Historical Development of Inorganic Photochemistry

Barbara N. Nunes, Cristiane L. de Barros, Detlef W. Bahnemann, and Antonio Otavio T. Patrocinio

Contents

Abstract

In this chapter, a brief summary of some key facts that marked the history of photochemistry is presented. Photochemistry is defined by the International Union of Pure and Applied Chemistry (IUPAC) as the field of chemistry concerned with the chemical effects of light. Naturally, the evolution of photochemistry as a scientific field occurred concomitantly and benefited from the development of other fields in chemistry, physics, and engineering. Along the centuries, a myriad of discoveries and theories

developed by different scientists have contributed for the understanding of excited state properties of different compounds. Light-induced chemical changes are in the core of the creation of the Universe, allow the existence of life as we know, and are fundamental to many modern technologies. Thus, the concepts and developments involved in this field continue to motivate scientists of different backgrounds. In the following sections, some concepts and findings that contributed for the field are discussed: in the first section, an introduction about how photochemistry is present in our daily life, along with early scientific observations is exposed. In the second part, the consequences of the quantum mechanics in the interpretation of photochemical and photophysical properties are summarized, and, then in the Sect. 1.3, some instrumental developments are highlighted. Finally, in the last section particular attention is given for the photochemical properties of inorganic compounds.

Keywords

Photochemistry · Inorganic compounds · Coordination complexes · Semiconductors · Solar energy conversion

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1.1 Introduction: The Beginnings of Photochemistry

Light-induced reactions are one of the key processes that shaped our planet and create the conditions to the development of lived systems. As soon as the dust began to settle in the planet after the accretion phase, hydrocarbons present in the atmosphere started to be transformed by high UV fluxes coming from the Sun and, after billions of years, the environmental conditions to have life were created. Sunlight has driven the production of more complex molecules like proteins and nucleic acids from simple hydrocarbons and cyanocarbons present on the atmosphere [1]. Then, over the

time, nature as we know has been developed by transforming light into chemical energy through photosynthesis. Plants, algae, and certain bacteria developed the ability to produce their own fuel by absorbing solar energy and converting water and CO_2 into energy-rich compounds [2]. The natural photosynthesis had as "co-product," molecular oxygen, which was accumulated in our atmosphere and is essential for the animal life. This photoproduct also takes part in another photoreaction, the photodissociation of O_2 by high energy UV light ($\lambda < 240$ nm) forming O_3 (Chapman mechanism [3]). Accumulation of ozone in the stratosphere ($\sim$20 km above the surface of the Earth) created a protection layer for the human and animal life against the harmful high energy photons coming from the sun [4].

In fact, even before all scientific knowledge about the role of light-induced reactions on the lived systems be developed, different cultures along the centuries associated light with welfare. This is due a physicologic perception coming from the vision as well as physiologic effect, associated for example with the synthesis of D vitamin and other hormones (see Box 1.1). As the human society has developed, the idea of light-induced chemical transformations, that is, photochemistry, was conceived based on numerous daily observations such as bleaching of exposed materials, spoiling of gun cottons, etc. The myriad of existing colors and the innumerous physical and chemical phenomena involving the interaction between light and matter have always fascinated the humans. Moreover, the will to understand and mimic the main mechanisms of life and nature, where light has a major rule, is in the core of the scientific development. There are plenty of examples in the human history in which photoinduced processes were empirically explored. Alexander the Great, about 330 B.C., designed for his troops a bracelet impregnated with a dye that, under sunlight exposition changed colors, allowing the coordination of the troops [5, 6]. The well-known burning mirror of Archimedes (287–212 B.C.) is another ancient example of "artificial" sunlight application. The attempt to use sunlight for laboratory experiments initiated about 1600 when scientists intended to exploit the heating energy. Some examples are the, distillations setups developed by Conrad Gesner (1599) and John French (1653) and thermal reactions carried out by Joseph Priestley (1790) [5].

**Box 1.1 Examples of Photochemical Reactions in the Human Body**
The eyesight mechanism that occurs inside retina is just possible because of photoreceptors, that is, molecules that are able to absorb light and drive electrical signals. There are two types of photoreceptors: rods, more sensitive and responsible for vision in low-light levels (scotopic vision), and cones. The later can be distinguished in L, M, and S cones, which refers to the spectral sensitivity (long, middle, and short wavelengths, respectively, Fig. 1.1). When both rods and cones are activated, the so-called photopic vision is reached allowing the color perception [7, 8]. This process starts by the photoinduced isomerization of the *cis*-11-retinol, which triggers several other reactions that allow us to notice and recognize the world by vision in wavelengths between 400 and 800 nm [9].

Light is not only essential for vision, but sun exposure is also fundamental for the human life maintenance. One typical photoreaction is the production of vitamin D from light absorption on the human skin. As shown in Fig. 1.2, at first step, 7-dehydrocholesterol or provitamin D (a sterol produced by human body and incorporated to the fat tissue) absorbs UV light from the sun and undergoes a partial oxidation to produce the so-called previtamin D. This last compound is finally converted into vitamin D in the skin by a thermal reaction [10, 11]. Vitamin D plays a very important role in intestinal calcium absorption and, consequently, in human skeleton formation and maintaining. It would be also possible to obtain Vitamin D directly from food, but most it do not contain enough quantities to supply normal body necessities. Thus, lack of sun exposure and, consequently, vitamin D deficiency can cause rickets in children and osteoporosis in adults, and also it is associated with cancer, cardiovascular diseases, multiple sclerosis, diabetes mellitus (type 1), and rheumatoid arthritis [12, 13].

Another example of practical relevance was the reproduction of the quality and variety of natural colors. Drawing and painting are activities that made possible to humans express themselves, their ideas, feelings, history, and discoveries since prehistorical ages. At first, some elements from nature as plants, earth, soot, charcoal, and minerals were used as dyes and pigments. It was possible because of the presence of molecules that are able to absorb light in visible range. Nevertheless, those natural colorants would be limited in color diversity or even difficult to obtain [14]. In fact, production of dyes from natural sources (ores or natural extracts) has an ancient history. Some pigments dated from before Christ and were employed by the Egyptians, Chinese, Greeks, and Romans [15]. However, in that time a limited range of pigments was available.

The first completely synthetic pigment was accidentally prepared by a chemist and painter in Berlin, Germany, in 1704. Heinrich Diesbach, trying to produce a red pigment with iron sulfate and contaminated potash, ended up with a
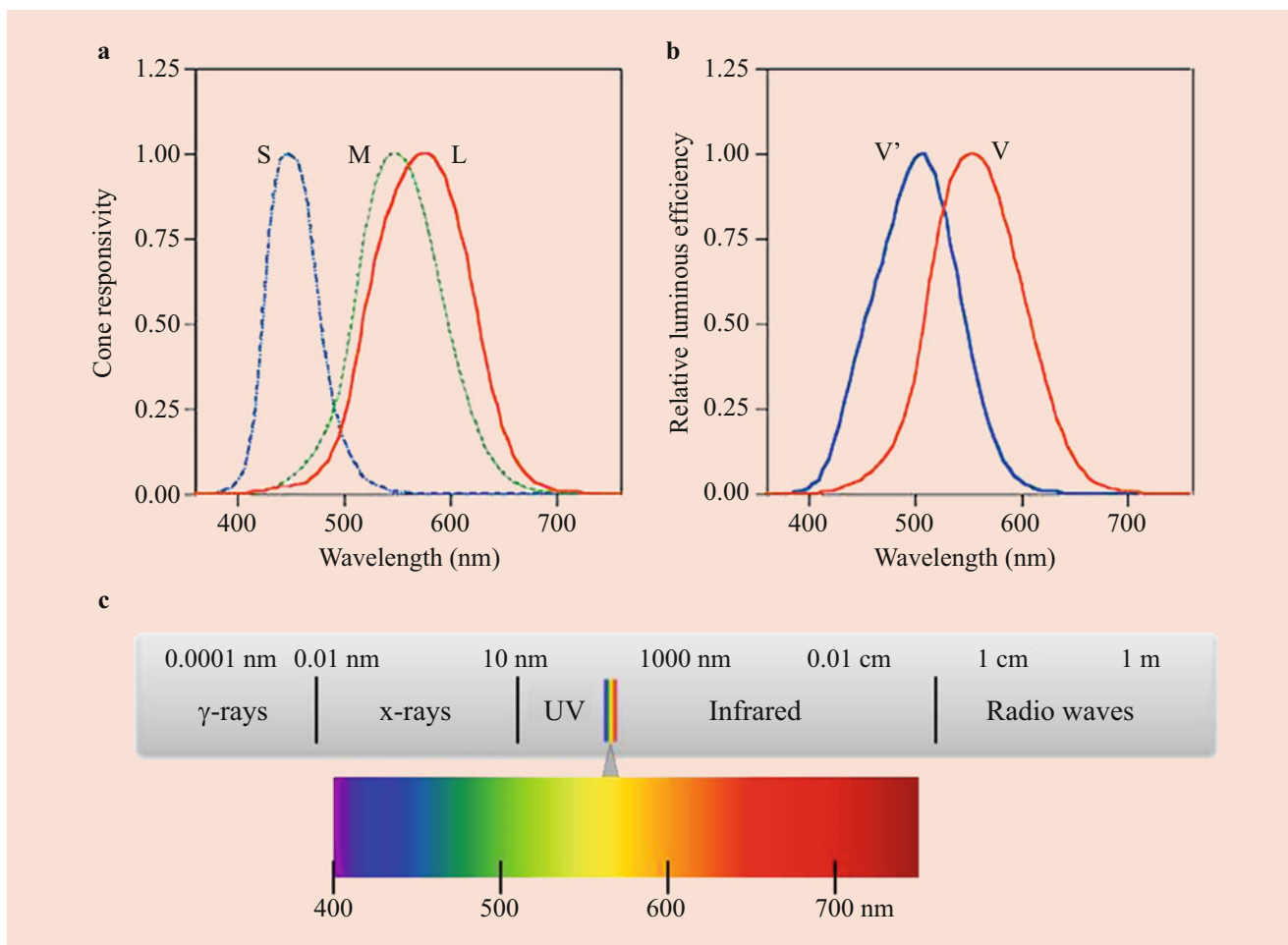
Fig. 1.1 (**a**) Spectral responsivity of L, M, and S cones, (**b**) luminous efficiency functions for scotopic (V′) and photopic (V), and (**c**) the electromagnetic spectrum. (Adapted from reference [8])
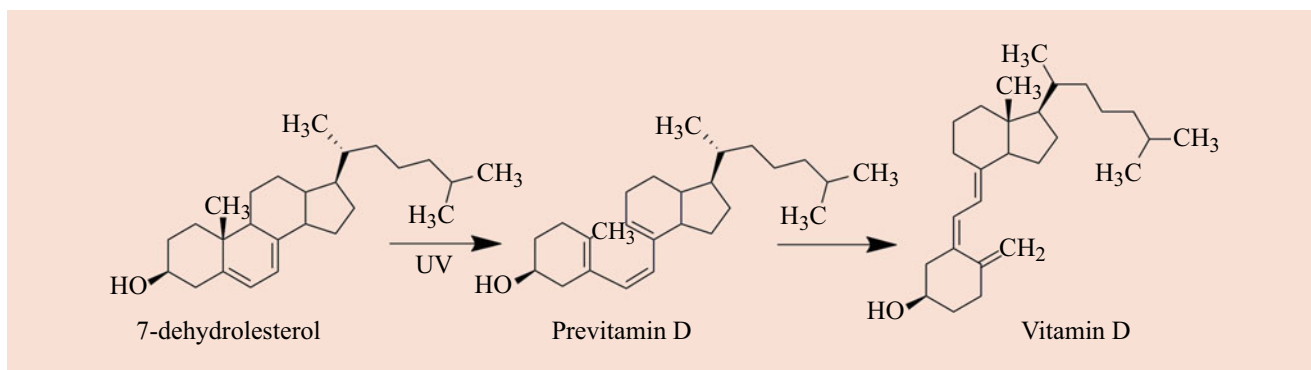
Fig. 1.2 Reaction mechanism for vitamin D production by UV light irradiation

blue pigment: Berlin blue or Prussian blue [16]. Before this compound had been synthesized, the most famous and very expensive blue pigment was ultramarine composed by grinding the *Lapis-lazuli* rock into a powder [15]. For this reason, blue was a highly prized color and after Diesbach's

discovery, this color became more popular and common in artwork. Beside the art and painting aspects, Prussian Blue also contributed substantially in inorganic chemistry development since it is considered the first synthetic inorganic complex. Moreover, because it was accidently produced,

numerous investigations and speculations about the origin of blue color and the structure and bonding of Prussian Blue were speculated [17].

As the industrial revolution took place, development of large-scale synthetic chemistry has also preceded, especially the dye syntheses. William Perkin in 1856 accidentally discovered an intense purple compound, mauveine, the first synthetic organic dye, Fig. 1.3. At that time he was only 18 years old and was a student in the Royal College of Chemistry, supervised by August Wilhelm Hofmann and received the task to prepare quinine, the only known medication to treat malaria. Based on the assumption of quinine empirical formula was $C_{20}H_{24}N_2O_2$, he tried to make it by an oxidation reaction with aniline hydrogen sulfate $((C_6H_5NH_2)_2H_2SO_4)$ and potassium dichromate. Using contaminated aniline with considerable quantities of toluidine, he obtained a black precipitate that when washed with methanol yielded a product with a strong purple coloration. To produce and commercialize the new pigment, Perkin's father and his brother Thomas Dix Perkin established the Perkin & Sons industry at Greenford Green, England, in 1857. Perkin further prepared other dyes by modifying the mauveine structure, and also designed new technologies to increase and improve the manufacturing process, which also contributed to different industrial processes. Synthetic organic colorants, inks, polymers, adhesives, paints, cosmetics, detergents, pesticides, and medicines are some examples of products in modern world that are related to Perkin's revolutionary industrial efforts [18–21]. The growth of the synthetic dye industries

with the industrial production of Indigo and indanthrene dyes by the *Badische Anilin & Soda Fabrik* (BASF) helped to drive attention of researchers on the correlations between color, molecular structure, and photostability.

Another practical application that had called attention to photochemical reactions is image acquisition through photography. The first paper that showed some scientific character concerning photoreactions was the work of Carl Wilhelm Scheele (1742–1786) [23]. He described in 1777 the effect of light on AgCl, the principle of photography. He noted that this salt blackened in sunlight and identified the reduction of Ag^+ to metallic silver when AgCl is exposed to light. Scheele makes others important discoveries about the relationship between light and silver chloride. He observed that blackened of this salt was wavelength dependent by exposing a sheet of silver-chloride coated paper to the solar spectrum. For example, red light blackened the salt after about 20 minutes, while the violet light blackened it almost instantly [23]. Scheele wrote only one book entitled "ChemischeAbhandlung von der Luft und demFeuer" (*Chemical Treatise on Air and Fire*), Fig. 1.4. By 1830s, photography became well established in several countries and, during the early 1840s, photography and photochemistry were almost indistinguishable [24, 25].

In 1817, a German physicist Theodor von Grotthus (1785–1822) formulated what is known as the first law of photochemistry. In his study of thiocyanate and cyanide complexes of iron(III) and cobalt(II) in alcoholic solutions, Grotthus observed that the solution faded when exposed to
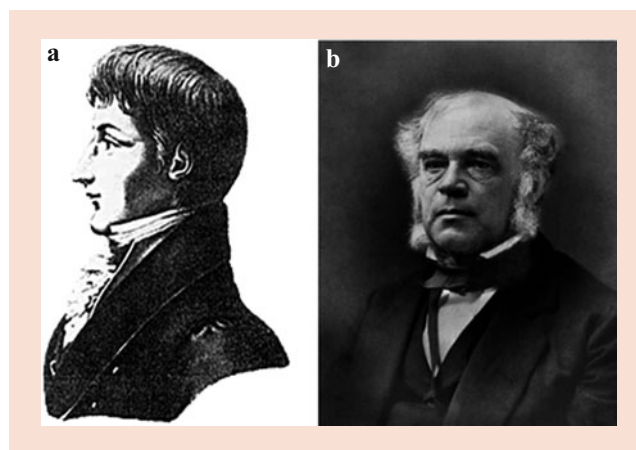

Fig. 1.3 Portrait of Thomas Dix Perkin, R Williamson and William Henry Perkin (the middle three from left to right) [20] and one fabric dyed with mauveine [22]
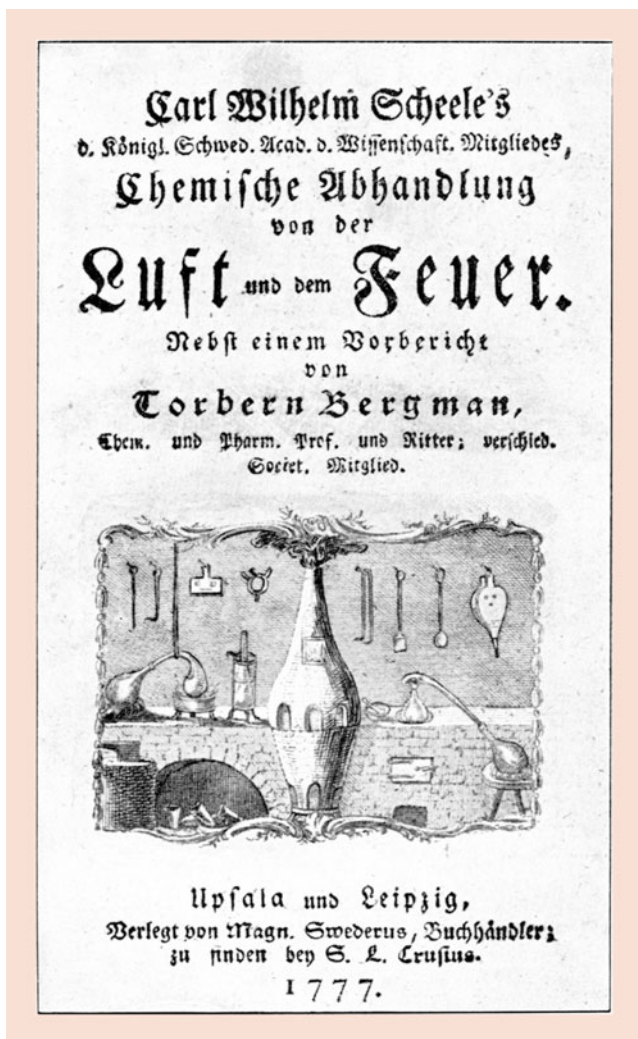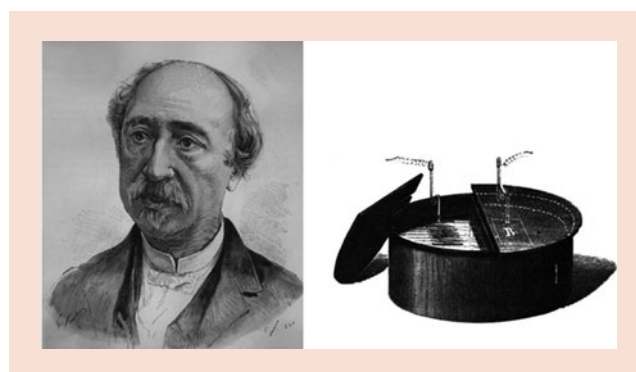
Fig. 1.4 Title page of Scheele's book *Chemische Abhandlung von der Luft und dem Feuer* [23]

Fig. 1.5 Portrait of Theodor von Grotthus (**a**) [28] and John William Draper (**b**) [29]

Fig. 1.6 Portrait of Alexander Edmond Becquerel [31] and his first invented photoelectric element in 1839 [32]

light and that the rate of fading was proportional to the duration of the exposure and the intensity of the light. From these observations, he proposed that light had to be absorbed in order to a photochemical reaction occurs [26]. After 24 years, the American chemist John William Draper (1811–1882) observed that the rate of photochemical reaction between moist hydrogen and chlorine gases was proportional to the intensity of the light absorbed [27]. The first law of photochemistry, also called the Grotthus-Draper law, emerged from these observations and states that only the absorbed light can generate a photochemical reaction (Fig. 1.5).

Another very important discovery for photochemistry occurred in 1839 with Alexander Edmond Becquerel (1820–1891), a French physicist. He discovered the so-called photovoltaic effect, also known as the Becquerel Effect. Becquerel enjoyed performing experiments in his father's laboratory and, at age 19, he created the first

photovoltaic cell while experimenting with a solid electrode in an electrolyte solution. In this experiment, silver chloride was added in an acidic solution and illuminated while it was connected to platinum electrodes. As a result, he realized that current and voltage were produced. Therefore, Becquerel could prove what he believed: "shining light on an electrode submerged in a conductive solution would create an electric current" [30] (Fig. 1.6).

After some years, Willoughby Smith (1828–1891), an English electrical engineer, discovered photoconductivity of elementary selenium [32, 33]. While working with the application of selenium rods on underwater telegraph wires, he observed that the conductivity of selenium increased significantly when exposed to sunlight and published an article in 1873 titled "Effect of light on selenium during the passage of an electric current" [32, 33].

In the late 1870s, a Professor of Kings College in England called William Grylls Adams (1836–1915) and his student Richard Evans Day performed several experiments on the photoconductivity of selenium. In one of these experiments,

they exposed a selenium rod to a candle and noted a strong deflection on their galvanometer. As the response was extremely fast, they dismissed the possibility that the heat of the candle flame had produced the current. Therefore, the researchers concluded: "it was clear that a current could be started in the selenium by the action of the light alone" [34]. So, they discovered that light caused "a flow of electricity" through a solid material and called the current produced by light of "photoelectric." Some years later, in 1883, an American inventor called Charles Edgar Fritts (1850–1903) applied the as-discovered photoelectric effect in solid materials and developed the first photovoltaic module, Fig. 1.7. He made the modules by spreading a thin layer of selenium onto a large plate of copper and then coated it with a thin semi-transparent gold-leaf layer. Fritts noted that the module produced a current "that is continuous, constant, and of considerable force" even when exposed to diffused daylight or candle light [35]. An important scientist of the time Werner von Siemens (1816–1892) declared to the scientific world that the photoelectricity was "scientifically of the most far-reaching importance" and the great scientist James Clerk Maxwell (1831–1879) agreed [36]. The discovery of photovoltaic effect enabled the direct conversion of solar energy into electricity and the development of solar cells.

Another milestone in the scientific development of photochemistry occurred with the formulation of the Beer–Lambert law. In 1729 Pierre Bouguer (1698–1758) observed the attenuation of a light beam in a transparent medium. Bouguer formulated that "in a medium of uniform transparency the light remaining in a collimated beam is an exponential function of the length of its path in the medium" [38]. This law was cited by Johann Heinrich Lambert (1728–1777), a Swiss


Fig. 1.7 The first solar panel installed on a roof of New York City by Charles Fritts in 1884 [37]

polymath, in his book called Photometriain 1760. Lambert stated that the absorbance of a material is directly proportional to its path length and the law became known as Lambert's law [39]. Years later, in 1852, a German mathematician and chemist called August Beer discovered another light attenuation relationship. Beer noticed that light absorption decreased with the increase of the amount of the attenuating species in the material sample and stated that absorptive capacity of a dissolved substance is directly proportional to its concentration in a solution [40]. The law known today as the Beer–Lambert law combines the formulations of Lambert and Beer and correlates the absorbance to both the path length of the beam in an absorbing medium and the concentrations of the absorbing species.

In the same year that Beer formulated the light absorption law, Sir George Gabriel Stokes (1819–1903) published his famous paper entitled "On the refrangibility of light" [41]. In this paper, Stokes reported his experiments with several organic and inorganic fluorescent materials. One of these experiments was very notable and simple. Stokes filled a test tube with a solution of quinine and moved it through the solar spectrum formed by a prism. When the tube passed through the visible part of the spectrum, nothing was observed and the solution remained transparent. But in the ultraviolet part, a blue light emission was observed. From this experiment and several others, Stokes realized a common phenomenon, in which the emitted light was always of longer wavelengths than the incident light. Stokes also observed that the emitted light occurred in all directions and he called this phenomenon of true internal dispersion or dispersive reflection. Later, he introduced the word fluorescence after the mineral fluorspar or fluorite (CaF_2), which exhibits the abovementioned property. So, Stokes stated that in fluorescence the wavelengths of emitted light are always longer than the wavelength of the excitation light [41]. Then, this statement became known as the Stokes law or Stokes shift.

It is little commented that in 1842 Becquerel had already stated that the emitted light is of longer wavelength than the incident light in his paper entitled "Mémoire sur la constitution du spectresolaire" [42]. In this paper, Becquerel exposed calcium sulfide deposited in a paper to ultraviolet light and observed a bluish emission. The difference between the observations of Stokes and Becquerel is that the former observed the fluorescence and the latter reported the phosphorescence. Stokes considered fluorescence to be an instantaneous scattering process that stopped immediately when the exciting light is ceased. Already Becquerel considered that phosphorescence and Stokes's fluorescence were the same phenomenon with a finite duration that was shorter or longer in the case of fluorescence or phosphorescence, respectively. Furthermore, he suggested that the term fluorescence be abandoned [43].
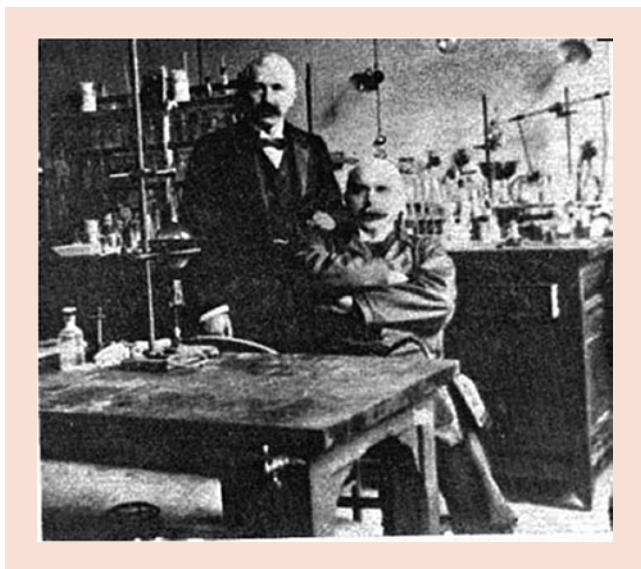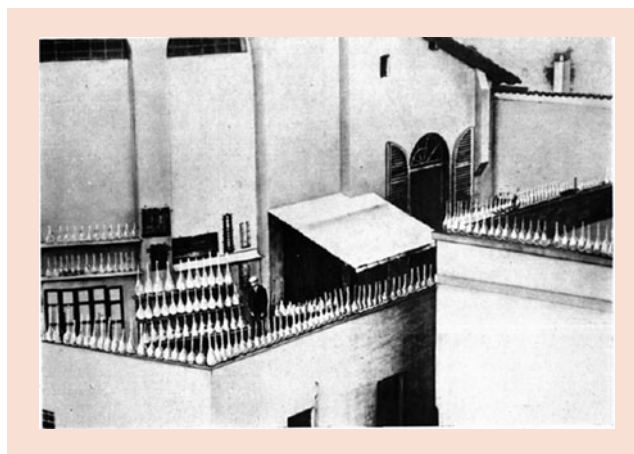
Fig. 1.8 Giacomo Ciamician at left and Paul Silber at right in their Bologna Laboratory. (Courtesy, Margherita Venturi) [45]

Fig. 1.9 Giacomo Ciamician surveys his collection of tubes and flasks exposed to the sun on the balcony of his institute. (Courtesy, Margherita Venturi) [45]

Fig. 1.10 *The Instituto di Chimica "Giacomo Ciamician"* Università di Bologna. (Courtesy, Margherita Venturi) [45]

Around the year 1900, a professor of Chemistry at the University of Bologna called Giacomo Luigi Ciamician (1857–1922) started his work on organic photochemistry, Fig. 1.8. He was fascinated by the ability of plants to carry out photosynthesis, so he started to investigate the chemistry of green plants and the chemical effects of light. Due to its pioneering research into photochemical reactions in a systematic way, Ciamician is considered the father of photochemistry [44].

Together with his coworker and close friend Paul Silber (1851–1932), Ciamician performed outdoor experiments in which he exposed to the sunlight various tubes and Erlenmeyer flasks containing different chemical compounds, Fig. 1.9. The experiments were carried out in the Chemistry department of Università di Bologna, which would be later named after Prof. Ciamician, Fig. 1.10. These experiments and others resulted in the discovery of different photochemical reactions, such as photochemical cycloaddition of olefins; photoreduction of aldehydes, ketones, quinones, and nitro compounds; phytohydrolytic fragmentation of ketones; intramolecular photochemical disproportionation of *o*-nitrobenzaldehyde, and photodimerization of olefins [46].

In 1912, Ciamician published an important article entitled "The Photochemistry of the Future" where he discussed the potential benefits of large-scale photochemical processes for the society and proposed that the new photochemical reactions should be used for the preparation of chemicals arising from coal distillation and of raw materials extracted from plants. So, he believed that the industry could take advantage of the chemical effects produced by light. Furthermore, he predicted the use of solar light as primary energy source in the near future [46]. The studies of Silber and Ciamician

resulted in more than 50 papers published in "Azionichimichedellaluce" and "Chemisches Lichtwirkungen." Furthermore, they have made photochemistry world-famous and have become well-known as Joseph Louis Gay-Lussac, Pierre and Marie Curie, etc. [46]. Due to the relevance and importance of his work, Ciamician was nominated for the Nobel Prize in Chemistry for nine times and received numerous academic honors during his career. In 1887, he was awarded with the Prize of the Royal Academy of Lincei; years later, he became a member of different academies, such as the Italian National Academy of Forty, the American Chemical Society, Royal Chemical Society, among others [45].

Facing so many practical experiences about photoreactions, a theoretical description of the interactions between chemical species and light that could explain all experimental

observations was intriguing. In this sense, scientific development of photochemistry and its theoretical foundations had benefited from the development of the so-called modern atomic theory and the quantum-mechanical physics.

1.2 The Advent of Quantum Theory and Its Applications on Photochemistry

After Planck [47] and Einstein [48] hypothesized that an electromagnetic field could be described as "packets" of energy with a well-defined energy (hv), Johannes Stark (1874–1957), a German physicist, started to correlate the absorbed radiation and the excited state formation in a molecule that could lead to chemical reaction. At that time (1906), as extraordinary Professor at the *Teschnische Hochschule* in Hannover and then as Professor at *Rheinisch-WestfälischeTechnische Hochschule* of Aachen (1909), he worked on what can be considered as the first true photochemical concept since he could distinguish between primary and secondary processes in a photoreaction [49]. In his papers [50, 51], Stark discussed not only the photochemical equivalence but gave also a clear distinction between the mechanism of direct and indirect reactions, including sensitized cases, proposing the mechanism of photochemical changes [52]. In his arguments [51], he proposed that chemical species would change its bound valence electrons by absorption of radiation. In this way, primary photochemical process can be considered the immediate photon absorption which separates a valence electron producing an ion or a split molecule. Then, the resulting species would initiate a second process that occurs in the dark [53, 54]. These statements are known as The Second Law of Photochemistry or Einstein-Stark Law or even photochemical equivalence, which was first enunciated by Stark in 1908 and later by Einstein in 1912: *One quantum of light is absorbed per molecule of absorbing and reacting substance that disappears* [page 5 of ref. 1]. Stark became famous for describing the effect of an electric field on the optical spectra of an atom, similarly to the magnetic field effect detailed by Zeeman. This phenomenon, known as Stark effect, is an important tool in atomic and molecular spectra investigations [55, 56]. For his work on the *"discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric field,"* he was awarded with the Nobel Prize for in 1919 [56].

In fact, light absorption does not necessarily induce a chemical reaction, but there may be several routes for an excited state returns to the ground state. Those deactivation processes can occur by radiative (emissive) or nonradiative transitions. The first one, also known as photoluminescence, is generally subdivided into fluorescence and phosphorescence. Francis Perrin (1901–1992) in 1929 in his doctoral thesis [57, 58] and inspired by his father's work, Jean Perrin
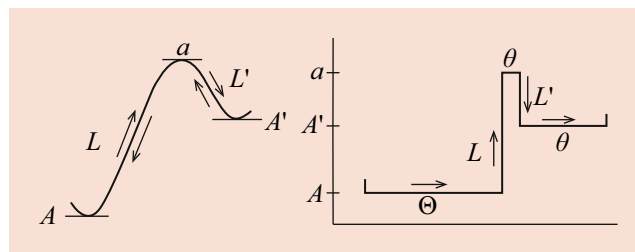

Fig. 1.11 Diagrams of Jean Perrin to explain different energy states during the time which L and L' are radiations designated in quantity, A and A' are different stable states, α is a critical state, and θ, Θ, and Θ' are average lifetimes [60]

(1870–1942), was one of the first to apply the quantum theory ideas to molecular absorption and emission processes, as in Fig. 1.11, in which J. Perrin explained metastable states by diagrams [59, 60].

Using diagrams to describe all those different processes trigged by light absorption and subsequent relaxation is extremely important even today. In this sense, these processes can be represented minutely thanks to Alexander Jablonski's (1898–1980) work, who is considered as the father of fluorescence spectroscopy because of his numerous achievements in this field. He was born in Voskeresenovka, Ukraine, and in 1916 began his studies about atomic physics at the University of Kharkov, and then, in 1918 he went to the Warsaw University. His scientific career was interrupted two times since he served Poland in the First and Second World Wars [61, 62]. In Warsaw, his early work included measurements of absorption spectra in solution and the observation that, in general, the fluorescence spectra intensity is independent of the excitation wavelength [63]. He also elucidated the Stokes shift of fluorescence and absorption spectra. By considering in the luminescence phenomenon both, the luminescent center and its vicinity, he explained the main features of fluorescence in liquid medium using the Franck-Condon principle [64–68], which was formulated years before by James Frank and Edward Condon.

In his article of 1933 [65], Jablonski proposed a diagram where he has distinguished a short-lived fluorescence state and a metastable long-lived fluorescence state. Based in Kautsky's experiments that demonstrated experimentally metastable levels of dyes adsorbed on gels [69], Jablonski proposed a diagram consisting of three energy levels, as shown in Fig. 1.12a, where M is one metastable energy level, F a level reached immediately after absorption (responsible for fluorescence transition), and N normal or ground state. Thereby, different transitions among those levels could suggest different effects: a-absorption, b-fluorescence, c-transition to metastable level, d-thermal excitation, e and f-phosphorescence, and g-absorption of very small transition probability [68]. Thereafter, that simple diagram resulted in
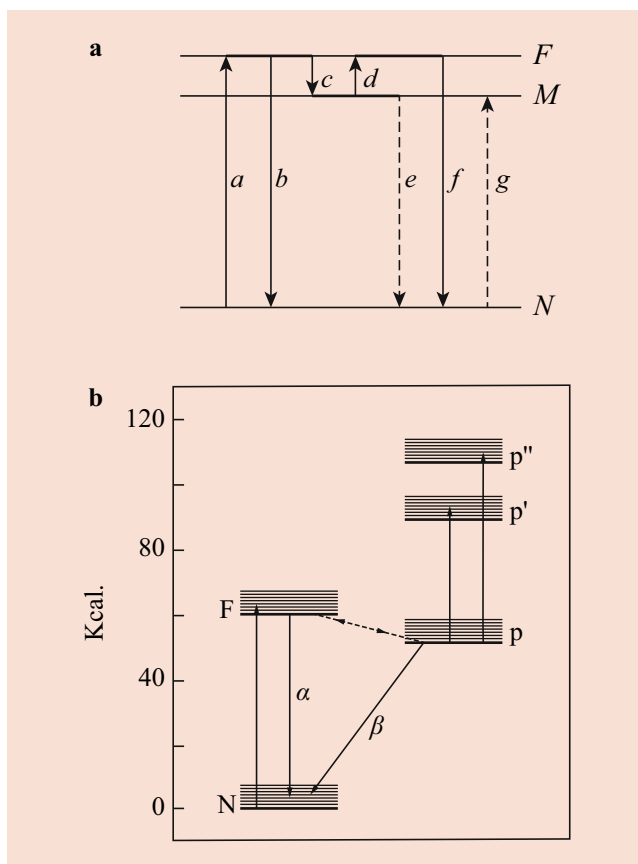
Fig. 1.12 (**a**) Jablonski's original diagram for three energy levels [65] and (**b**) energy diagram of fluorescein in boric acid designed by Lewis [70]

new discussions that he published in 1935 [64]. By a simple kinetic equation for dye decay from level M, he could get formulas to calculate the lifetime of M to F levels in presence or absence of thermal excitation and obtain quantum yields for fluorescence and phosphorescence reactions as well as the phosphorescence exponential decay law [67].

Jablonski diagram was the basis to further concepts about different excited states of different multiplicities. Gilbert N. Lewis (1875–1946) and coworkers have performed several spectroscopic studies using fluorescein in boric acid due its strong blue luminescence aiming at the investigation of the different electronic transitions and excited state relaxation [70]. The authors observed a phosphorescence spectrum at room temperature, characterized by a strong band near 485 nm (alpha band) of the spectrum along with a weaker band at 570 nm (beta band). When the temperature of the solution was successively lowered, the blue band gradually disappeared, and, at all temperatures below −35 °C (238 K), just the beta band was observed. Based on these experimental observations and Jablonski's work, Lewis designed a more detailed diagram, Fig. 1.12b. Furthermore, considering that there are broad absorption and emission bands which are

characteristic of the dyes, Lewis concluded that in addition to main levels there are various vibrational levels. He stated "*when the normal molecules absorb light they pass to various states of the F group and then drop to the basic F level in a time which is supposed to be short compared to the life of the fluorescent state. These molecules now produce fluorescence by dropping not to the basic N state but to some state of higher vibrational energy. Similarly, the molecules from the P state fall back to the vibrational N levels and the most probable level reached is not necessarily the same as the one reached by the F molecules. In other words, the difference in energy of the maxima of the alpha and beta bands need not be exactly equal to the difference in energy between the basic levels F and P*" [page 3012 of ref. 70].

Those previous statements introduced by Lewis, along with the development of the modern atomic theory, were extremely important for the development of concepts about multiplicity, which were explored by Michael Kasha (1920–2013) [71]. Kasha was born in Elizabeth, New Jersey (USA), into a poor and simple family of Ukrainian immigrants. From early age, during high school, he was extremely interested in chemistry, so that he built a lab in the basement of his home. After he finished high school, he got a job at the Pure Research Division of the Merck Chemical Co. under supervision of Dr. Karl Folkers who encouraged Kasha to take chemistry studies. In 1943, when he obtained his bachelor's degree, Kasha started to work with Gilbert N. Lewis at University of California, on the triplet-state origin of organic phosphorescence molecules [71, 72]. Lewis and Kasha published in 1944 [73] one paper of fundamental importance for the development of modern molecular photophysics, as well as for that of photochemistry and photobiology [71]. In this work [73], they reported spectroscopic data about the phosphorescence of 89 molecules. They were able to identify the nature of phosphorescence as a triplet-to-singlet state transition and thus introduce the new concept of triplet state. Until then, phosphorescence emission from organic dyes in cryogenic matrices was attributed to aggregated forms and impurities. Kasha and Lewis successfully purified a myriad of organic species such as α-nitronaphthalene, α-naphthaldehyde, 2-nitrofluorene, and 4,4′-dinitrobiphenyl, which exhibited an unique phosphorescent state. Experimental apparatus used by them can be seen in Fig. 1.13a). They deduced that complex phosphorescence bands of a single substance are due to processes involving a single phosphorescence state. Therefore, different bands resulted from a phosphorescent decay to several vibrational states, and the spectrum was independent of the solvent. Ground state had to have paired electrons and the excited state could be composed by singlets, with opposite-spin orientation, or triplets with same spin orientation. So a selection rule expresses that transitions between singlets and triplets are forbidden. However, the transition happened anyway, even weakly, leading
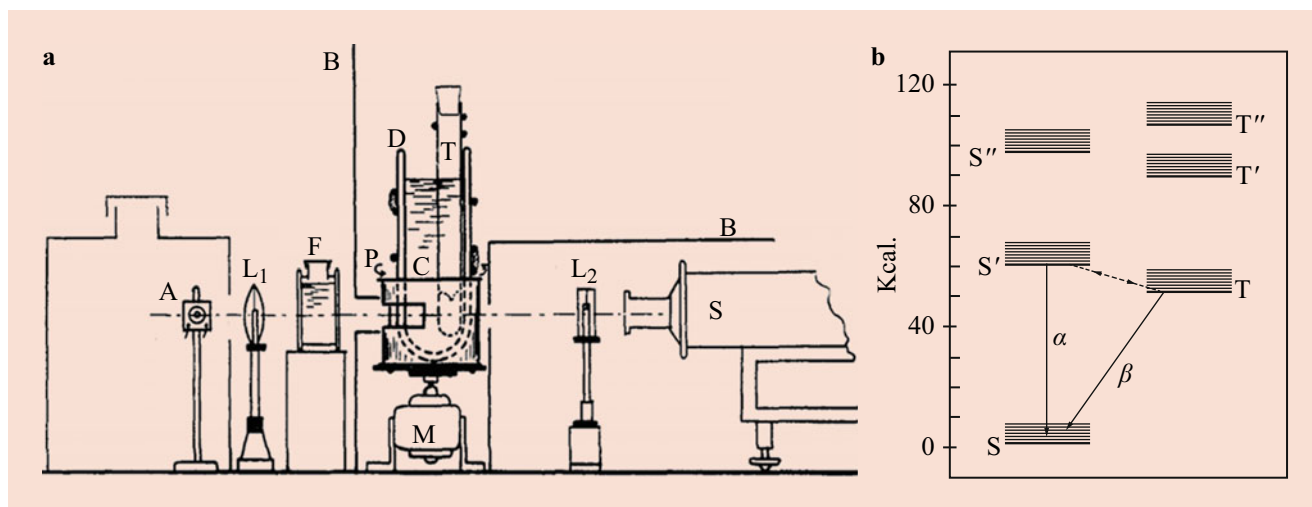
Fig. 1.13 (**a**) Apparatus used by Lewis and Kasha composed by (A) mercury lamp, (L₁) quartz condensing lens, (F) filter of aqueous copper sulfate, (B) light-baffle of blackened cardboard, (P) rotating can, (D) dewar, (C) liquid air, (T) quartz sample tube, and (L₂) lens that focuses the phosphorescent light upon the slit of the spectroscope and (**b**) energy diagram proposed by Lewis [73]

to long phosphorescence lifetimes. Thus, the slower decay rate of the phosphorescent state, compared with that for the fluorescent state, could be attributed to a quasi-prohibited decay and such prohibition was originated from a transition between two states of different multiplicities in which the phosphorescent molecule is in a triplet state [73–75]. They also proposed a Jablonski diagram to describe those transitions based on previous work of Lewis [70] but using other letters to designate the several states in conformity with the new theory (Fig. 1.13b).

The new theory incited numerous critical comments, mainly because singlet-triplet transitions were forbidden by quantum mechanical rules [71]. Then, Kasha published a classical review with some observations to refute those criticisms [76]. He elucidated that "*the mechanism of excitation of the triplet state involves an intersystem 'crossing' of potential curves for the $^1\Gamma^*$ and $^3\Gamma$ states. The mechanism sequence may be outlined as follows: primary absorption of light ($^1\Gamma^* \leftarrow {}^1\Gamma$), rapid vibrational cascade to the vicinity of the zero-point level of the $^1\Gamma^*$ state, with simultaneous intersystem crossing ($^1\Gamma^* \rightarrow {}^3\Gamma$), followed by vibrational cascade to the zero-point level of the $^3\Gamma$ state. Thereafter, spontaneous phosphorescence emission ($^3\Gamma \rightarrow {}^1\Gamma$) may occur*" [page 410 of ref. 76].Intersystem crossing was then more precisely defined in the work published in 1950 [77] as the spin-orbit-coupling-dependent internal conversion and, in most cases, this is a radiationless transition from the lowest excited singlet level to the lowest triplet level of the molecule. He also defined internal conversion as the rapid radiationless combination of excited electronic states of same multiplicity. Along with those important definitions, in this work, Kasha also enunciated one of the most important and known fundament of photophysics and photochemistry, so it is called

Kasha's rule: "*The emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity*" [page 15 of ref. 77]. According to International Union of Pure and Applied Chemistry (IUPAC), Kasha rule is also enunciated as "*polyatomic molecular entities luminesce with appreciable yield only from the lowest excited state of a given multiplicity*" [page 360 of ref. 78]. One of the few examples of "anti-Kasha" fluorescence was studied by Kasha himself. Azulene molecules have shown a large energy gap between S_1 and S_2 states so fluorescence occurs favorably from S_2 instead of internal conversion to S_1 [79].

Another important concept resulted from Kasha's work was published in 1952, it is the so-called external heavy-atom effect or Kasha effect [80]. Considering the intersystem crossing, singlet–triplet transitions could be induced by incorporating the corresponding orbital angular momentum, in other words, a spin–orbit coupling. In this sense, Kasha used two colorless compounds, α-chloronaphthalene and ethyl iodide, and when they were mixed without any reaction at 20 °C, a yellow color was produced instantly. A naphthalene-based compound was chosen because its lowest triplet state which exhibits very weak absorption in a different region of the singlet absorption. Specifically, chloronaphthalene was selected because it is liquid at 20 °C and the spin-orbital perturbation is weak. It was observed that the presence of iodide increased the intensity of singlet to triplet band (T ← S) resulting in the yellow color, Fig. 1.14. Thus, the effect was attributed to a collisional spin-orbital perturbation in which the π-orbital of the naphthalene molecule strongly overlaps with the halogen p-orbitals through an acid-base interaction. Therefore, external or intermolecular heavy-atom spin-orbital effect can be described as a spin-orbital coupling induced in a molecule by a species with

heavy atoms, as a stable molecular complex or as a collision pair or even by lattice formation into close proximity to each other. Similar internal or intramolecular effect can also occur when spin-orbital coupling results from covalent binding of high atomic number to an aromatic system, or from variation of the metallic component of an aromatic metallochelate [81].

1.3 Instrumental Developments

Simultaneously to the new concepts, instrumental spectrometric methods also developed largely in the last centuries. The first step for it was given by Isaac Newton in 1666, when he noted that white light could be separated into a series of colors through a glass prism resulting in a spectrum.
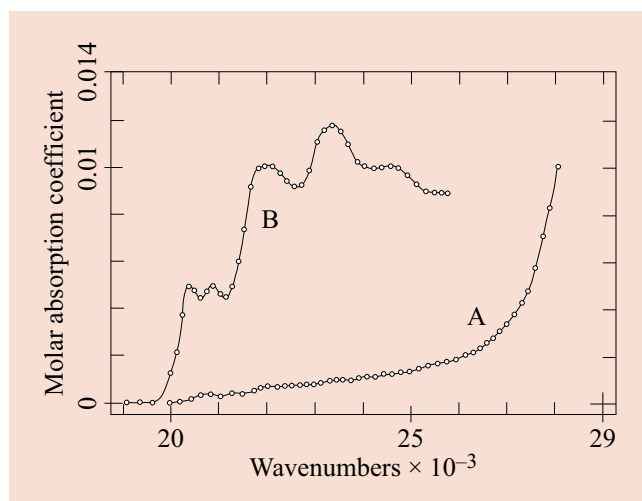

Fig. 1.14 Absorption spectrum of α-chloronaphthalene (curve A) and 1:2 volume mixture of α-chloronaphthalene and ethyliodide (curve B) [80]

Moreover, he also observed white light formation when he passed individual colors through reverse position of the prism. Then, around 1800, a German optician, Joseph von Fraunhofer (1787–1826) analyzed some dark lines in sunlight spectrum and designed achromatic, aplanatic lenses, and optical instruments to make a better spectroscope. That instrument enabled him to observe more than 500 dark lines in solar spectrum and measure some wavelengths (Fig. 1.15). Anders J. Angstrom, in 1868, measured the wavelengths of about 1000 Fraunhofer lines and expressed them in units of 10^{-10} m, a unit that currently is called after his name [82, 83].

Gustav R. Kirchhoff showed that the Fraunhofer lines correspond to different elements that absorb a specific portion of sunlight. Kirchhoff established important fundaments of spectroscopy that is known as Kirchhoff's Laws. In 1859, Kirchhoff and Robert W. Bunsen, who created the famous "Bunsen's burner," developed the first practical spectrometer, and then, they investigated different spectral lines and also concluded that they are unique to each element [83–85]. Spectroscope of Bunsen and Kirchhoff is shown in Fig. 1.16, where A is an inside dark box with two oblique side walls at an angle of 58° to carry two small telescopes B and C. The ocular lenses of the first were removed and replaced by a gap in which there is a space formed by two brass cutting edges, which is placed in the focal point of the objective lens. In front of the gap, lamp D is standing so that the edge of its flame touches the axis of tube B. Just below this point, there was a thin platinum wire supported by the E bracket, where the compound to be investigated would be placed. Between B and C is located one hollow prism F filled with carbon disulfide. The prism rests on a brass plate, which is rotatable about a vertical axis. At the lower end of this axis is located the mirror G and above it the arm H, which serves as a handle to rotate the prism and the mirror. There is a small telescope against the mirror, showing to the eye the reflection of a
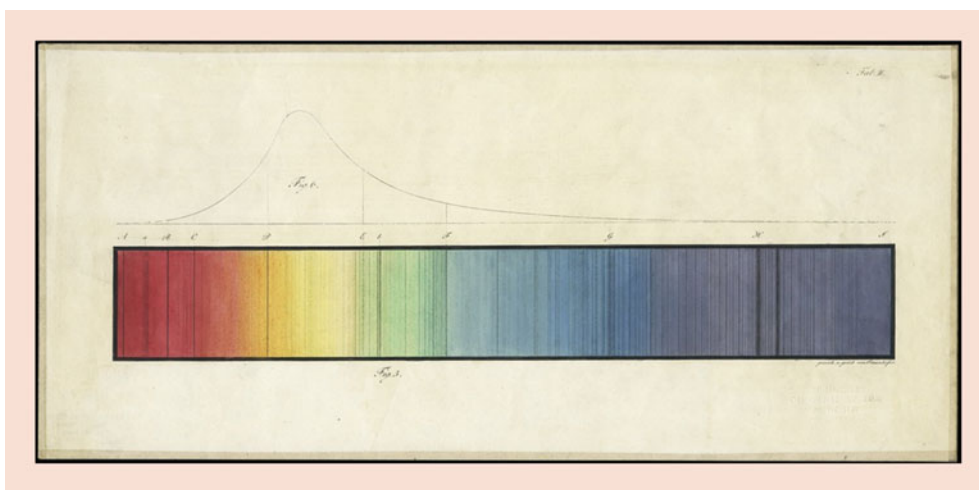
Fig. 1.15 Joseph Fraunhofer's spectrum lines [84]
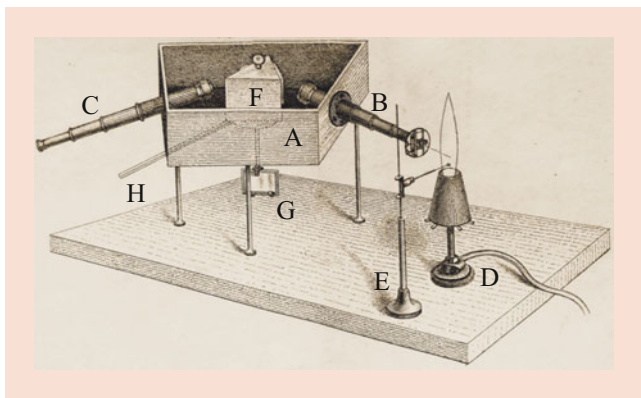
**Fig. 1.16** Bunsen and Kirchhoff's Spectroscope [86]

horizontal scale mounted at a short distance. By rotating the prism, it was possible to pass the entire spectrum of the flame on the vertical line of the telescope C and to match each point of the spectrum with that line. The development of the first spectrometer and concepts by Fraunhofer and after Bunsen and Kirchhoff established the basis of modern spectroscopy [86].

Such findings made possible the discovery of different elements as cesium, rubidium, thallium, helium, argon, etc. Since Bunsen flame could vaporize a limited number of elements, the development of arc lamps allowed the investigation of all elements, and some really important works for science like those of J. J. Balmer, Niels Bohr, Plank, and Einstein [82, 84]. August Beer made use of a color comparator that was one of the first instruments to use absorbance of light to determine concentrations which relied on Beer's law. The color comparator measures the light transmitted intensity through a solution with unknown concentration in relation to a standard solution of known concentration. Then, the more less inaccurate detection by human eye was replaced by photodetectors, and, in the 1930s, a new instrument called colorimeter or spectrophotometer was developed using a grating or prism to isolate a specific wavelength for spectral analysis. The earliest UV-visible spectrometer, Cary 11, was produced by Varian in 1947 [83, 87].

Previous Kasha and Lewis' work about emission of light from the lowest excited state and triplet multiplicity [73] made possible new spectroscopic and physical investigations. However, by 1945 the progress in reaction kinetics was limited since there are no available techniques to probe free radicals and other short-lived intermediates [89]. In this sense, Norrish and Porter [89] used a 7.5 kW mercury arc mounted in a searchlight to produce detectable amounts of CH_2 radicals by the photolysis of a gas flow containing ketene or diazomethane. Then, in 1949 [90], they introduced the technique of flash photolysis which consisted of the irradiation of a sample with a very short high intensity flash of light and the changes in light absorption could be

followed photographically in a wide wavelength range by a second weaker flash or photoelectrically at a single wavelength by a continuous source of light [91]. Before flash photolysis, reactions were studied just under steady-state conditions where intermediates could not be detected. Initially, the flashes lasted about one millisecond, but by 1950 this time had already been reduced to one microsecond. Therefore, rapid reactions such as combinations of atoms and free radicals could be studied, and intermediates of reactions could be detected [92]. The first experimental flash-photolysis setup is illustrated in Fig. 1.17. In 1952, Porter and Windsor studied triplet absorption spectra by flash photolysis in ordinary solvents at room temperature since by that time, Kasha and Lewis described triplet states just using rigid solutions at low temperatures. Porter and Windsor succeeded and observed that triplet state lifetimes under mild conditions were of the order of a millisecond, ideal for studies by flash photolysis [88]. Norrish and Porter shared the 1967 Nobel Prize with M. Eigen "*for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy*" [93].

Over time, new technologies could increase sensitivity and efficiency of optical instrumentation and among them, introduction of Light amplification by stimulated emission of radiation or LASERs was a great impulse to the whole field of spectroscopy. The origins of the laser are in the early 1950 by the development of the MASER (Microwave Amplification by Stimulated Emission of Radiation) [94]. However, it was not continuously operable using only two levels and when the lower level became sufficiently populated, the maser action stopped. Then, Basov and Prokhorov developed a three levels system which worked continuously by optical pumping. Along with Townes, they shared the 1964 Nobel Prize in Physics "*for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle*" [94, 95]. The first laser device was the ruby laser with two lines in the red around 694 nm. It was designed in 1960 by Theodore Maiman, using a cylinder of ruby as the active medium and crystal electric fields surrounding the Cr^{3+} ion [96]. The ends of the ruby crystal were silver coated to make a Fabry–Perot cavity [94]. The improvement and the application of lasers allowed studying faster reactions in nano- and femtosecond scales. Around 1968 Porter [88, 97] had successfully developed a flash photolysis system using pulsed laser whose flashes lasted nanoseconds and it allowed the analysis of absorption spectra of excited singlet states, short-lived excited triplet states, and chemical events in the nanosecond time region. The experimental arrangement, Fig. 1.18, was constituted by a ruby laser with vanadyl phthalocyanine Q-switch that delivered a pulse doubled in frequency by an ammonium dihydrogen phosphate crystal.
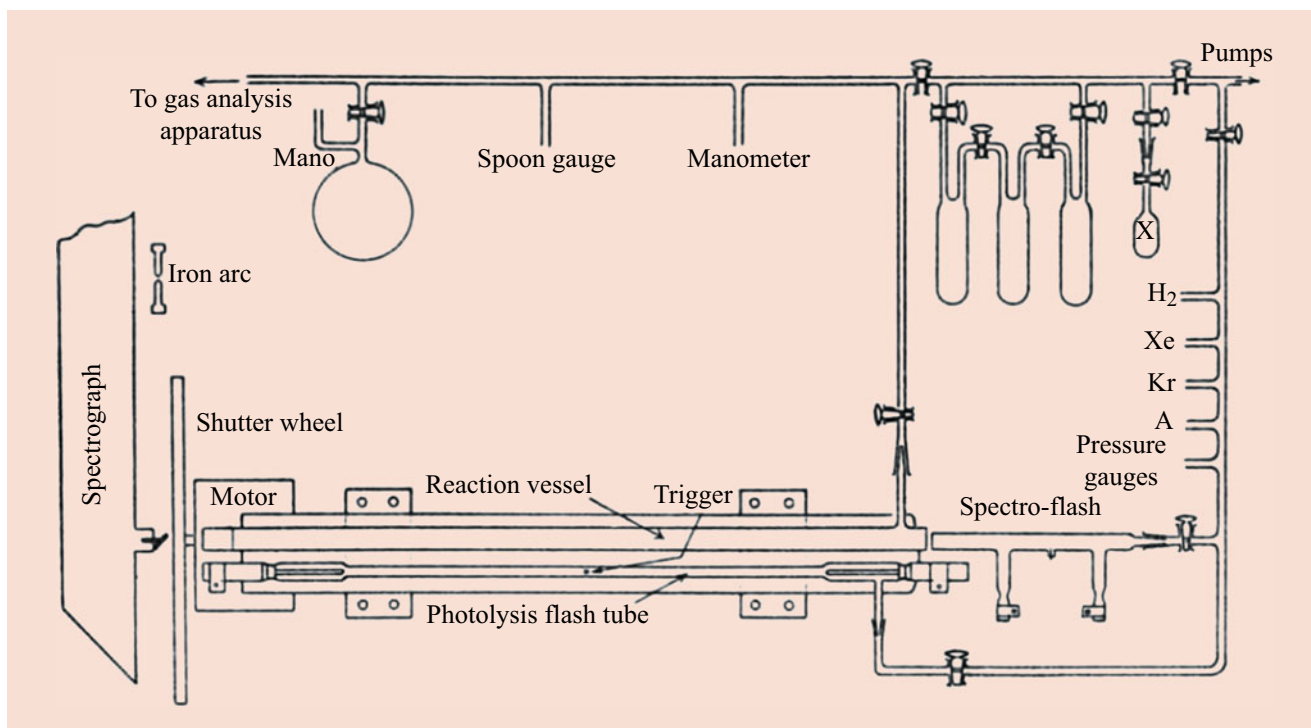
Fig. 1.17 Norrish and Porter's diagram of experimental flash photolysis setup [90]
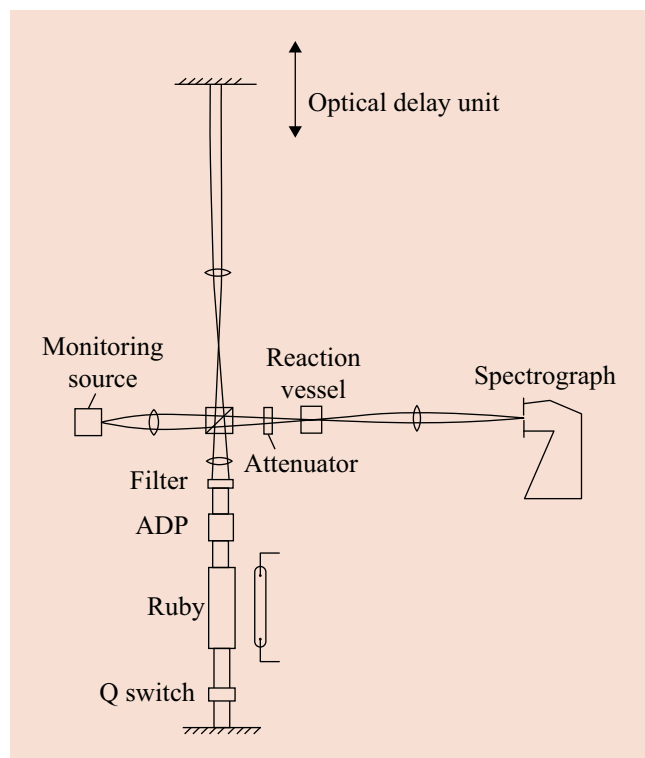
Fig. 1.18 Experimental apparatus for nanosecond photolysis of G. Porter and M. R. Topp [101]

The shaft of light was filtered to reduce red light and light scattered and it was divided by two, one passed directly to the reaction vessel to act as photolysis flash and the second one was delayed up to 100 ns and reflected to the beam splitter and into a cell with fluorescent solution of 1,1,4,4-tetraphenylbuta-1,3-diene. This last one emitted a pulse lasting 18 ns and had a continuous spectrum from 400 to 600 nm and it passed through the cell and into the spectrographic slit [88]. Simultaneously, Novak and Windsor also developed a spectroscopic recording technique to obtain absorption spectra of transient intermediates with lifetimes in the nanosecond scale [98, 99]. The experimental apparatus was composed by a Q-switched ruby laser coupled to potassium dihydrogen phosphate crystal to convert beam partially to second harmonic at 347 nm. Those beams, both with duration of 30 nanoseconds, were separated by a prism which ultraviolet one was used to excite the sample. Then, the red one was focused to a point in a gas-filled cell to generate a spark bright and record a continuous background spectrum on a Hilger small-quartz spectrograph. They have named this technique as laser photolysis and spectroscopy [100].

After more progress in Lasers instruments, it was possible to analyze faster process. Some advances in relation to very short flashes were succeeded primarily at the AT&T Bell Labs in New Jersey (USA), led primarily by researchers Charles V. Shank (1943–) and Peter M. Rentzepis (1934–). In the 1970s, these researchers and

their collaborators were able to obtain flashes of up to one picosecond, and in the 1980s, it was possible to obtain flashes of few femtoseconds [92]. Ultrafast laser techniques allowed the development of methods to investigate chemical reactions with femtosecond time resolution. In 1979 Ahmed H. Zewail and coworkers started to work in ultrafast chemistry by pulsed lasers and molecular beams. After pulsating lasers with 10 fs flashes appeared, Dantus, Rosker, and Zewail in 1987 probed spectroscopically transition states of reaction of iodine cyanide decomposition [102]. The Nobel Prize in Chemistry 1999 was awarded to Ahmed H. Zewail "for his studies of the transition states of chemical reactions using femtosecond spectroscopy" [103]. Zewail's work was pioneered to develop modern dynamics instruments and for studies of the dynamics of the chemical bond at the atomic level. In general, femtochemistry can be subdivided into structural dynamics, which determine the time-dependent atomic positions, and reaction dynamics, which study the energy flow between diverse electronic states [104]. It allows the detection of ultrafast modifications of molecules, crystal lattices, unstable intermediates, and stages of distortion, giving information about the structures of molecules and the dynamics of crystal lattices, liquids, individual molecules, or even biological systems [105]. Some modern techniques applied in photochemical and photophysical studies are described in detail in Part C of this handbook.

1.4 The Photochemistry of Inorganic Compounds

Most of the early fundamental studies on photochemistry were carried out with organic molecules. Hence, the main reason for it was the fact that the nature of the bonding on metal complexes was not fully understood before the Werner's seminal work. The intriguing properties of inorganic salts, such as the luminescence of fluorite, and the myriad of colors of the inorganic pigments had always called attention of the scientists. In 1777, Carl Wilhelm Scheele described the effect of light on AgCl when he observed that the decomposition of silver chloride occurred in different degrees depending of the region of the solar spectrum. Scheele is also responsible for important compound discoveries as oxygen, ammonia, hydrochloric gas, and different organic and inorganic acids [106]. The silver halides were largely employed in the beginnings of the photography.

The rationalization of the photochemical and photophysical properties of inorganic compounds started in the end of nineteenth and beginning of twentieth century with the work of Alfred Werner on metal complexes and the contributions of different scientists on the light-induced reaction at semiconductor surfaces. Since the discovery of Prussian blue, some metal complexes were studied but the results were based just on visual and experimental observations with very limited scientific meaning. In this sense, Alfred Werner (1866–1919) further explained the nature of bonding in inorganic complexes and provided the foundation for the field of transition-metal coordination chemistry. Werner was born in 1866, in Mulhouse, France, and his first Chemistry classes occurred during his mandatory year of service in the German army at the Technical High School in Karlsruhe. His initial publications, as his doctoral work, were in organic chemistry concerning the stereochemistry of nitrogen compounds. So, he was used to look at the molecules in three dimensions which contributed to his further studies. His previous interest in nitrogen-based compounds and organic stereochemistry led him to study ammonia or organic amines bonded to metal centers [107]. By that time, the scientific community was trying to deal with the fact that some elements would have shown multiple valencies.

Initially, Werner's work was based on experimental data of Sophus Mads Jørgensen who have studied complexes of chromium, cobalt, rhodium, and platinum. Jørgensen has explained the structures of these compounds by the theory of Christian Wilhelm Blomstrand that had proposed -NH_3-chains analogous to -CH_2- bounds in hydrocarbons. He observed that different numbers of chloride ions are dissociated from different adducts. So, he interpreted that halogen ions that did not precipitate immediately by silver nitrate were bonded directly to the metal atom and the ones that could be precipitated immediately were bonded through the ammonia chains [108, 109]. However, Werner did not agree with the pentavalency of nitrogen and neither the Kekulé concept of constant or fixed valence with directed force and fixed number of definite spatial distribution units.

In 1893, as full professor at Zurich University, he proposed a new hypothesis for Jørgensen's compounds (Fig. 1.19a) and also assumed two types of valence [110]: "*The conception of valence as an individual force does not explain how an atom, which is divalent, is able to chain six complexes directly to one another. If we think of the metal atom as a sphere, the six complexes directly connected to it in a first sphere and the other lying outside of this first sphere as being in a second sphere, then we can find that the valence of the radical formed by the metal atom and the six complexes of the first sphere (MA_6) is equal to the difference between the valence of the metal atom and the valency of the monovalent groups of the first sphere, quite independently of that in the first sphere*." In 1902 [111], Werner established a primary or ionizable valence (Hauptvalenz), corresponding to the oxidation state of the central metal and the secondary or nonionizable valence

(Nebenvalenz) defined by coordination number, the number of ligands around the metallic center that could be substituted by other groups. Thus, primary sphere could be filled only by anions and second sphere could be supplied by both anions and other neutral species containing donor atoms such as oxygen, nitrogen, sulfur, and phosphorus [112].

At the beginning, Werner's theory was mostly without experimental proofing. Therefore, in front of the criticism coming from the scientific community and mainly by Jørgensen, Werner devoted his career to a series of experimental studies, which resulted in approximately 700 cobalt compounds and several different metallic compounds referring to Werner and associates (Fig. 1.19b) [113, 114]. He investigated dissociation properties of the complex compounds by electrical conductivity and also studied its colors, chemical reactions, and optical properties. It was done by using some compounds series such as $[Co(NH_3)_6](NO_2)_3$ to $K_3[Co(NO_2)_6]$ and $[Pt(NH_3)_6]Cl_4$ to $K_2[PtCl_6]$ in a very systematic way. Werner not only identified the bound type in the coordinating compounds but also elucidated different geometric configuration and optical isomerism of them. So, he was also able to explain the existence of two differently colored isomers such as that observed for $[Co(en)_2Cl_2]Cl$ [114, 115]. Even without any techniques such as UV-vis spectroscopies or X-ray crystallography, Werner clarified essentially spatial formulas and geometric structures for hundreds inorganic compounds. Due his brilliant and devoted research, Alfred Werner was awarded the Nobel Prize in 1913 "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry" [115].

After Werner's great contribution to understanding the bonding structure of the coordination compounds, some theories were proposed to explain the bounds between the central metal and ligands in a complex. The first one was the valence bond (VB) theory suggested by Linus Pauling based on the work of Walter Heitler and Fritz London that could describe the chemical bonding based on quantum mechanical considerations [117]. By this theory, it was possible to deduce the structure and the stability of a given complex. However, the colors and mainly the electronic transitions of different coordination compounds could not be explained [118]. At that time electronic spectroscopy has become a well-established method to describe the bound structures and energy states of coordination compounds. The absorption spectrum of a coordination compound depends mainly on the ligands bounded to central ion but different solvents and contra-ions can also influence it [119]. Careful evaluation of ultraviolet and visible absorption spectra provide extensive information about the compound as its molecular structure and excited state energies since light absorption implicates electronic transitions between different levels of the chemical species.

In this sense, the development of the Crystal Field Theory was the first step to interpret electronic absorption spectra of coordination compounds. Its name makes reference to the original theory of Hans Albrecht Bethe (1906–2005), German physicist and Ph.D. in theoretical physics supervised by
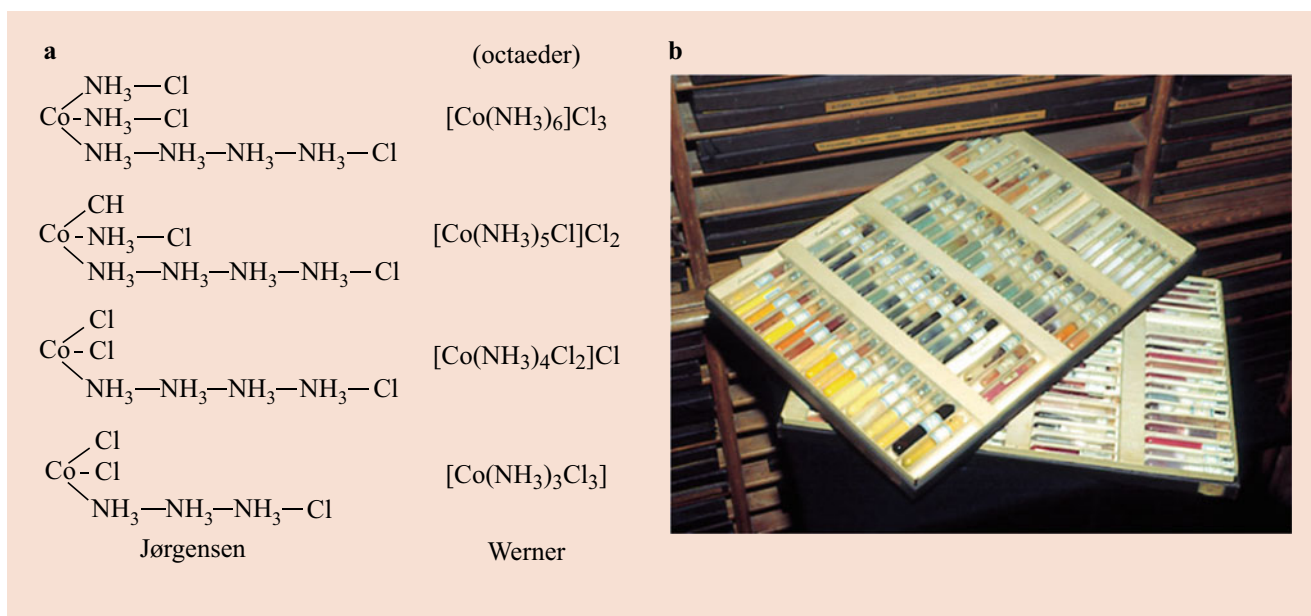
Fig. 1.19 (**a**) Structures proposed by Jørgensen and later by Werner for the ammine cobalt(III) complexes previous studied by Jørgensen [116] and (**b**) some original preparations from Alfred Werner's laboratory [116]

Prof. Arnold Sommerfeld on electron scattering in crystals in University of Munich [120]. In 1928, Bethe published his innovative theory that explained the influence of the ligands in transition metal complexes by considering the electrostatic crystal field between the ligands and the metal center: "If an atom is placed in a crystal, its energy levels are split. The splitting depends on the symmetry of the location of the atom in the crystal. The splitting is derived here from the Group theory" [121]. Parameters such as ligand field strength, asymmetric portion of the electron interaction, and the spin-orbit interaction allow the proposition of an energy level scheme. So, most of its results are the consequence of symmetry instead of the electrostatic model, which was an advantage since electrostatic field theory was not so realistic [120]. Bethe also worked with theory of atomic nuclei which led him to discover the reactions responsible for supply the energy in the stars and resulted in his Nobel Prize in 1967 "for his contributions to the theory of nuclear reactions, especially his discoveries concerning the energy production in stars" [122]. Until then, the ligands are represented by point charges and the Crystal Field Theory was entirely electrostatic. Moreover, John Hasbrouck Van Vleck, an American physicist and mathematician, included molecular orbital concepts in the theory to firstly explain some magnetic properties of metal complexes [120]. In his work [123], Van Vleck assumed partly covalent bonding between the ligands and the d-orbitals of the metal center [124]. This effect could result in the formation of different levels of energy, as represented in Fig. 1.20.

Thus, the Crystal Field Theory modified by these covalent contributions becomes the Ligand Field Theory [118]. Therefore, the Ligand Field Theory was mainly applied to explain some magnetic details and the small difference in energy of the ground state levels. In 1977, together with Philip Warren Anderson and Sir Nevill Francis Mott, J. H. Van Vleck was awarded the Nobel Prize in Physics "for their fundamental
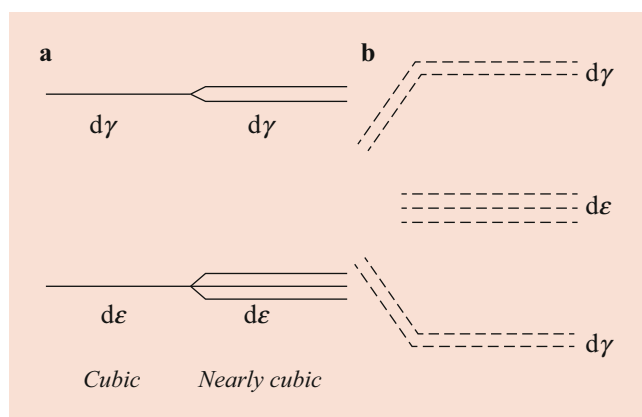
theoretical investigations of the electronic structure of magnetic and disordered systems" [125]. The first application of that theory to describe absorption spectra of coordination compounds was made by R. Finkelstein and Van Vleck. In their work published in 1940 [126], the entire energy levels, including spin-forbidden transitions, for the d^3 configuration of Cr^{3+} in the $(KCr(SO_4)_2.12H_2O)$ complex was described using spectroscopic data. After that, some works concerning the study of transition metal complexes and their energy levels by absorption spectrums were published [119]. F. Ilse and H. Hartmann [127] published a systematic study using absorption spectra of $Ti(H_2O)_6^{3+}$. They changed some aqua ligands by chlorine to observe the interactions between ligand and the central ion regarding electrostatic forces. One of the most known scientific works was the one of Tanabe and Sugano in 1954, where they explain the origin of absorption bands and lines of some octahedral iron complexes [128].

The crystal field theory could provide the nature of low lying electronic levels in the vast majority of complexes containing unfilled d orbitals. Nevertheless, higher lying states or charge transfer states with no d electrons as MnO_4^- were still unsure [129]. More precise description of molecular electronic structure, considering both ionic and covalent behaviors, was then provided by the Molecular Orbital Theory (MOT) [118]. After the introduction of Quantum Mechanics by Heisenberg (1901–1976) and Schrödinger (1887–1961), MOT took the wave properties of electrons to describe bonds as a combination of atomic orbitals [130]. In principle, this theory was developed to describe diatomic molecules and their spectroscopic properties. The pioneer work was done mainly by the physicist Friedrich Hund and the chemist Robert Mulliken, both spectroscopists, and then John Lennard-Jones and John C. Slater contributed to the theory development as well [131]. In 1927, using the quantum mechanics theory of Heisenberg and the adiabatic correlation of atoms and their nuclei combination, Hund developed the principles of the molecular orbital theory to detail the electronic structure of diatomic molecules [132]. Then, in a review published in the next year, Mulliken extended Hund's concepts and proposed a detailed description of quantum numbers and energies of individual electrons in molecules. He considered the influence of a strong and axially symmetrical electric field and the effect of separating the united-atom nucleus into the two nuclei to form a molecule [133]. In 1966, Mulliken awarded the Nobel Prize in Chemistry "*for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method*" [134]. Thus, Hund and Mulliken ascribed a quantum notation to electron in a molecule individually. In 1929 [135], Lennard-Jones compared Hund and Mulliken works and proposed a simpler way to nominate bonding electrons and a linear combination of atomic orbital.

Fig. 1.20 Representation of different energy states for a paramagnetic cation surrounded by negative ions in octahedral arrangement [123]

So, he designed the most known interaction diagram that molecular orbitals are formed by separate atoms, resulting in lower and higher energy levels. Differently of the previous theories, MOT allows to explain the reason of the paramagnetism of O_2. Then, by John Slater studies and mathematical considerations, MOT could be applied to many-electron wave functions [136]. Regarding more complex organic molecules as unsaturated and conjugated compounds, the physicist Erich Hückel deeply contributed to their quantum mechanical description [137]. About 1960 Lipscomb and Hoffmann adapted the Hückel model and calculate electronic structures of three-dimensional molecules including organometallic and more complex inorganic molecules [138]. The theoretical prediction of electronic structures and excited state properties benefit greatly from the fast progress in the computational capacity. Such findings are discussed in part B of this handbook.

Femtosecond time-resolved absorption spectroscopy was fundamental for coordination chemistry development, mainly because it allows to characterize and identify not only structural rearrangements and electron transfer steps but also intramolecular vibrational relaxation (IVR), internal conversion (IC), and intersystem crossing (ISC) processes [139]. This methodology was used for the first time by Niels H. Damrauer and coworkers to characterize the ultrafast nature of excited-state evolution in the [Ru (bpy)$_3$]$^{2+}$. They described the metal-to-ligand charge transfer excited state (^{3}MLCT) formation and the initial evolution of the Franck-Condon state by femtosecond absorption spectroscopy [140]. Thus, the femtochemistry achievements were able to provide new understanding of light absorption in inorganic chromophores, and also confront assumptions concerning some fundamental theories such as the Born−Oppenheimer approximation and the Franck−Condon principle and the relative rates of non-radiative processes [141]. Nowadays, the femtochemistry concepts can be used in different techniques such as X-ray absorption and fluorescence, and even Raman and Infrared spectroscopies, allowing the investigation of structural, spin, and vibrational changes [141].

Therefore, electronic transitions and spectroscopy enlightenments achieved by ligand field and molecular orbital theories were essential to explain excited-state photochemistry and different colors of coordination compounds. Due this progress, new compounds were elaborated for different applications and more advanced spectrophotometers and lasers allowed the complete description of the excited state dynamics of these systems [142]. Around the world, diverse research groups have dedicated their activities to the understanding of different photoinduced processes in inorganic compounds, the fundaments and the state-of-the-art theories in energy/electronic transfer of which will be discussed in ▶ Chaps. 2 and ▶ 3 of this handbook. Further photochemical

processes in molecular and supramolecular systems are discussed in Parts D and E, respectively.

Besides the coordination compounds, the photochemistry of inorganic semiconductors, particularly metal oxides, have called great attention. Heterogeneous photocatalysis has been known as a great alternative for environmental remediation, solar energy conversion, organic synthesis, etc. In this sense, according to IUPAC, a photocatalyst can be defined as "a catalyst that, upon absorption of light, is able to produce chemical transformations of the reaction partners. The excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions" [page 384 of ref. 78]. According to N. Serponi and coworkers [143], the first time that the terms photocatalysis and photocatalyst were reported in the literature was in 1910 by J. Plotnikow in Russia (in Russian, photokatalyse and photokatalytisch) [144]. Then, the term was used in 1911 by Alexander Eibner, a German painter, to express the effect of ZnO illumination on paints and on the bleaching of Prussian blue [145–148]. In the same year, Bruner and Kozak published an article entitled "Information on the photocatalysis - the light reaction in uranium saltplus oxalic acid mixtures" where they described the photodegradation of oxalic acid in presence of UO_2^+ [149]. In 1920, the German chemist G. Tammann related that ZnO, a white powder, became gray when it was exposed to light in the presence of $AgNO_3$ or $AgSO_4$ solution [149]. Then, in 1924, E. Baur and A. Perret published an article about the ZnO photoactivity to reduce Ag [148]. They suggest a "molecular electrolysis" where zinc oxide absorbed light and then both cathodic and anodic process occurs, as represented in the scheme of Fig. 1.21. In further works, Baur also described the photolysis of methylene blue [151] and the photocatalytic formation of hydroperoxide [152] both in the presence of zinc oxide.

Carl Renz reported the first application of TiO_2 as photocatalyst in 1921 at the Swiss University of Lugano [153]. Actually, in his paper, Carl investigated not only TiO_2 but different oxide as CeO_2, Nb_2O_5, and Ta_2O_5. By color changing, he observed that, in presence of organic compounds, the oxides were partially reduced by sun irradiation. Some years later, based on Baur mechanism, Renz demonstrated the formation of metallic gold and silver by

$$ZnO \begin{cases} \oplus \ + \ OH' \ = \ \tfrac{1}{4}O_2 \ + \ \tfrac{1}{2}H_2O \\ \ominus \ + \ Ag^\bullet \ = \ Ag \end{cases}$$
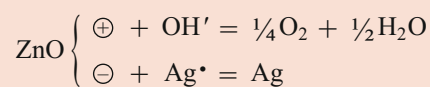
Fig. 1.21 Scheme of photoreaction of ZnO proposed by Baur and Perret [150]

photoreduction with a plenty of diverse oxides such as Al_2O_3, Y_2O_3, La_2O_3, ZrO_2, TiO_2, Nb_2O_5, and others [154]. Goodeve in 1936 then discussed the photoactivity of white oxides in terms of their absorption spectra by diffuse reflectance experiments [155]. He used a light beam from hydrogen discharge tube which was continuous in the UV region of the spectrum since some previous work in literature had evidenced that TiO_2 and ZnO were activated in that region only. The resulted spectra of some of the investigated materials can be observed in Fig. 1.22. Therefore, he observed a strong absorption band with a fairly sharp threshold indicating the region in which those substances were photoactive. He proposed that the energy adsorbed by an electron would form an exciton (term proposed by Frenkel in 1936 [155]) which was found as an excited electronic state in the spectrum. Then, they could move to the surface to promote the oxidation or reduction reactions. In his articles in 1938 [156, 157], he

investigated TiO_2 as photocatalyst for bleaching the dye Chlorazol SkyBlue FF, because its absorption is minimum in the blue and near ultraviolet, where TiO_2 absorbs strongly. By analyzing the spectrophotometric data and the determined quantum yields, he suggested that the dye was oxidized by a chemical reaction between surface TiO_2 and adjacent dye molecules. So, he stated that the energy absorbed may be transferred on collision to a second molecule by physical process or the metal oxide be dissociated into atoms or free radicals acting as catalysts or chain carriers for the main reaction, later recombining to form the unchanged compound.

The research group of Terenin in Russia provided a great contribution in the photocatalysis development between 1930s and 1970s. Terenin published several papers about photochemical process as absorption, luminescence quenching, and photoreactions using different systems and
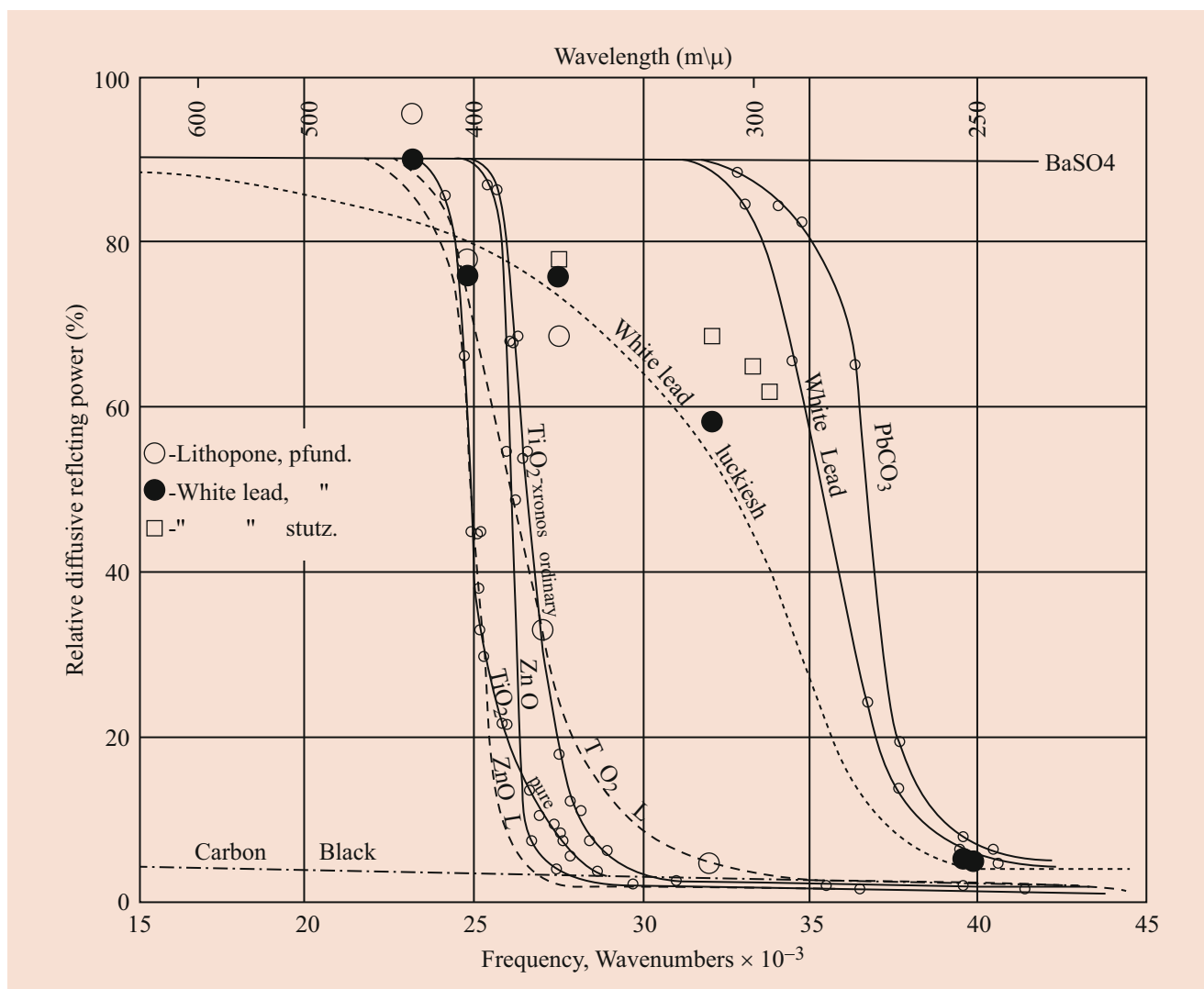

Fig. 1.22 Diffuse reflectance spectrums of TiO_2, ZnO, white lead, and $PbCO_3$ [155]

compounds as thalium iodide, Al_2O_3, MgO, ZnO, TiO_2, Fe_2O_3, among others. In the 1950s, ZnO was one of the most studied oxides for photocatalytic applications, mainly to clarify the mechanism of hydrogen peroxide production [158]. Maria C. Markham and coworkers studied the kinetics of hydrogen peroxide formation under UV light and proposed that it was caused by an electron transfer to adsorbed water that dissociates into free radicals [159]. In 1958, Markham and coworkers investigated the photooxidation of glycerol, benzyl alcohol, and some aliphatic alcohols by ZnO [160]. It was found out that the mechanism occurs by an electron transfer from ZnO to absorbed O_2 producing O_2^-. So, the organic compounds were oxidized either by the photopositive zinc oxide surface or by hydrogen abstraction by the peroxide radical ion to form HO_2^-.

The photocatalytic activity of TiO_2 turned more popular mainly in Japan since 1956 by Kato and Mashio sequence of reports entitled "Autooxidation by TiO_2 as a photocatalyst" [161]. They published a remarkable work in 1964 in which 12 different commercial anatase TiO_2 and three different rutile TiO_2 powders were tested toward oxidation of organic solvents under UV radiation. They recognized that anatase TiO_2 phase was more active than the rutile one. During the late 1960s, A. Fujishima investigated the photoelectrolysis of water using TiO_2 as photoanode, since its positive valence band edge is suitable for O_2 production and it is highly stable in aqueous electrolyte solution [161]. Moreover, in the 1970s, crude oil prices increased rapidly, a period known as oil crisis, and the oil and energy scarcity became a critical concern. This was an additional motivation to the research in alternative energy sources [162]. Then, in 1972, Fujishima and his coworker K. Honda published their seminal work in *Nature* [164]. For the first time, H_2 and O_2 were produced by water splitting simultaneously by employing a photoelectrochemical cell with a TiO_2 photoanode connected with a platinum electrode (Fig. 1.23). When the TiO_2 surface was irradiated with wavelengths smaller than 415 nm at -0.4 V vs NHE, O_2 was produced at TiO_2 surface and H_2 at the platinum counterelectrode. These observations contributed to the development of several works focusing on the production of hydrogen and oxygen from water as a means of converting and storage solar energy. It soon became apparent that such redox reactions could also be induced by the irradiation of a wide range of semiconductors. The investigation of photocatalytic processes at semiconductors surface evolved as a very exciting field in inorganic photochemistry, triggered mainly by the society demand for clean energy production using the sun as primary source. The concepts and aspects involved in photoinduced interfacial electrons transfer process on semiconductor surfaces are discussed in ▶ Chap. 4 of this handbook as well as in Part F.
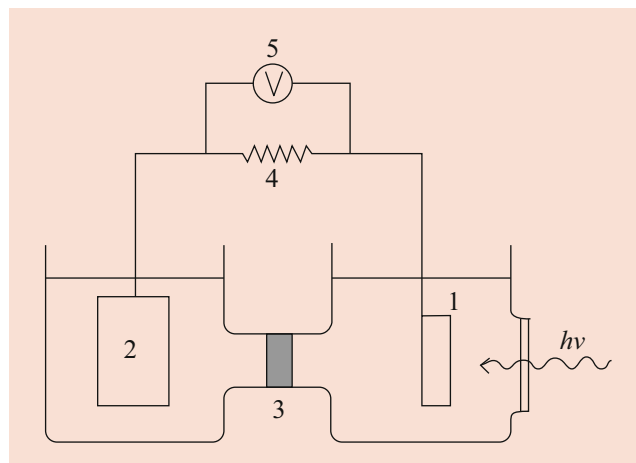
Fig. 1.23 Photoelectrochemical cell scheme with (1) TiO_2 electrode, (2) platinum electrode, (3) salt bridge, and (4), (5) external circuit [163]

1.5   Concluding Remarks

As a fundamental part of the world and life as we know it, the interactions between light and matter have always attracted increasing interest. Photochemistry as a modern scientific field is dedicated to the rationalization of these interactions, combining chemists, physicists, engineers, and biologists in a multidisciplinary environment. As it will be shown in next sections of this handbook, state-of-the-art fundamental studies on photochemistry and photophysics of inorganic compounds continue to be an intriguing and dynamic field in science, which finds application in many fields, such as medicine, energy, photonics, and catalysis. These applications are discussed in the detail in Parts G to L of this handbook. The historical development of photochemistry is in the core of the way and how we understand the matter at atomic level and its continuous progress will certainly pave the advance of science and society.

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