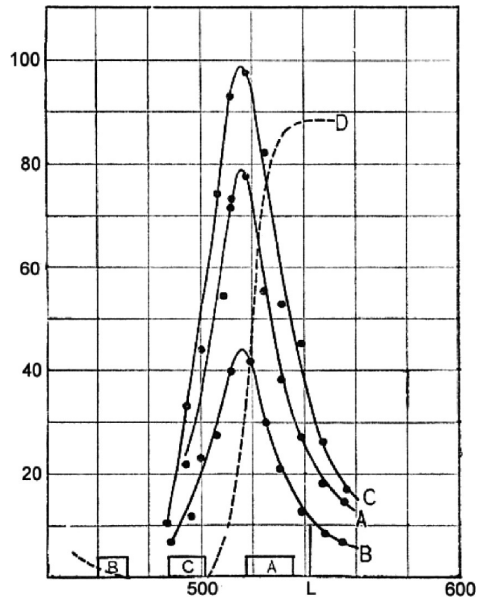


Figure 9. Fluorescence spectra of fluorescein upon excitation by various sources (A, B, C) whose wavelength ranges are represented on the horizontal axis (values in nm). L represents the longest excitation wavelength providing fluorescence. D is the transmittance of the sample. (Adapted from ref 31).

A major event in the turn of the 19th century was the Planck theory of quanta that Albert Einstein applied to the photoelectric effect and also to luminescence. Considering that the energy of the absorbed and emitted light quanta (later on called photons) should be proportional to their respective frequencies, the Stokes law simply obeys the first law of thermodynamics (conservation of energy). But how can the exceptions to the Stokes law be explained? The bell-shaped intensity curves for emission suggest a statistical process. Einstein proposed that molecular motion provides the additional energy required for the violation of the Stokes law. If this assumption is correct, then the departure from the Stokes law should be larger at higher temperatures. A discussion between Einstein and Joseph von Kowalski on this topic led the latter to study the effect of temperature on the emission of rhodamine. The results showed agreement (within an order of magnitude) with calculations based on Einstein's assumption.[33] As vibrational energy is converted into radiation, cooling of the medium can occur upon anti-Stokes emission. An interesting consequence is laser cooling of solids, a subject where significant developments occurred over the past decade.[34]

BECQUEREL'S PIONEERING WORK ON TIME-RESOLVED PHOTOLUMINESCENCE

Edmond Becquerel did not participate in the controversy on the Stokes law. He showed great interest for various aspects of light,[24] but his most important contribution concerns phosphorescence. In fact, Kayser and Konen[35] considered that Becquerel introduced a revolution in this field. In particular, Becquerel

Milwaukee Electric Tool Corporation
Ex-1019
Page 5 of 8

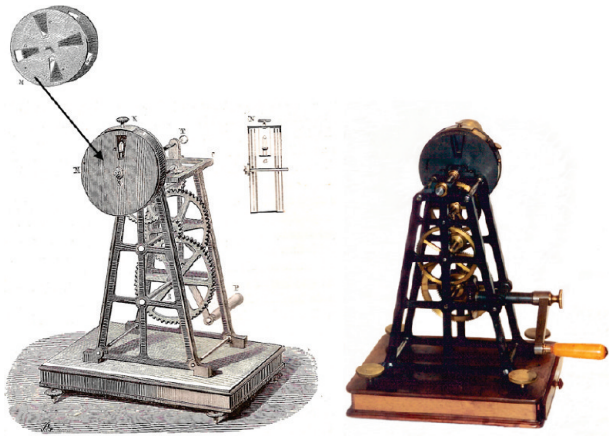


Figure 10. Two of Edmond Becquerel's phosphoroscopes: (left) drawing from ref 24 and (right) photo of the phosphoroscope at the Musée des Arts et Métiers in Paris. The speed of rotation of both disks bearing four windows can reach 3000 rev/s, which allowed Becquerel to analyze phosphorescence decays whose time constant is shorter than 0.1 ms. The authors of the present article had the privilege to operate it very carefully, with special gloves! It still works very well.

measured the decay times of the phosphorescence of various compounds by means of his outstanding phosphoroscope built in 1858: this was the very first time-resolved photoluminescence experiment.

Becquerel designed his phosphoroscope at the Conservatoire Impérial des Arts et Métiers, where he was appointed to the chair of physics from 1852 to 1891. The instrument consists of two disks rotating together at variable speeds up to 3000 revolutions per second (rev/s). The sample is placed between the two disks. Each disk possesses four windows in such a way that the incident light cannot go through the second disk (Figure 10), and therefore, there is a time lag between excitation and observation of emission that depends on the speed of rotation. By changing the latter, the intensity of emission can be measured as a function of time. Phosphorescence lifetimes shorter than 0.1 ms could be determined in this way. The first results were published in 1861.[24]

For the description of the experimental phosphorescence decays, Becquerel used an exponential of time and also a sum of two exponentials. However, in the case of inorganic solids, he obtained a better fit with the following equation:

$$i^2(t + c) = c \qquad (1)$$

where i is the normalized intensity so that $i(0) = 1$, t is time, and c is a time constant. Later, he proposed a more general equation in the form:[36]

$$i^m(t + c) = c \qquad (2)$$

where $1 \geq m \geq {}^1/_2$. He obtained good fits for alkaline-earth sulfides. Equation 2 can be rewritten as

$$i(t) = \frac{1}{(1 + t/c)^{1/m}} \qquad (3)$$

Because m is less than 1, this function decays faster than a hyperbola (for which $m = 1$) and can thus be called a *compressed* or *squeezed hyperbola*. But owing to Becquerel's pioneering studies, and reviving a now almost forgotten terminology,[37] we suggest calling this function the *Becquerel decay law*.[38] We have recently shown that this function is of great interest in the analysis of complex luminescence decays with underlying distributions of decay times.[39−41]

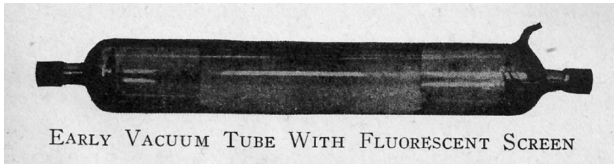


Figure 11. Photograph of an early fluorescent tube made by W. S. Andrews in 1912 (reproduced with permission from ref 43; Copyright 1941 Chemical Publishing Co.).

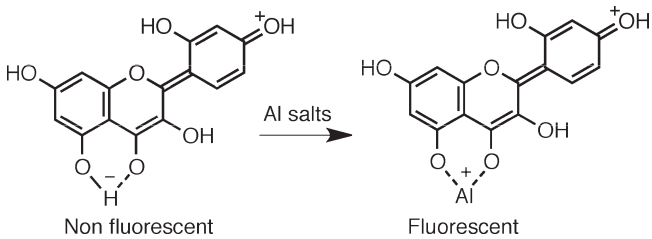


Figure 12. Complexation of morin with aluminum ion leads to a fluorogenic effect (enhancement of fluorescence intensity).

EARLY APPLICATIONS OF PHOTOLUMINESCENCE[2,6,42−44]

The fluorescent tube was one of the oldest applications of fluorescence. Edmond Becquerel in 1857, and probably German scientists at the same time, conceived the idea of coating the inner surface of an electric discharge tube with a luminescent material (Figure 11). Such tubes are similar to the fluorescent tubes that are made today. In fact, the inner coating is nowadays made of Eu^{II}, Eu^{III}, and Tb^{III}, so that addition of blue, red, and green lights yields white light.

In the field of chemistry, fluorescence has long been used as an analytical tool for the determination of the concentrations of various neutral or ionic species.[6,45] Stokes had this idea in mind since his 1852 paper, where one of conclusions states[4]

> *[The phenomenon] furnishes a new chemical test, of a remarkable searching character, which seems likely to prove of great value in the separation of organic compounds. The test (...) leads to the independent recognition of one or more sensitive substances in a mixture (...).*

He lectured "on the application of the optical properties to detection and discrimination of organic substances" before the Chemical Society and the Royal Institution in 1864.

Victor Pierre[46] who was a professor in Prague and later in Vienna, published papers in 1862 where he studied solutions of single fluorescent compounds and mixtures. He noticed that bands of fluorescent spectra were characteristic of a particular substance. He noted also the effect of solvent and acidity or alkalinity. A well-known application of fluorescence to analysis was reported by Göppelsröder[d] in 1868:[47] the complexation of morin (a hydroxyflavone derivative) with aluminum produces a drastic enhancement of fluorescence intensity (Figure 12), offering a straightforward way to detect this metal. It was the first time that the term *fluorescence analysis* was employed.

Milwaukee Electric Tool Corporation
Ex-1019
Page 6 of 8

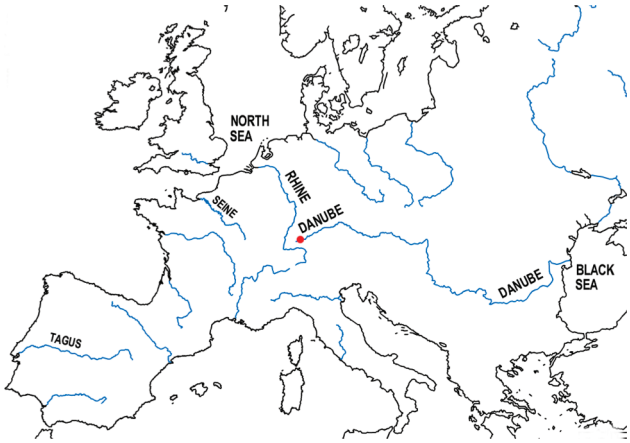


Figure 13. Map showing that the Danube springs in the Black Forest and flows into the Black Sea. By means of uranin as a fluorescent tracer, it was demonstrated that most of the spring water flows into the North Sea. The red point indicates the location of Immendingen.

Among the old applications of fluorescence, it is worth mentioning that uranin (the disodium salt of fluorescein) was used for the first time in 1877 as a tracer for monitoring the flow of the Danube river.[48] On all maps, it is shown that the Danube springs in the Black Forest and, after many hundreds of kilometers, flows into the Black Sea (Figure 13). But there are several sinks (swallow holes) in the bed of Danube. The biggest one is near Immendingen (red point in Figure 13). Ten liters of a concentrated solution of uranin were poured by Knop into the bed of the upper current of the Danube, and 50 h later, the fluorescence could be observed in the water of the river Aache 12 km to the south. This river flows into the lake Constanz that feeds the Rhine. Therefore, only a small part of the water from the Danube spring arrives at the Black Sea. Most of it flows into the North Sea! Nowadays, fluorescence tracing is currently used in hydrogeology, especially to simulate and trace the discharge of pollutants.[48]

CONCLUSION

Photoluminescence is an attractive topic that deserves various discussions in the classroom related to (i) the excited states of atoms and molecules, (ii) the various types of emission of light by matter, (iii) the distinction between luminescence and incandescence, (iv) the thermodynamic aspects of photoluminescence in the frame of a historical controversy, (v) the Stokes law and its violation, (vi) the temporal characteristics of photoluminescence exemplified by the early time-resolved measurements, and (vii) the early applications of fluorescence that are still used today.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (B.V.) bernard.valeur@cnam.fr; (M.N.B.-S.) berberan@ist.utl.pt.

ADDITIONAL NOTE

[a] The spin multiplicity is the number of possible orientations, calculated as $2S + 1$, of the spin angular momentum corresponding to a given total spin quantum number (S), for the same spatial electronic wavefunction. A state of singlet multiplicity has $S = 0$ and $2S + 1 = 1$. A state of triplet multiplicity has $S = 1$ and $2S + 1 = 3$.

[b] We find the same root in the common name of $COCl_2$, phosgene (*generated by light*), the infamous poisonous gas first synthesized by Davy in 1812 by the photodissociation of chlorine in the presence of carbon monoxide.

[c] According to a contemporary writer, most mineral shops were located at Alston, in the Alston Moor district, under whose name the fluor spar from the area (including the green variety characteristic of Weardale) was known, see Sopwith, T. *An Account of the Mining Districts of Alston Moor, Weardale and Teesdale in Cumberland and Durham*; Davison: Alnwick, 1833; p 110.

[d] The first paper of the series written by F. Göppelsröder (*J. Prakt. Chem.* **1867**, *101*, 408) is often erroneously cited as the first reported application of fluorescence to analysis. In fact, the application to aluminum detection was not described in this paper.

REFERENCES

(1) (a) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, 2002. (b) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2006. (c) *Molecular Luminescence Spectroscopy*; Schulman, S. G., Ed.; Wiley Interscience: New York, 1985−1993; Parts 1−3.

(2) (a) Valeur, B. From Well-Known to Underrated Applications of Fluorescence. In *Fluorescence of Supermolecules, Polymers and Nanosystems; Springer Series on Fluorescence*, Vol. 4; Berberan-Santos, M. N., Ed.; Springer Verlag: Berlin, 2008; pp 21−43. (b) Valeur, B. Molecular Fluorescence. In *Encyclopædia of Applied Spectroscopy*; Andrews, D., Ed.; Wiley-VCH: Weinheim, 2009; pp 477−532.

(3) Braslavsky, S. E. et al. ; *Glossary of Terms used in Photochemistry*, 3rd edition (IUPAC recommendations 2006), *Pure Appl. Chem.* **2007**, *79*, 293−465.

(4) Stokes, G. G. *Philos. Trans.* **1852**, *142*, 463–562.

(5) Perrin, F. *Ann. Phys. (Paris, Fr.)* **1929**, *12*, 169–275.

(6) Harvey, E. N. *A History of Luminescence from the Earliest Times until 1900*; The American Philosophical Society: Philadelphia, PA, 1957; Reprinted by Dover publications.

(7) Goldberg, M. C., Weiner, E. R. The Science of Luminescence. In *Luminescence Applications*; Goldberg, M. C., Ed.; ACS Symposium series 383, American Chemical Society: Washington DC, 1989; pp 1−22.

(8) Valeur, B. On the origin of the terms fluorescence, phosphorescence and luminescence. In *New Trends in Fluorescence Spectroscopy: Application to Chemical and Life Sciences*; Valeur, B., Brochon, J. C., Eds.; Springer: Berlin, 2001; pp 3−6.

(9) Safford, W. E. *Ann. Rep. Smithsonian Inst.* **1915**, 271–298.

(10) Partington, J. R. *Ann. Sci.* **1955**, *11*, 1–26.

(11) Muyskens, M. *J. Chem. Educ.* **2006**, *83*, 765–768.

(12) (a) Acuña, A. U.; Amat-Guerri, F. Early History of Solution Fluorescence: The Lignum nephriticum of Nicolás Monardes. In *Fluorescence of Supermolecules, Polymers and Nanosystems; Springer Series on Fluorescence*, Vol. 4; Berberan-Santos, M. N., Ed.; Springer Verlag: Berlin, 2008; pp 3−20. (b) Acuña, A. U. *J. Chem. Educ.* **2007**, *84*, 231. (c) Acuña, A. U.; Amat-Guerri, F.; Morcillo, P.; Liras, M.; Rodriguez, B. *Org. Lett.* **2009**, *11*, 3020–3023.

(13) Clarke, E. D. *Ann. Philos.* **1819**, 34–36.

(14) Bill, H.; Sierro, J.; Lacroix, R. *Am. Mineral.* **1967**, *52*, 1003–1008.

(15) (a) Przibram, K. *Irradiation Colours and Luminescence*; Pergamon: London, 1956. (b) Calderon, T.; Khanlary, M.-R.; Rendell, H. M.; Townsend, P. D. *Nucl. Tracks Radiat. Meas.* **1992**, *20*, 475–485.

Milwaukee Electric Tool Corporation
Ex-1019
Page 7 of 8

(16) Haüy, R.-J. *Traité de Minéralogie*, 2nd ed.; Bachelier: Paris, 1822; Vol. 1.
(17) Brewster, D. *Trans. R. Soc. Edinburgh* **1834**, *12*, 538–545.
(18) Herschel, J. F. W. *Philos. Trans.* **1845**, *143*−*145*, 147–153.
(19) Brewster, D. *Philos. Mag.* **1848**, *32* (16), 401−412 (also published in *Trans. R. Soc. Edinburgh* **1849**, *16*, 111−121).
(20) Valeur, B. *Lumière et Luminescence*; Belin: Paris, 2005.
(21) Stokes, G. G. *Philos. Trans.* **1853**, *143*, 385–396.
(22) Becquerel, E. *Ann. Chim. Phys.* **1842**, *9*, 257–322.
(23) In *Cosmos* **1854**, *3*, 509-510.
(24) Becquerel, E. *La Lumière. Ses Causes et ses Effets*; Firmin Didot: Paris, 1867; Vol. 1.
(25) Malley, M. *Ann. Sci.* **1994**, *51*, 203–224.
(26) Wiedemann, E. *Ann. Phys. Chem.* **1888**, *34*, 446–463.
(27) Malley, M. *Arch. Hist. Exact Sci.* **1991**, *42*, 173–186.
(28) Lommel, E. *Ann. Phys. Chem.* **1871**, *143*, 26–51.
(29) Stenger, F. *Ann. Phys. Chem.* **1886**, *28*, 201–230.
(30) von Wesendonck, K. *Ann. Phys. Chem.* **1897**, *62*, 706–708.
(31) Nichols, E. L.; Merritt, E. *Phys. Rev.* **1904**, *18*, 403–418.
(32) Lommel, E. *Ann. Phys. Chem.* **1878**, *3*, 251–283.
(33) Kowalski, J. *Le Radium* **1910**, *7*, 56–58.
(34) Ruan, X. L.; Kaviany, M. *J. Heat Transfer* **2007**, *129*, 3–10.
(35) Kayser, H.; Konen, H., *Handbuch der Spectroscopie*; Herzel: Leipzig, 1908; Vol. IV, pp 643−649.
(36) Becquerel, E. *La Lumière. Ses Causes et ses Effets*; Firmin Didot: Paris, 1867; Vol. 1, p 295.
(37) Curie, D. *Luminescence in Crystals*; Methuen: London, 1963.
(38) Berberan-Santos, M. N.; Bodunov, E. N.; Valeur, B. *Chem. Phys.* **2005**, *317*, 57–62.
(39) Berberan-Santos, M. N.; Valeur, B. *J. Lumin.* **2007**, *126*, 263–272.
(40) Souchon, V.; Leray, I.; Berberan-Santos, M. N.; Valeur, B. *Dalton Trans.* **2009**, *20*, 3988–3992.
(41) Martins, S.; Fedorov, A.; Afonso, C. A. M.; Baleizão, C.; Berberan-Santos, M. N. *Chem. Phys. Lett.* **2010**, *497*, 43–47.
(42) Radley, J. A.; Grant, J. *Fluorescence Analysis in Ultraviolet Light*; Van Nostrand Co.: New York, 1933.
(43) Dake, H. C.; De Ment, J. *Fluorescent Light and Its Application*; Chemical Publishing Co.: Brooklyn, NY, 1941.
(44) Pringsheim, P.; Vogel, M. *Luminescence of Liquids and Solids and Its Practical Applications*; Interscience: New York, 1943.
(45) O'Haver, T. C. *J. Chem. Educ.* **1978**, *55*, 423–428.
(46) Pierre, V. "Über die Anwendung der Fluorescenz zur Erkennung von fluorescirenden Stoffe " [On the use of fluorescence for the detection of fluorescent compounds] . *Sitzber. Böhm. Ges. Wiss. Prag.* **1862**, *2*, 66−82; 82−85.
(47) Göppelsröder, F. "Über eine fluorescirende Substanz aus dem Kuba-holze (Fortsetzung) and über Fluorescenzanalyse" [On a fluorescent substance extracted from Cuba wood and on fluorescence analysis]. *J. Prakt. Chem.* **1868**, *104*, 10–27.
(48) Käss, W. *Tracing Technique in Hydrogeology*, Balkema: Rotterdam, 1998.

Milwaukee Electric Tool Corporation
Ex-1019
Page 8 of 8