PART I

A HISTORICAL OVERVIEW

1

THE FIRST DECADES AFTER THE DISCOVERY OF CD AND ORD BY AIMÉ COTTON IN 1895

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1.1. SCOPE: SUBJECTS AND TIME FRAME TO BE REVIEWED

The story of the Cotton effect begins with its discovery in 1895. Although the news was hailed by leading physicists and chemists, studies to extend, exploit, and apply Cotton's findings developed at a slower pace than one might have anticipated. One of the reasons for this delay was simply the necessity of the researchers to construct their own optical apparatus. Gradual technical improvements eventually allowed one, in the 1920s, to take chiroptical measurements in the ultraviolet as well as the visible, thus making accessible in principle a great many Cotton effects in colorless (mostly organic) compounds. Despite the paramount importance of such developments, neither the technical details nor the physics involved will be discussed in the following. Rather, a chemist's view will prevail, paying attention chiefly to experimental results and the application of chiroptics to chemical problems.

Since much of the work during the first 20 or so years after Cotton's discovery was done by physicists and physicochemists, it is not surprising that many investigations were interconnected with or even motivated by the concomitant progress of the theory of optical activity. But also the discussion of this part of (theoretical) physics will be curtailed in the following. The exclusion in this chapter appears justified, because various comprehensive reviews are readily available, as they are for the field of optical instrumentation.

By about 1935, Cotton effect measurements were possible with most organic and inorganic chromophores. It is rather surprising that not much use was made of the chiroptical techniques, especially by organic chemists. On the other hand, physical chemists had demonstrated the feasibility of Cotton effect studies in various classes of chemical compounds, but seemed satisfied with this result. Likewise, the advancement of optical

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instruments for chiroptical measurements slowed down. All this led to a certain climax of chiroptical studies in the early 1930s, to be followed by a near standstill. It is not unreasonable to symbolically connect this phenomenon with the death in 1936 of T. M. Lowry, one of the most active scholars in the field.

Arguably, the death of T. M. Lowry ended the first, pioneering period of chiroptical studies. The present chapter will concentrate on reviewing these first "historical" decades.

Some work on the experimental study of the Cotton effect continued after 1936 until World War II on a minor scale, on, for example, organic compounds (S. Mitchell) or platinum complexes (I. Lifschitz). But at exactly the same time, new developments took place in the theory of optical activity and its application to chemical problems: Werner Kuhn's calculation of the absolute configuration of lactic acid in 1935 rang in a new era. The waning interest of the experimentalists contrasts with the increased activity of theoretical chemists like J. G. Kirkwood, E. U. Condon, H. Eyring, or W. Kauzmann, who in the late 1930s advanced different models of optical activity. Still, chemistry had to wait for the period of 1950–1960 for a revitalization of chiroptics. Some reasons for the animation are: (1) the development of X-ray scattering methods for the determination of the absolute configuration, thus anchoring the stereochemistry unambiguously, following J. M. Bijvoet's seminal publication of 1951; (2) the advent of new, commercially available measuring devices of ORD and CD; and (3) growing interest in natural products chemistry and, generally, optically active systems. But to discuss these topics would need another chapter.

1.2. EARLY CHIROPTICAL STUDIES

The discovery of optical activity is credited to the two distinguished French mathematicians, physicists, astronomers, and geodesists (and more) Dominique-François Jean Arago (1786–1853, of Catalan origin) and Jean-Baptiste Biot (1774–1862) [1]. Arago and Biot had been closely associated at least since 1806 in the pursuit of other scientific subjects, and they sometimes published together. Both investigated the optical activity of quartz, and apparently they also shared their equipment to some extent. If, on the one hand, Arago was the first to go into print, Biot, on the other hand, soon became more active in this field and extended the studies. He undoubtedly observed optical activity for the first time in organic compounds such as natural oils and terpenes, or solutions of camphor [2] and cane sugar [3]. Biot continued his research on optical activity throughout his life, later concentrating particularly on tartaric acid. He noticed the wavelength dependence of the optical rotation even at the very beginning of his studies, albeit in a rather qualitative way. Whereas eventually the rotatory dispersion of quartz could be elucidated satisfactorily (which led to Biot's law, stating that the rotation is inversely proportional to the square of the wavelength), similar solution studies were seriously impeded by experimental deficiencies, particularly the lack of suitable monochromatic light sources.

Genuine chiroptical studies were, therefore, rather infrequent until the end of the nineteenth century. One of the most important papers here is a report by the Norwegian physicist Adam Arndtsen, who discussed his studies of aqueous solutions of (+)-tartaric acid [4]. Using sunlight, he was able to visually determine the angle of rotation at some of the principal Fraunhofer lines, that is, C (656), D (589), E (527), b (517), F (486), and e (438 nm). He could confirm and extend Biot's earlier finding that the rotation exhibits a maximum in the spectral region studied, with its wavelength shifting from the blue to the red on increasing concentration. This unexpected and intriguing result led the Swiss chemist Hans Landolt (an important pioneer of the investigation and application of optical activity, as well as one of the "fathers" of Physical Chemistry) in 1877 to introduce the expression "*anomale Rotationsdispersion*" (anomalous rotation dispersion) [5], which since has become established for the description of such rotatory dispersion curves that run through a maximum or minimum, or show a reversal of sign.

It had thus become apparent that spectropolarimetry promised to develop into an interesting field in the future. In his last and comprehensive paper on optical activity, Biot [6] suggested, therefore (translation from the French by the present author):

> I should like to draw the attention of experimentalists to a class of phenomena which, hitherto, has been little studied but which, nevertheless, for both theoretical and practical purposes, ranks in importance with that of the optical rotatory power itself of which it is a constituent element. I refer to the specific mode of dispersion that each optically active substance or compound imparts to plane polarized light of different wavelengths [literally: refrangibility].

Despite this exhortation, reports on rotatory dispersion remained scarce until the end of the century. This is also evident from the very first book on optical activity, where all data known at that time are summarized, which was published in Germany in 1879 by Landolt [7]. Here, he also describes in detail the optical equipment used by himself and his predecessors. Therefore, it is not necessary to dwell at this point on the measuring devices and optical methods. Although most of the rotations listed (many of which had been determined or redetermined by Landolt himself) refer to the sodium D line only, his book also has short sections on normal and anomalous rotatory dispersion. It is important to realize that so far all reported optically active liquids or solutions were based on organic compounds without absorption bands in the visible. In fact, Landolt emphasized that there is not a single inorganic substance known which shows optical activity in solution (or in the gas phase), from which he tentatively—but incorrectly—concluded that optical activity might be restricted to carbon compounds, except for the solid phase. Surprisingly, he gave no reference to any optically active transition metal complex, although at least Fehling's solution (a mixture of several Cu(II) tartrate complexes) had been around since 1848 [8]. One might speculate whether such coordination compounds (of a still unknown nature) were ignored as a result of theoretical considerations.

It should also be mentioned that measurements in general were limited to practically colorless samples and to merely certain frequencies of the visual solar spectrum. The only other reasonably monochromatic light sources available were based on lithium, sodium, and thallium salts heated in a Bunsen burner (invented in 1866), giving access to the wavelengths 671 nm (Li), 589 nm (Na), and 535 nm (Tl), respectively.

It is worthwhile to briefly turn to the "anomalous" refractive dispersion using unpolarized light—that is, the characteristic sigmoidal variation of the index of refraction in the absorption region, running through a maximum and minimum, instead of steadily increasing as the wavelength decreases, as in normal dispersion. This behavior had been discovered in iodine vapor in 1862 by the French physicist F.-P. Leroux [9], and around 1870 it attracted the attention of several investigators, who published independently on anomalous dispersion in the visible, using solutions of organic dyes like fuchsine [10]. There was some dispute as to priority among the Danish physicist Christian Christiansen, the Swiss chemist and physicist Jacques-Louis Soret, and the German physicist August Kundt. While it is clear that Christiansen was the first to publish, the most extensive studies were carried out by Kundt. The relevance of these findings to the present subject lies in the fact that here was proven the possibility of successfully studying the index of refraction even near absorption bands in the visible. Consequently, a similar anomalous dispersion could be expected to exist for the optical rotation, keeping in mind the relation between the velocity of light, the index of refraction, and the optical rotation. This anomalous dispersion feature of the rotation should have been accessible by existing techniques, if only suitable colored optically active samples had been available. It took more than two decades, however, before this problem was addressed.

1.3. THE DISCOVERY OF THE COTTON EFFECT

In 1895, two short papers ("notes") appeared in the fortnightly journal of the French Academy of Sciences, entitled "*Unequal absorption of right and left circularly polarized light by certain optically active substances*" [11] and "*Anomalous rotatory dispersion of absorbing substances*" [12]. The author was the 26-year-old physicist Aimé Auguste Cotton (Bourg-en-Bresse 1869–Sèvres 1951), a PhD student at the prestigious École Normale Supérieure in Paris. The first of these papers describes and names the property of "*dichroïsme circulaire*" (what we now call "CD") associated with an absorption band of an optically active compound in solution, and the second one introduces the corresponding effect in the dispersion mode (now called "ORD"). The full paper of 85 pages, also incorporating studies on magnetic optical activity, was published in 1896 under the heading "*Investigations of the absorption and the dispersion of light by optically active media*" [13]. It summarizes A. Cotton's *Thèse de Doctorat*, which he prepared from November 1893 to July 1896 at the Physics Laboratory of the École Normale with Professors Marcel Brillouin and Jules Violle as advisors. Based on his important discoveries, Cotton was accorded the degree of *Docteur ès Sciences* in 1896.

In his thesis, Cotton for the first time reports data of (a) optical rotations close to both sides of an absorption band in the visible, using solutions of Cu(II) and Cr(III) coordination compounds with tartrate or malate ligands, and (b) the associated circular dichroism. It is quite obvious that Cotton was successful to a large degree owing to both the quality of his optical components and the skillful and precise construction of the measuring devices, especially for the determination of very small values of the ellipticity, but also to his power of observation, and—last but not least—to a fortunate choice of optically active samples. In this chapter, however, his technical equipment and the underlying physical principles shall not be discussed in detail, because Cotton himself gives a full description in his major paper, and there are also comprehensive reviews elsewhere as, for example, in the books by Mitchell and Lowry (see below).

While Cotton's expression "*dispersion rotatoire anomale*" (anomalous rotatory dispersion) is self-explanatory, a comment concerning his novel term "*dichroïsme circulaire*" (circular dichroism) may be appropriate. Cotton did not always measure directly or indirectly the difference in absorption of left- and right-circularly polarized light by his sample [*i.e.*, $(\varepsilon_L - \varepsilon_R)$], but rather the ellipticity of the emerging elliptically polarized light. In this case, his measuring device included, apart from a Nicol prism to provide plane-polarized light, a "double circular polarizer" consisting of two quarter-waveplates placed side by side in the plane-polarized light beam in such a way that their principal axes are at 90° to one another and at 45° to the plane of the incident light. This arrangement allowed the observation of left- and right-circularly polarized light beams next to each other. On the introduction of a sample showing circular dichroism, the beams would be differently absorbed, which could be detected visually or photometrically. The field of vision was thus divided into two halves by these $\lambda/4$ plates. When he used white instead of monochromatic light for the examination of his optically active sample solutions, these two halves showed different colors. This reminded him of the dichroism observed with certain doubly refracting crystals, where the ordinary and the extraordinary ray are absorbed unequally, as found by Biot in tourmaline and later by the Austrian mineralogist Haidinger in many other cases [14]. Cotton therefore chose the term "*circular dichroism*." In fact, Haidinger had already discovered this phenomenon in amethyst quartz in 1847 [15].

Nowadays, the expression "*circular dichroism*" probably just awakens vague memories of the original visual observations; this context has been largely forgotten nowadays, with the advent of automated electronic spectropolarimeters. Actually, Cotton himself had already performed some photometric measurements, but had found them inferior to his visual results.

1.4. THE FIRST CD AND ORD CURVES

Cotton's measurements obviously were not only restricted to the visible, but also quite limited as to the wavelengths available. Even under favorable conditions, at most eight spectral lines were at his disposal, namely, 657 (red, near C), 589 (yellow, sodium D line), 581 (orange, near D), 562 (greenish yellow), 522 (green, between E and b), 475 (blue, near F), 459 (blue-violet), and 437 nm (violet, near e) [the letters C, D, E, b, F, and e refer to the Fraunhofer lines so designated]. A comparison with Arndtsen's paper of 1858 [4] shows that hardly any improvement of the spectral availability had taken place until the end of the nineteenth century. However, on the positive side it can be seen that these lines are spread rather evenly across the whole visual region. Nevertheless, the generation of continuous absorption and rotation curves, as often published, on the basis of observations at some of these individual wavelengths, leaves much to the whim of the draftsman, especially concerning the position and magnitude of any maxima and minima. Such "data" should not be overinterpreted. This situation would prevail in the decades to come.

It is not unexpected that, at the onset of his investigations, Cotton chose Fehling's solution ("*liqueur de Fehling*") for his studies. It is, after all, in the direct line of Biot's research to look at derivatives of active tartaric acid. Secondly, the only area of importance where the application of optical activity had become established was saccharimetry; and thirdly, Fehling's solution was a proven and powerful reagent in carbohydrate chemistry [16]. It seems that Cotton systematically progressed from the complex and notoriously unstable Fehling's solution to simpler alkali copper(II) tartrates, the preparation of which he describes in detail. By the way, it is amusing to note that in one case he reports the precipitation of copper tartrate from a copper sulfate solution by adding the aqueous solution of a crystal of Seignette salt (potassium sodium tartrate); this crystal had been prepared by Pasteur himself. Unfortunately, these copper complexes proved to be very unstable; they changed or simply decomposed with time or at elevated temperature and were also light-sensitive. Furthermore, the chemical composition of these aqueous solutions was unknown (and, to some extent, still is), and attempts at isolating any well-defined compound failed. A solution of crystalline copper malate, perhaps more stable, did not show any observable circular dichroism. Despite these drawbacks, Cotton did obtain many ORD and some CD data, but obviously the reproducibility of the experiments remains questionable, and the curves shown in print [13] should be interpreted with caution.

The most convincing chiroptical effects, however, were observed with aqueous solutions of potassium chromium(III) tartrate, prepared *in situ*. They shall be discussed here in some detail. Figure 1.1 is Cotton's Figure 18 on page 408 of reference 13, and it shows a complete "*Cotton effect*" in the ORD and the CD near 570 nm. Because of its seminal importance, this figure has been later reprinted by others a number of times. The actually measured data are given as follows: 657 nm, rotation $\rho + 1^\circ 26'$, ellipse [sic] $\phi + 32'$; similarly: 589, $+2^\circ 30'$, $(-3^\circ 40')$; 581, $+1^\circ 46'$, $-4^\circ 54'$; 562, $-1^\circ 21'$, $-4^\circ 16'$; 522, $-2^\circ 50'$, $-1^\circ 25'$; and 475, $1^\circ 52'$ [no sign given in the paper; from the curve it is evident that ρ must be negative], $+28'$. Data were thus collected at six wavelengths only, because the onset of a second strong absorption band made observations at shorter wavelengths impossible. The parentheses around the ellipticity value at the sodium D line are Cotton's and indicate that this number results from photometric measurements.

Despite its beautiful appearance, there are unfortunately some flaws in this figure and the data as printed. A comparison of the figure with the data listed above makes evident two discrepancies at 562 nm: In the figure, the angle ϕ is given as $-4^\circ 46'$ (not $-4^\circ 16'$), and the corresponding angle ρ is given as $-0^\circ 21'$ (not $-1^\circ 21'$). On reexamination, the true values were verified to be $\phi - 4^\circ 46'$ and $\rho - 1^\circ 21'$. The figure should be redrawn, therefore, using this value of ρ. Such a modification would necessarily modify the shape of the ORD curve, while not basically changing it. Cotton gives these corrections in

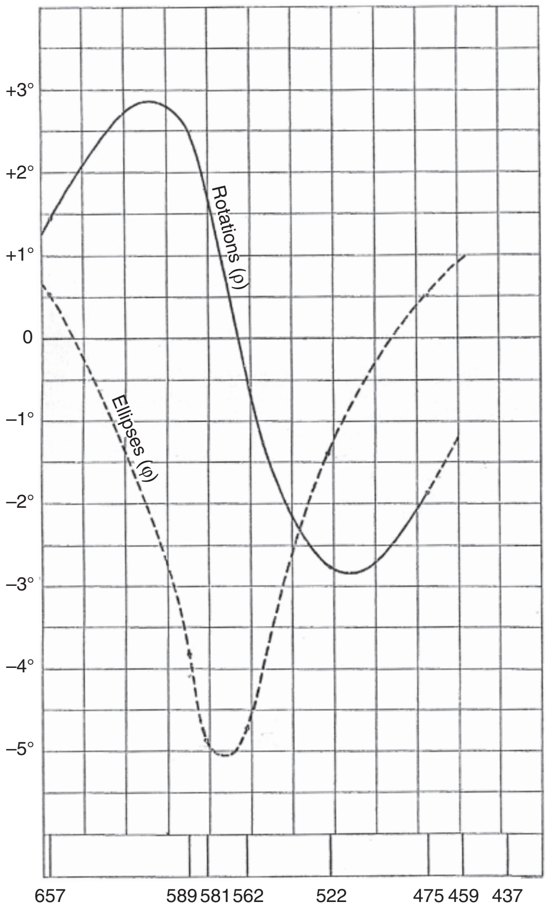

Figure 1.1. CD and ORD of potassium chromium(III) tartrate (solvent H_2O). (From A. Cotton, *Ann. Chim. Physique* **1896**, [7] *8*, 347; Figure 18, p. 408.)

a letter to Professor Ladislas Natanson in Cracow, Poland, quoted on pages 33/34 of reference 17. He explains the first error as a misprint, and he states that the second one is a mistake by the "*dessinateur*" (draftsman).

However, the really important disagreement between the ORD and CD, as we can see immediately from the curves—with hindsight—lies in the incompatibility of their signs. If we accept the rotation values as correct, as seems reasonable, the sign of the CD is in error. And so it is! Cotton himself redressed this flaw two years later [18] in a paper, the first sentence of which runs as follows (translated from the French): '*It is easy to be mistaken as to the sense of a circular vibration*.' Admitting his mistake in the assignment of the direction of the rays circularly polarized by a Fresnel rhomb, he imputed it to his misinterpretation of some of Billet's tenets in the latter's "*Traité*" [19]. Apparently, Billet had used the expression "*principal section*" of a mica crystal in an unorthodox way and had also treated this crystal as positive, contrary to the common practice. Therefore, all of Cotton's CD curves, and the sign of all ellipticities published before 1898, ought to be inverted.

But not everyone read or responded to this correction; others did so, but without indicating it. The confusion that might have been generated was fortunately curtailed by the fact that very few scientists, apart from Frenchmen, studied the circular dichroism in the following decades. But as late as in 1923, (Ms.) N. Wedeneewa in Moscow (for example) still used the earlier "wrong" sign of the CD, when she reported the ORD and CD of camphor quinone [20]. Similarly, T. M. Lowry just reprinted Cotton's Figure 18 in his famous classic of 1935 [21] without any comment, whereas S. Mitchell in his treatise on the Cotton effect [22] of 1933 simply shows an inverted CD curve in ostensibly the same figure (see Figure 1.2), also without any further comment.

Another point of criticism could be raised because of the all-too-vague identity of the samples investigated. Although Cotton carefully describes the preparation of his samples, as mentioned earlier, their inherent instability cannot preclude changes with time, perhaps also as the result of shifting equilibria between the several complexes present. Indeed, small changes even in the synthesis of the tartrate complexes can lead to the total inversion of the anomalous rotatory dispersion, as has been observed by Wedeneewa [20]. All this calls for caution with respect to the early ORD and CD publications. However, concerning the key compound discussed at length, potassium chromium(III) tartrate, all doubts were finally set to rest by W. Kuhn [23], who much later very carefully repeated Cotton's work and found it fully correct (Figure 1.3).

1.5. THE REACTION OF THE LEARNED WORLD TO COTTON'S DISCOVERIES

Cotton's papers raised the immediate attention of Wilhelm Ostwald (Nobel Prize 1909), who, one year after the publication of the original notes in the *Comptes Rendues* [11, 12], wrote two abstracts thereof himself for his journal *Zeitschrift für Physikalische Chemie* [24]. This was followed by his six-page review of Cotton's full paper [13] in the same year [25], with several CD and ORD curves reprinted, including Cotton's original Figure 18, discussed above.

It should be pointed out that the lack of correspondence of the sign of the ORD and the CD could not have been noticed by Ostwald at that time, since the necessary theoretical background had not yet been provided. With these reviews, Ostwald acquainted the chemical world with Cotton's results, and his name carried much weight. It is certainly unusual that preliminary notes by a foreign physics student and extracts of his

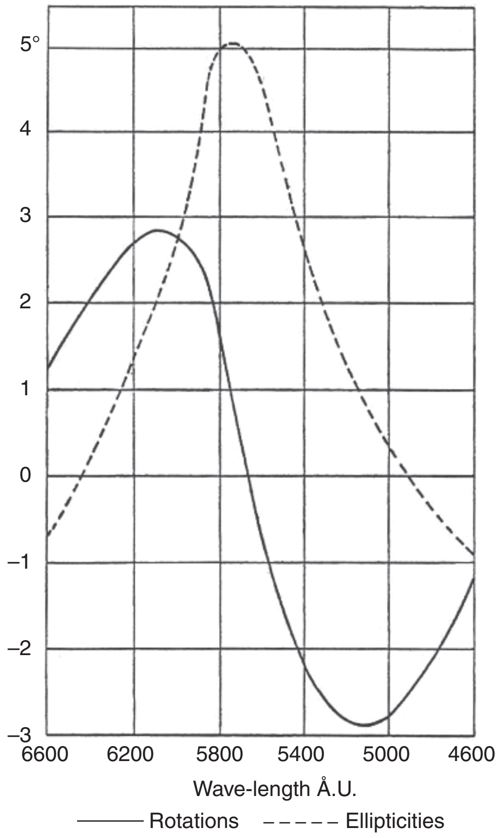

Figure 1.2. CD and ORD of potassium chromium(III) tartrate (solvent H_2O). (From S. Mitchell, *The Cotton Effect*, Bell, London, 1933; Figure 12, p. 23; reproduced with permission.)

thesis should induce an already famous physical chemist to such a presentation. Incidentally, already the “sponsoring” of Cotton’s notes by the renowned physicist Gabriel Lippmann from Luxembourg (Nobel Prize 1908)—such notes had to be presented by an academician—attests to the importance attributed to them. One might well say that chiroptics had a splendid start.

The speed with which the news was reported and hailed is altogether breathtaking. For example, the physical chemist Landolt referred to Cotton’s studies already in the second edition of his book, published in 1898 [7]. Mention should also be made of the German physicist Paul Drude, who included a treatment of Cotton’s “(anomalous) rotary dispersion” in his famous *Lehrbuch der Optik* of 1900 [26].

So, by the beginning of the twentieth century, the international world of physics and physical chemistry was well aware of Cotton’s results.

It took only a few additional years before a thorough theoretical treatment was provided by L. Natanson, Professor of Theoretical Physics at the Jagiellonian University Kraków (Cracow, Poland). The title of his important paper, “*On the elliptic polarization of light transmitted through an absorbing naturally-active medium*” [27], with a supplementary note [17], needs no further comment. Here, Natanson treated the interdependence of absorption, optical rotation, and circular dichroism. Probably in order to spread his results further, also an amalgamated and shortened French translation of both papers by the Count of Ballehache was published very shortly thereafter [28]. The relations presented here between the sign of the rotation and the circular dichroism have become known as the “*Règle de Natanson*” or “*Natanson’s Rule*” [29]. This finally allowed the

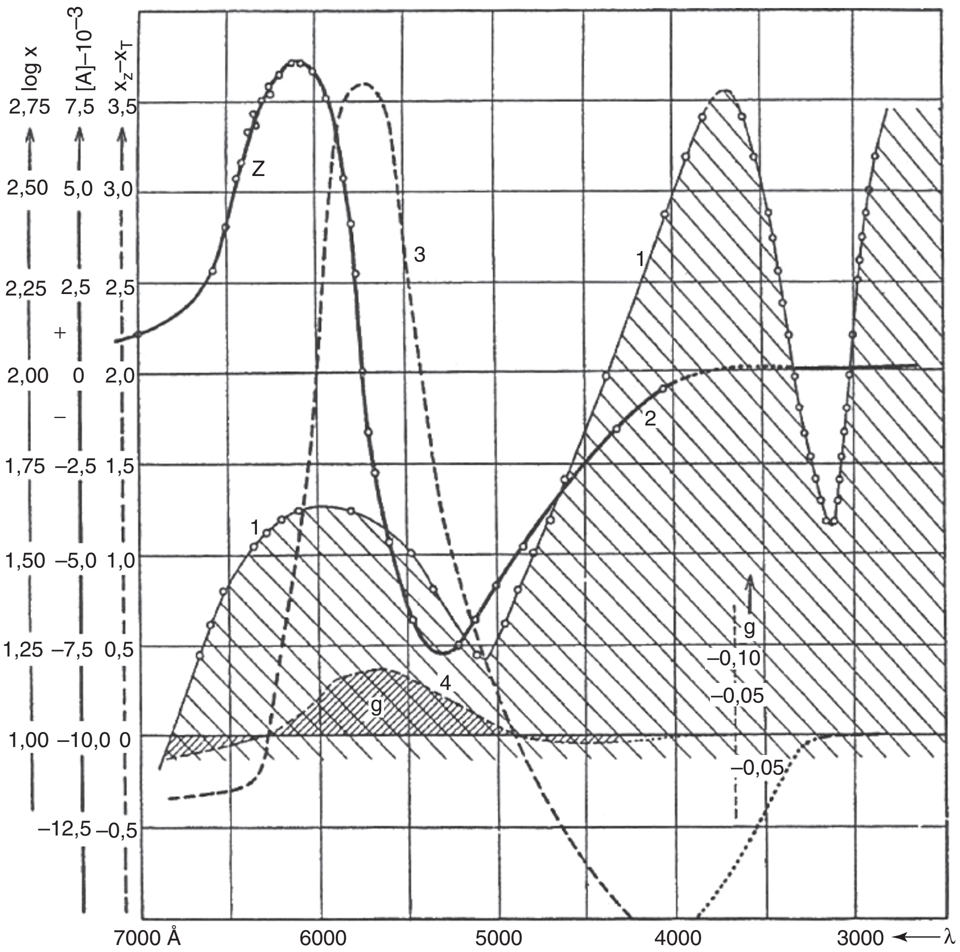

Figure 1.3. UV, CD, and ORD of potassium chromium(III) tartrate (solvent H_2O). (From W. Kuhn, A. Szabo, *Z. Phys. Chem.* **1931**, *B15*, 59; Figure 1, p. 62; Oldenbourg Wissenschaftsverlag München, reproduced with permission.)

prediction of the sign of the circular dichroism associated with a specific absorption band, based on just the anomalous rotation curve, which should not be too difficult to obtain.

Natanson's papers included the following sentences on the first page: "*Effects of this kind have been observed and investigated by Monsieur A. Cotton*" [27] and "*Des phénomènes de ce genre ont été observé et analysés par M. Cotton*" [28]. Here we find the seed that has developed into the important technical terms "*Cotton's Phenomenon*" and "*Cotton Effect*," which have been used ever since, with the first one preferred in the early decades of the twentieth century.

At this point it may be timely to more formally give a definition of the Cotton effect as we understand it today. It may be interesting to compare the definition given in 1933 by Stotherd Mitchell on page 24 of his book on the Cotton effect (incidentally the first monograph of this kind) [22] with the definition by Werner Kuhn from 1960 [30].

Mitchell wrote: "A maximum ellipticity and zero rotation are found in this region [of the absorption band]. The rotation reaches a maximum value on one side of the band and a minimum on the other. This variation of rotation and ellipticity in the neighbourhood of an absorption band has been called the *Cotton effect*." [Mitchell's italics]

Kuhn stated: "[Cotton] found that optical rotatory power as a function of the wavelength often shows, in the region where the substances show ordinary absorption, a characteristic *anomaly* which is associated with a *circular dichroism* in the absorption region and which after the name of its discoverer is called a *Cotton effect*." [Kuhn's italics]

It is satisfactory that both definitions, published some 30 years apart, fully agree with one another; furthermore, we still can subscribe to both of them, even 50 years later. Many similar definitions can be found over the last 80 years, all of them stressing the point that the ensemble of rotatory dispersion and circular dichroism in the absorption region *collectively* constitute the Cotton effect. Nevertheless, quite commonly the term Cotton effect has loosely been used to characterize merely the "anomalous" rotation features, since in the decades following Cotton's discoveries the available data were mostly limited to the optical rotation. In fact, in many cases it has been considered sufficient to have reached the first maximum of the rotatory dispersion curve, still outside the absorption band, to apply the term Cotton effect. In recent decades, when ORD effectively disappeared in favor of CD, the term usually means the CD curve only.

1.6. MORE TARTRATES: THE PHYSICIST'S PLAYGROUND

Cotton's discovery of circular dichroism raised so much interest in Brace's Physics Laboratory at the University of Nebraska that it was decided to construct an improved and more sensitive apparatus for measuring both elliptical polarization and rotation, in order to repeat and extend the French findings. The American physicist DeWitt Bristol Brace was himself active in the field of optical activity and had in 1904 described an elliptical polarizer and compensator that was incorporated not only in the optical system used in Nebraska, but also later in Europe. Brace died in 1905 and had, therefore, no part in the further development. The first results on, for example, complex chromium, copper, cobalt, and nickel tartrates and copper malate were presented by M. F. McDowell in 1905 [31]. The ellipticity had been measured in "all parts of the spectrum," which means at some 10 different wavelengths of the visual solar spectrum.

Unfortunately, the calculation of the ellipticity was found to be incorrect, and some compounds were irreproducible. This was carefully rectified at the same laboratory in 1912 by L. B. Olmstead, who studied tartrates, malates, and lactates of chromium, copper, cobalt, and manganese [32]. Also here, the so-called "monochromatic" light, with a spectral band width of perhaps 20 nm, was obtained from sunlight. Although the optical part of the investigation seems to be impeccable (except that Cotton's first—incorrect—sign protocol of the circular dichroism was still used), the identity of the compounds studied is uncertain. Olmstead himself points out: "No chemical analyses of the compounds were made; *the names assigned being merely for convenience*, and not indicating that the chemical formulæ are known." [Olmstead's italics]. He observed that Cotton's results for potassium chromium tartrate could be repeated quantitatively when the sample was prepared from potassium dichromate and potassium tartrate, but an oppositely signed Cotton effect developed when the potassium dichromate was replaced by chromium acetate. Undoubtedly, the samples consisted of a mixture of complexes, as was also indicated by color changes of the solutions, depending on variations of the concentration and with time. As a result, even these carefully collected data are of a qualitative nature only.

The same qualifications pertain to a large number of papers of the early twentieth century on the rotatory dispersion of transition metal complexes with optically active ligands. In addition, the rotatory dispersion data were often collected at only four or five rather ill-defined spectral bands in the visible. Examples are found in the report by H. Grossmann and A. Loeb on copper tartrate and malate coordination compounds [33], as well as in the paper by H. Volk on copper, nickel, and cobalt complexes with lactate ligands [34]. Also these investigations were initiated, by the way, in order to verify and extend Cotton's findings.

Cotton himself did not continue his work on the optically active tartrates, but motivated his student Georges Bruhat to address the problem again [35]. Bruhat tried to synthesize and isolate individual, well-defined compounds, but succeeded with most tartrates and malates in part only, because of the easy decomposition of the respective solutions. He did isolate and investigate uranyl tartrate that seemed to be stable and showed a Cotton effect near 500 nm. His optical equipment limited the quality of his measurements rather severely, however. After a disruption of the research by the First World War, he resumed his studies again in 1919 with a much more advanced apparatus. This allowed him to reduce the spectral band width from 30 nm to 10 nm, which was essential to avoid "flattened-out" dispersion curves. In this way, he obtained splendid CD and ORD data for uranyl tartrate and ammoniacal cobalt tartrate [36], for example. But regrettably, not even the high quality of the physical data allows any better analysis of the compounds responsible.

The interest in this topic was not yet put to rest in Cotton's laboratory. In the earlier work, the copper complexes had been particularly unsatisfactory. Therefore, the study of alkaline copper tartrate solutions was taken up again in order to enhance the quality of the samples [37]. Somewhat later, complex chromium [38] and cobalt tartrates [39] were reinvestigated. Good CD data could be collected, but the chemical identity of the species in solution remained uncertain, despite Mathieu's extensive experiments.

Such tartrate studies were not wholly limited to Paris. Also W. Pfleiderer in Basel, Switzerland, had returned to measuring the optical rotation of aqueous alkaline solutions of copper tartrate, and he found his data to qualitatively agree with Cotton's of 1895 [40]. The chiroptical instability that Nina Wedeneewa in Moscow, Russia, had encountered with alkaline chromium tartrates in the absorption region has been mentioned already [20]. Last but not least, attention is drawn to W. Kuhn's reevaluation of the same problem, as outlined earlier [23].

The overview presented here is not exhaustive. Because of the similarity of the problems, the preceding discussion pertains also to, for example, optically active lactates, malates, and "sucrates" of transition metals. The respective chiroptical results are not basically different from those with tartrate ligands.

It remains to report that even many years later the chemical identity of these complicated coordination compounds has not been fully understood, with several questions still unsettled even today [41]. While some of the variability observed is certainly caused by the gradual replacement of coordinated water by the organic ligands, condensation processes leading to multinuclear species also seem to be involved.

It is intriguing that the chiroptical properties of tartrate complexes dominate the study of circular dichroism for three decades. In fact, during these years very few CD measurements have been carried out outside of this area (see later). One might speculate whether this conservatism would perhaps result from the fact that practically all researchers were physicists, who might have had limited awareness of colored optically active compounds in other fields of chemistry. After all, with, for example, organic xanthates, such compounds did exist, but their investigation was largely confined to only one chemical research group in Russia, as will be seen.

The question might well be asked, What motivated these tenacious tartrate investigations? It is obvious that genuine chemical topics were not addressed, such as the stereochemical correlation and the application of optical activity to the study of reaction mechanisms, or as a tool in the elucidation of the chemical constitution. This contrasts with the aims in connection with the Werner complexes, to be discussed in the following section of this report. But as to tartrates, the investigators were primarily interested in the circular dichroism in its own right. They tried to effect improvements in the optical instrumentation in order to enhance the sensitivity and precision of their measuring devices. For testing the various theories of optical activity and to compare calculated and experimental data, the latter should be measured with a maximum of accuracy and reliability. It might well have been felt that the continuation with "well-known" samples like the complex tartrates would be advantageous, with a host of data already existing for comparison.

1.7. WERNER COMPLEXES: INORGANIC CHEMISTS LEARN TO MAKE USE OF THE COTTON EFFECT

According to common practice, the tartrate systems discussed in the previous section can be considered to belong to the realm of inorganic chemistry. But they were chosen for chiroptical research without paying much attention to their chemical nature. Chemists have performed hardly any systematic studies of these compounds and have instead tended to neglect them.

The situation was quite different with regard to the chemically and structurally well-defined octahedral transition metal complexes, following the Alsatian Alfred Werner's (1866–1919) introduction in 1893 of his geometric model for centers with the coordination number six [42]. At that time, Werner worked in the laboratory of his doctoral advisor, Professor Arthur Rudolf Hantzsch, at the University of Zurich, Switzerland. He had obtained his doctoral degree only in 1890, but was quickly promoted to a chair of chemistry at this University in 1895. Although his revolutionary concept eventually secured him the Nobel Prize in 1913, it met much resistance among his chemical colleagues. The opposition diminished, however, after he had achieved the resolution of some of his complexes into enantiomers [43], since the occurrence of optical activity was hard to reconcile with other than the octahedral geometry. The optically active compounds, mostly Co(III) complexes, were of greatly varying chemical and optical stability, often racemizing at room temperature within a few hours. It was found that chelating ligands like oxalate ions (O,O'-donor ligands) or 1,2-diamines (N,N'-donor ligands) led to increased stability. In the beginning, the optical rotation at only one wavelength was considered sufficient to characterize a specific complex. But it was soon realized that the stereochemical correlation should not be based on such an individual value, since it varied too much in magnitude and even in sign from one complex to the next, notwithstanding a close chemical relationship. Furthermore, as the enantiomeric purity of the compounds was often uncertain, a particular, selected rotation value could be quite misleading. On the other hand, these complexes were well-suited to measurements of the Cotton effect due to their color, which often brought them within the range of visual observation. The sign of this Cotton effect, associated with electron transitions at the coordinating metal center, was found to be a reliable, characteristic feature. Consequently, measuring the rotatory dispersion including, hopefully, a more or less complete Cotton effect became a common goal.

The first Werner complex for which both ORD and CD data through an absorption band were obtained, namely, potassium (trisoxalato)iridate(III) dihydrate, $K_3[Ir(C_2O_4)_3]\cdot 2\ H_2O$, was resolved by M. Delépine [44], and its chiroptical properties were determined by G. Bruhat [45]. A Cotton effect near 450 nm was found. This is, incidentally, one of the rare instances where the circular dichroism of a Werner complex has been determined in the early part of the twentieth century. In practically all other cases, the term Cotton effect just refers to the rotatory dispersion near or at an absorption band in the visible.

Werner himself had already reported similar dissymmetric, optically active complexes with bidentate ligands like $[Co(en)_3]^{3+}$ or $[Cr(ox)_3]^{3-}$ (en = 1,2-diaminoethane; ox = oxalate ion $C_2O_4{}^{2-}$), but without any further spectropolarimetric data [46]. It is amusing to see that in some other cases the Cotton effect—or, rather, the anomalous rotatory dispersion—rests on measurements at only three different wavelengths as for $[Rh(ox)_3]^{3-}$, for example [47].

Werner's concept achieved its final breakthrough when he published the resolution of the "completely inorganic" complex $[Co\{Co(NH_3)_4(OH)_2\}_3]Br_6$, an octahedral Co(III) complex with bidentate O,O' ligands. This complex, without any carbon atom, is sterically related to the simpler $[Co(en)_3]^{3+}$ system. It showed a Cotton effect near 600 nm [48]. This finding finally put to rest the long-lived but obsolete theory that the presence of carbon atoms was essential for the unfolding of optical activity. Werner showed no particular interest in the Cotton effect in its own right, however, but rather made use of it for the stereochemical correlation and the characterization of his compounds. A further example which may be mentioned is $[Co(NO_2)_2(en)(pn)]$, with pn = 1,2-diaminopropane, with either *rac*-pn or *l*-pn, that had Cotton effects in the 530- to 540-nm range [49]. In general, Werner's interest in spectropolarimetry remained limited, and usually he left further chiroptical studies to others. Even when he reported Cotton effects, it is not always clear how, where, and by whom the data were obtained.

Meanwhile, a new "center of gravity" for the examination of Werner complexes was developing in Groningen in the Netherlands. Here, the stereochemist Franciscus Mauritius Jaeger (1877–1945), Professor of Inorganic and Physical Chemistry at the Rijksuniversiteit Groningen (RUG) from 1908 to 1945, had by 1915 embarked on a program of the comprehensive investigation of these systems [50]. A great many new, and some already known, Werner complexes were synthesized and studied. Jaeger's interests lay largely in their crystallographic description, but he also included optical activity in his research program. Most of the spectropolarimetric data generated "plain" ORD curves only, because the anticipated Cotton effect was often beyond the wavelength limit of the optical devices or inaccessible because of too strong an absorption. In Jaeger's extensive paper of 1919 [51], many such plain curves are reported, but only two cases of a *bona fide* Cotton effect, namely, in $K_3[Cr(ox)_3]$ (Cotton effect near 565 nm) and $K_3[Co(ox)_3]\cdot H_2O$ (near 620 nm). The chromium compound had already been synthesized and resolved by Werner in 1912, but had not been investigated by spectropolarimetry, whereas the (trisoxalato)cobaltate(III) was new.

It was very advantageous that Jaeger could induce Israel Lifschitz (1888–1953), Private Docent at the University of Zurich, to join his laboratory in 1921. Lifschitz, whose special area of research had been the absorption spectroscopy and photochemistry of organic compounds, now became Private Docent of Electrochemistry and Photochemistry and tenured staff member at RUG. He turned to the spectroscopic study of transition metal complexes, with particular attention to spectropolarimetry. Largely owing to his efforts, the laboratory developed into a center of chiroptical spectroscopy, of international repute. Lifschitz had taken his doctorate in 1911 with A. Hantzsch in Germany (Hantzsch had changed from Zurich to the University of Leipzig) and had moved to Switzerland in 1914. It is interesting to note that he there worked close to Werner, who also had been a student of Hantzsch. Perhaps the shift of Lifschitz from organic photochemistry to coordination stereochemistry has thereby been influenced, but presently nothing is known of a personal interaction with Werner. It is difficult to assay in detail Lifschitz's contribution to the Groningen laboratory, except for his own publications, since Jaeger as laboratory head regularly included the research results of his local colleagues in his own publications, without giving any individual credit. This procedure was rather common in those days. Only sometimes is Lifschitz mentioned in a vague way as a "*collaborateur*" (coworker).

In 1923 Lifschitz started a series of papers called "Investigations of Rotatory Dispersion" [translated from the original German]. In the first paper, he presented and discussed ORD data of complexes of Cr(III), Co(III), Ni(II), and $UO_2{}^{2-}$ ions with optically active camphor derivatives, including nitrocamphor. These compounds exhibited Cotton effects in the visible. The paper is also noteworthy, because here the technical term "Cotton effect" was introduced into the chemical literature; the earlier term had been "Cotton phenomenon" [52]. In the second paper of this series, Lifschitz reported the ORD Cotton effects of Co and Cu complexes with amino acid ligands (alanine, asparagine), and also of the complex $[\mathrm{Cu}\text{-}(l\text{-pn})_2]\mathrm{SO}_4$ (effect at 510 nm) [53]. Slightly later, Jaeger extended the chiroptical studies to cobalt complexes with 1,2-diamino ligands, and he reported the Cotton effects in $[\mathrm{Co}(\textit{rac-trans}\text{-1,2-diaminocyclopentane})_3]\mathrm{Cl}_3 \cdot 4\mathrm{H}_2\mathrm{O}$ at 470 nm and in $[\mathrm{Co}(\textit{rac-trans}\text{-1,2-diaminocyclopentane})(\mathrm{en})_2]\mathrm{Br}_3 \cdot 2\mathrm{H}_2\mathrm{O}$ at 500 nm [54].

A few years later, some of these Werner complexes were reinvestigated by Werner Kuhn, making use of advanced instrumentation. Measurements had now become possible down to 280 nm. With potassium (trisoxalato)cobaltate(III), for example, the Cotton effect at ~600 nm was measured both in rotatory dispersion and in circular dichroism [55]. But now the aim had shifted from using the spectropolarimetric data for chemical and stereochemical correlation, as had been the purpose in Zurich and Groningen, to probing the stereochemistry in depth, with the elucidation of the absolute configuration in mind, and to testing new theoretical models of the optical activity. But it would take a few additional decades before eventually another experimental reinvestigation of the circular dichroism of some of these complexes, in connection with an analysis based on an improved theory, led to the desired knowledge of both the structure in solution and the absolute configuration. To this end, once again the circular dichroism of the (trisethylenediamine)cobalt(III) cation [56] and of the (trisoxalato)cobaltate(III) anion [57] was studied. But to trace this development would far exceed the scope of the present overview.

1.8. THE COTTON EFFECT IN ORGANIC CHEMISTRY, A RUSSIAN DOMAIN

It would not be correct to claim that organic chemists neglected optical activity in the early twentieth century, except to characterize compounds by their D-line rotation. As an example to the contrary can be cited a series of papers by the Swiss chemist Hans Rupe (1866–1951) on the influence of the constitution on the rotatory power of optically active compounds, starting in 1903 [58]. However, usually colorless solutions were examined in the visible, as also done by Rupe, and could provide data on "plain" rotatory dispersion only. These investigations are, therefore, outside of the scope of the present overview.

However, it must be admitted that, in general, organic chemists seem to have been less interested in chiroptical effects than their inorganic or physicochemical colleagues. Thus the study of organic molecules, as much as there is, had to rest on the "good will" of people from the latter fold. Here, credit is to be given first to the distinguished English physical chemist, Thomas Martin Lowry (1874–1936). Lowry's interest in optical activity dates back to 1898, when he noted the change of optical rotation on nitrocamphor with time and introduced the term "mutarotation" to characterize this phenomenon [59]. He greatly improved the mathematical treatment and the theoretical understanding of rotatory dispersion and circular dichroism, based in part on the experimental data collected in his own research group in London, and later in Cambridge. It is interesting to see that there was a certain lack of understanding of the theory of optical activity on the part of some organic chemists. Even Rupe himself, for example, maintained as late as in 1921 that there had not been established with certainty any connection between the Cotton effect and the absorption of light [60]. In the earlier period of his career, Lowry dealt mostly with features outside of absorption bands; that is, he did not penetrate by experiment into the Cotton effect region itself. The state of the research on optical activity by the year 1914 has been summarized in the report "*Optical Rotatory Power. A general Discussion*" [61], and later in Lowry's classic book [21], and it need not be described further in this paper. Lowry's work in the early 1930s on the Cotton effect of organic molecules will be discussed later in this section. The most active pioneer in the study of the rotatory dispersion of organic molecules, and the only one who obtained data for the Cotton effect before World War I, is undoubtedly the Russian Leo [Lev] Alexandrovitsch Tschugaev (1873–1922) [62].

Tschugaev was a prolific research worker, who from the beginning of his career engaged in the chemistry of compounds like terpenes and camphor and, secondly, that of transition metal complexes. It was probably the study of optically active natural products that aroused his interest in optical activity generally. Eventually, he turned to a third research topic, after he had become Professor of Inorganic Chemistry at the Imperial University of St. Petersburg, and began in 1909 a series of papers on (anomalous) rotatory dispersion [63]. Tschugaev was fully aware of Cotton's ground-breaking discoveries, and he was also aware of the problems inherently connected with the samples chosen for this early work. Therefore, he proudly, and correctly, pointed out in his initial papers that he now for the first time employed well-defined compounds for the study of the rotatory dispersion (he himself had no instrument that would allow him to measure the circular dichroism, in addition). But also he was still limited to visual observations at certain spectral lines. He used samples from two different families of sulfur-containing colored derivatives of optically active terpene alcohols like borneol, menthol, or fenchol, namely, xanthates $RO{-}C(S){-}SR'$ and related compounds, along with "dithiourethanes" $RO{-}C(S){-}NPh{-}C(S)Ph$ (with $Ph = C_6H_5$) and similar compounds. In all cases he found an anomalous dispersion of the rotation, but for different reasons. The xanthates give colorless or yellowish solutions, because there are no absorption bands in the visible. The anomalous rotatory dispersion detected is, therefore, of the type already observed for tartaric acid by Biot, and it is not caused by a Cotton effect in this spectral region. The red dithiourethanes, however, do show an absorption band at ~520 nm, and the rotatory dispersion features indeed result from a Cotton effect associated with this absorption.

It must be admitted that Tschugaev was only able to detect the first maximum of the ORD curve, because of the onset of high absorption near 450 nm precluding measurements of the short-wavelength part of the dispersion curve. Therefore, it might be considered stretching a point rather far to speak of his truly having detected Cotton effects, since this depends on quite some interpolation and interpretation. But his contention was much strengthened by G. Bruhat, to whom he had sent samples of both the *d*- and the *l*-bornyl dithiourethane mentioned above. Bruhat was able to measure the circular dichroism, both in toluene solution and in the melt [35, 64]. The CD maximum at 520–530 nm coincided with the absorption maximum at 520 nm. Bruhat could confirm, but not extend, Tschugaev's ORD data, by the way. This then not only proved that Tschugaev's interpretation of his rotatory dispersion curves had been correct, but also provided the first example of circular dichroism observed in a well-defined (organic) compound.

With Tschugaev's papers at hand, it is interesting to follow the progress of his search for a fitting technical term to describe what he initially calls an anomalous rotatory dispersion "in the sense of Cotton," until he finally in 1912 arrived at the "Cotton phenomenon." This then became the internationally accepted term to be used for two decades, until it lost ground against Lifschitz's "Cotton effect."

T. M. Lowry revisited Tschugaev's compounds in 1932, confirming the earlier data and extending the wavelength range of the observations, thanks to improvements in the optical instrumentation and the introduction of photography. He also performed calculations on a more advanced basis in order to analyze and simulate the data [65]. Now it had become possible to take photographic readings at many points of the wavelength scale down to 325 nm. Lowry not only supplemented and slightly extended Tschugaev's earlier ORD results, but now he could additionally make available circular dichroism data for the xanthates. These compounds, with a weak absorption at 360 nm (which Tschugaev had missed) and a strong one at 280 nm, exhibit a CD maximum at ~355 nm. The steep rise of the absorption toward shorter wavelengths still precluded the precise observation of the second ORD maximum at about 330 nm. It is notable that Lowry found his photographic CD measurements of the dithiourethanes in the year 1932 less exact than Bruhat's visual measurements of 1911.

Colored organic compounds were not unknown apart from the sulfur-containing derivatives discussed above, but were not easily available in optically active form. For chiroptical studies they should advantageously stem from the pool of optically active natural compounds or their derivatives, because the organic chemists of those days seem to have tended to avoid resolutions, contrary to their colleagues in the field of Werner complexes. Therefore, it is not surprising that the yellow camphor quinone attracted the attention of physical chemists and physicists alike. The Russian physicist Nina Wedeneewa detected in this compound a Cotton effect near 490 nm by ellipticity and rotatory dispersion measurements; although the work had been done in 1919, its publication was delayed until 1923 because of the political turmoil in Russia [20]. Her main interest was the analysis of the data in terms of the Drude theory of optical dispersion. Slightly later, in 1925, Israel Lifschitz also had tried to measure the optical rotation of camphor quinone near the absorption region, but could reach the first maximum only [53]. Lowry later repeated, confirmed, and extended Nina Wedeneewa's findings, thereby tacitly correcting the sign of her circular dichroism data, as he studied camphor quinone both in solution and in the vapor phase [66].

Also this second case, in which the circular dichroism of an organic molecule has been measured successfully, in addition to Tschugaev's/Bruhat's dithiourethane, stems from Russia. Unfortunately, the First World War, the Russian Revolution, and Tschugaev's premature death interrupted and eventually ended a period of intensive research on chiroptics in that country.

Intriguing colored organic compounds are the "nitrosites" (1,2-nitroso-nitrites) and "pseudo-nitrosites" (1,2-nitroso-nitro compounds), which can be made by the addition of (formally) N_2O_3 to olefins. These compounds exhibit green or blue colors in solution, provided that the nitroso group is monomeric. E. Deussen, working with the blue optically active caryophyllene nitrosite, had noticed an anomalous rotatory dispersion, minimalistically based on readings at just two wavelengths [67]. The suggestion by Tschugaev, that this might be caused by a Cotton effect in the visible [68], led Stotherd Mitchell in Glasgow in 1928 to check the chiroptical properties of this compound [69], but with readings taken at eight wavelengths between 691 and 436 nm. Indeed, a Cotton effect was found in the CD at ~680 nm. It might be remarked that the absorption curves were measured separately with right- and left-circularly polarized light, whereas in practically all earlier cases data on ellipticities had been collected.

In summary, the circular dichroism of only three (colored) organic compounds had become known by 1928. Although in some cases the claim has been put forward to have seen in such compounds a Cotton effect by rotatory dispersion, this should be taken with a grain of salt, because this cannot normally be substantiated by presenting the whole sigmoidal dispersion curve. Usually one wing of the curve is missing (commonly on the high-energy side of the absorption band), for reasons discussed above. It may come as a surprise, therefore, that as early as 1910, Eugène Darmois, one of Cotton's students, published the ORD Cotton effect of even a colorless organic compound, namely, camphor, at ~300 nm [70]. It is true that he had not been able to obtain rotation data at the absorption maximum itself, but only on either side of it (with a gap between 313 and 265 nm), but the dispersion curve can be easily completed by interpolation. This finding is all the more remarkable, because it demonstrated for the first time the possibility of taking rotation values down to ~250 nm in the ultraviolet. Regrettably, the response of the chemical community was slow, probably because of the technical difficulties involved in the construction of a suitable spectropolarimeter. It took some 20 years before Darmois's work could be taken up again; then, W. Kuhn published ORD, CD, and UV data of camphor, taken right through the absorption band [71], and T. M. Lowry likewise reported data of the related camphor-β-sulfonic acid [72].

It seems rather daring that Darmois [70] also tried to measure the chiroptical properties of olefins like α- and β-pinene or limonene, but—not unexpectedly—without much success. This chromophore still resisted the efforts of R. Servant in 1932, but at least this time some indication of a first ORD maximum seemed to be suggested at around 280 nm in the case of the pinenes [73].

From the foregoing it appears that rather suddenly, by around 1930, many more types of compounds were studied by chiroptical techniques. This resulted from the progress in instrumentation, to be related briefly in the next section. Now, a great many additional chromophores in colorless organic compounds, like nitro, azido, nitrito, and particularly carbonyl groups, opened the way for studies of the circular dichroism and the rotatory dispersion. Nevertheless, just a few typical samples were used to be investigated for physical–chemical purposes. It would take many more years before organic chemists made use of the now accessible optical techniques for stereochemical correlations and the determination of the absolute configuration. But this then is far outside the scope of this overview. These newer developments since the early 1930s will not be treated here, because many summaries are already available. The major source of information for the organic chemist on these later chiroptical investigations is Carl Djerassi's book [74], which has become a "classic" in the field to which the reader should turn.

1.9. ADVANCES IN INSTRUMENTATION AND THEORY; THE WAY INTO THE ULTRAVIOLET

Very briefly, the technical advances shall be sketched here that, around 1930, led to the (short-lived) upsurge in chiroptical activity mentioned in the foregoing section. Details shall be omitted, because comprehensive reviews are readily available. In addition to Lowry's encyclopedic monograph of 1935 [21] and Mitchell's book of 1933 [22], one should pay particular attention to Bruhat's 1930 treatise on polarimetry, since most of the "newer" development of spectropolarimeters and ellipsometers resulted from the efforts at his laboratory in Paris [75]. Another active center was at the Technische Hochschule (Institute of Technology) Karlsruhe, Germany, where the Swiss physical chemist Werner Kuhn not only worked on theoretical and experimental chiroptics, but also developed his own apparatus [76]. Relevant optical instruments have also been reviewed by R. Descamps in Brussels, Belgium, who had himself constructed and perfected a spectropolarimeter for the UV region [77]. Of course, Lowry's important contributions from his Laboratory of Physical Chemistry in the University of Cambridge, UK, are by no means to be forgotten.

Progress in instrumentation for chiroptical studies meant, besides the obvious improvement of sensitivity and reliability, by and large the extension of the wavelength range into the ultraviolet. It was evident that the absorption bands of the vast majority of chemical compounds are located in the UV. It may come as a surprise that polarimetric measurements in the ultraviolet have been known for a considerable time and can be traced back to the nineteenth century. Various instruments for this purpose are described by Lowry [21], but the operation of the apparatus was laborious, the accuracy of the results questionable, and the accessible wavelength range rather limited. It does not seem, moreover, that these techniques have been applied to the detection of Cotton effects before the exceptional pioneering work of E. Darmois in 1911 [70]. One of the earlier attempts at measuring optical rotations in the UV was by Lowry himself, who in 1908 combined a half-shadow polarimeter with a UV spectrograph [78].

Darmois could collect data to the wavelength limit of 250 nm. But in order to make this wavelength range more generally accessible, and even extend it toward higher energy, three different problems had to be solved: first, with regard to the light sources; second, with the transparency of optical components to the UV light; and third, in connection with the efficiency of detectors.

1. The solar spectrum provided light in the laboratory only down to the limit of 300 nm, because of atmospheric absorption. Mercury vapor lamps allowed readings to be taken for another 50 nm, down to 250 nm. Beyond that wavelength, various other light sources have been used, in all cases providing an array of separate spectral lines—for example, the iron arc to 233 nm, or the cadmium spark to 210 nm.
2. The transparency limits of glass preclude its use in UV instruments for lenses, prisms, or similar optical devices, except for the near-UV range. Materials like Iceland spar (cutoff at 250 nm), fluorspar, or quartz had to be introduced to improve the transmittance of UV radiation. Even the Canada balsam used in

conventional Nicol prisms had to be replaced by, for example, glycerol, in order to allow their utilization below 340 nm.

3. As to the detectors, the fluorescent screens of the early days were soon replaced by photographic implements, but the evaluation of the developed plates posed new problems in its own right.

The improvements in all these areas led to the independent construction of two similar recording spectropolarimeters in the year 1926, giving access to UV measurements up to the high energy limit of 250 nm [79]. An important objective in the construction of these instruments was the desire to hold to a minimum the number of optical parts that had to be transparent to UV light. In Cotton's photographic spectropolarimeter, the optical density of the photographs had to be evaluated by means of a photometer or, better, by a microphotometer. Although the recording was automatic, it was not continuous, but consisted of discrete exposures. Bruhat, on his part, used a photoelectric device. The data analysis could still be cumbersome, but the measurement of rotations in the UV had nevertheless become relatively easy. Bruhat's polarimeter was perfected still further [80], to the extent that the photoelectric measurements became superior in precision to those obtained by the photographic method applied by Servant [73].

All the instruments mentioned so far are polarimeters. Similar advances had taken place in the construction of ellipsometers. Again, Bruhat was in the forefront with the development of a polarimeter–ellipsometer [81]. This widely used visual instrument consisted of an ordinary polarimeter, fitted with a mica $\lambda/4$ plate. Werner Kuhn developed an even more advanced photographic device for use in the ultraviolet [82]. It contained optical parts of quartz and fluorite only, and it allowed measurements to be taken all the way to 190 nm. This apparatus was the preferred instrument for many years to come and was marketed by the well-known makers of optical instruments in Berlin, Schmidt & Haensch. A similar ellipsometer was described by Mathieu in Paris [83]; it was designed particularly for the wavelength range of 450–280 nm.

In conclusion, in the beginning of the 1930s, the development of instrumentation to measure the optical rotatory dispersion and the circular dichroism (in terms of ellipticities) had progressed to a state of perfection that was hard to improve upon in the decades to come. But, although it had been convincingly shown now that the Cotton effects of a wealth of optically active (organic) compounds were accessible, the chemical community at large was slow to make use of the chiroptical techniques. This resulted probably in part from the fact that the importance of stereochemistry had not yet been realized widely, especially among organic chemists. Also, the necessary apparatus still had to be built individually, and the measurement of ORD and CD was still far from being routine. Only with the advent of commercial recording instruments for ORD [84] and CD [85] many years later was the field of chiroptical investigations opened to the general chemist.

Very few sentences must suffice on the contemporary development of the theory of optical activity, because this topic lies far away from the present overview. Paul Drude's theory of optical activity in isotropic media, as expanded in his famous book of 1900 [26], has been the standard with which most physical(–chemical) research had to contend for the first three decades of the twentieth century. Many experimental investigations, including Lowry's, have been motivated by the search for an improved version of the "Drude equation" of optical activity. An important step forward in this line was taken by L. Natanson, who in the year 1909 succeeded in deriving an equation that could approximate the optical dispersion within the absorption band, a problem that Drude's original equation could not handle [17, 27, 28]. An advanced theory of optical activity was published by Max Born (1882–1970, Nobel Prize 1954) in 1915 [86] and at about the same time by C. W. Oseen [87] and F. Gray [88]. Although the importance of these papers, especially Born's, was immediately recognized, practically no direct influence on the study of chiroptical properties was engendered. Likewise, the important paper by the Belgian physicist Léon Rosenfeld (1904–1974) on the quantum-mechanical theory of optical activity did not affect the chemical community at the time [89]. It took Werner Kuhn's (1899–1963) simplification of Born's theory into his coupled-oscillator model to attract the chemists' attention [76, 90]. Now the application of theoretical methods to actual problems of stereochemistry seemed to become realistic. Even the determination of the absolute configuration of molecules might come into reach. Indeed, Kuhn's conclusion that (−)-butan-2-ol had the (*R*) configuration was the culminating point of his theoretical work [91]. A comprehensive overview of these developments in theory is found in Mathieu's monograph on the molecular theories of natural optical activity [92].

1.10. SOME WORDS ON NOMENCLATURE: COTTON EFFECT, OPTICAL ROTATORY DISPERSION, CD, ORD

The expression "Cotton effect" (originally in German) was introduced by Israel Lifschitz in 1922. The earlier technical term, first used by Tschugaev in 1912 (also originally in German), is "Cotton's phenomenon." This latter expression developed gradually by the contraction of phrases like "anomale Rotationsdispersion im Sinne A. Cottons" (anomalous rotation dispersion in the sense of A. Cotton) [93] or "la manière de voir de M. Cotton" (literally: Mr. Cotton's way of viewing) and "phénomène de la dispersion anormale" (phenomenon of anomalous dispersion) [94]. Tschugaev never used the word "Cotton effect" in whatever language. It is slightly confusing, therefore, to find this term in his Russian collected works [95], but on closer inspection this turns out to appear in a posthumous translation of his German papers into Russian. He himself always wrote in Russian "явление Коттона" (*i.e.*, Cotton's phenomenon).

As can be seen from Table 1.1, both expressions were used side by side for a period of 10 years, but eventually "Cotton effect" was victorious.

The situation is slightly simpler with "rotatory dispersion." From the beginning in 1877, this term had become established, with minor variations as shown in Table 1.2. The only point meriting some attention is the question, Why has rotatory dispersion nowadays become "*optical* rotatory dispersion"? The "optical" was originally added in order to differentiate between the two effects of magnetic and optical rotatory dispersion, both of which were the subject of a series of papers by Lowry, with the first one appearing in 1913. Usually, however, it was considered unnecessary to point to this difference, because magnetic rotatory dispersion rarely plays a role in chemistry. The modern habit of always referring to "optical rotatory dispersion", which also led to the common abbreviation "ORD," seems to originate with Carl Djerassi, who used it since 1955 in a great many papers and who publicized it further by his textbook on ORD.

The counterpart expression with respect to circular dichroism should be "*optical* circular dichroism," in order to likewise differentiate between optical and magnetic circular dichroism. Indeed, the French "fathers" of modern CD instruments and their application in chemistry have used the term "dichroïsme circulaire optique" [96], but for reasons unknown, in this case the chemical community has continued to ignore the "optical."

For the first half of the twentieth century, abbreviations were not much used in (physical) chemistry. With fashions changing, this became a craze, however, in the second half, especially in the United States and the Soviet Union. Typical is the general use

TABLE 1.1. The Change from Cotton's Phenomenon to the Cotton Effect

The Cotton Phenomenon		The Cotton Effect	
1912	L. Tschugaeff: Cottonsches Phänomen[a]		
1913	L. Tchougaeff: phénomène Cotton[b]		
1914	L. Tschugaeff: Cotton's phenomenon[c]		
	M. Delépine: les phénomènes découverts par M. Cotton[d]		
1915	H. Rupe: Cottonsches Phänomen[e]		
1922	H. Grossmann: Cotton-Phänomen[f]	1922	J. Lifschitz: Cottoneffekt[g]
1922 [1925]	F. M. Jaeger: phénomène de Cotton[h]	1922 [1925]	F. M. Jaeger: l'effet de M. Cotton[h]
		1923	F. M. Jaeger: l'effet Cotton[i]
1926	W. Pfleiderer: Cottonsches Phänomen[j]		
		1928	S. Mitchell: Cotton Effect[k]
		1929	W. Kuhn: COTTON-Effekt[l]
1930, 1933	T. M. Lowry: Cotton phenomenon[m]	1930	G. Bruhat: l'effet Cotton[n]
		1935	T. M. Lowry: Cotton Effect[o]

Cotton effect (Engl.); Cottoneffekt (German, Danish); effet Cotton (French); Effeto Cotton (Italian); Efekt Cottona (Polish); эффект Коттона (Russian)

[a] L. Tschugaeff, *J. Prakt. Chem*. **1912**, [2] *86*, 545–550; L. Tschugaeff, G. Glinin, *Ber. Dtsch. Chem. Ges*. **1912**, *45*, 2759–2764.

[b] L. Tchougaeff, A. Kirpitcheff, *Bull. Soc. Chim. Fr*. **1913**, [4] *13*, 796–803.

[c] L. Tschugaeff, *Trans. Faraday Soc*. **1914**, *10*, 70–79.

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[e] H. Rupe, Liebigs Ann. Chem. **1915**, *409*, 327–357.

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of "RD" in C. Djerassi's book published in 1960, incidentally one of the first major applications of this abbreviation. It is amusing to note that here "RD" still refers to "rotatory dispersion," of course, while the same author had already adopted "*optical* rotatory dispersion" for some years. It was consistent with adding "optical" to "rotatory dispersion," to also add the letter "O" to the abbreviation "RD": The birth of "ORD" took place in Djerassi's environment in the early 1960s.

TABLE 1.2. From Rotatory Dispersion to Optical Rotatory Dispersion

	Rotatory Dispersion, Dispersion Rotatoire, Rotationsdispersion
1877	H. Landolt[a]: (anomale) Rotationsdispersion [German]
1895	A. Cotton[b]: dispersion rotatoire (anomale) [French]
1908	H. Grossmann[c]: (anormale) Rotationsdispersion [German]
1911	L. Tschugaeff[d]: anomale Rotationsdispersion im Sinne A. Cottons [German]
	L. Tschugaeff[e]: dispersion rotatoire ano(r)male [French]
1913	T. M. Lowry[f]: rotatory dispersion [English]
1914	T. S. Patterson[g]: (normal/abnormal) rotation-dispersion [English]
1915	T. M. Lowry[h]: an exact definition of normal and anomalous rotatory dispersion
1917	F. M. Jaeger[i]: rotatie-dispersie [Dutch]
1935	T. M. Lowry[j]: (normal and anomalous) rotatory dispersion [English]
	Optical Rotatory Dispersion
1913	T. M. Lowry[k]: magnetic and optical rotatory dispersion [English]
1926	W. Pfleiderer[l]: optische/magnetische Rotationsdispersion [German]
1955	C. Djerassi[m]: Optical Rotatory Dispersion Studies [1st paper] [English]
1959	F. Woldbye[n]: optical rotatory dispersion [English]
1960	C. Djerassi: Optical Rotatory Dispersion, McGraw-Hill, New York [English]

[a] H. Landolt, *Liebigs Ann. Chem.* **1877**, *189*, 241–337 (p. 274).

[b] A. Cotton, *C. R. H. Acad. Sci.* **1895**, *120*, 989–991.

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The abbreviation "CD" for circular dichroism was introduced at about the same time. Whereas "OCD" has never become popular, "MCD" for magnetic circular dichroism is a logical and accepted abridgment. In the same vein, a reasonable abbreviation for magnetic rotatory dispersion should be "MRD". The misnomer "MORD" (which in German means "murder," by the way) should fall into disuse. Details concerning these various abbreviations are collected in Table 1.3.

It remains to remind the reader that the terms "rotatory dispersion" and "circular dichroism" as well as their abbreviations might change, if languages other than English are used. Some examples are collated in Table 1.4.

1.11. BIOGRAPHICAL NOTICES: G. BRUHAT, A. COTTON, W. KUHN, I. LIFSCHITZ, T. M. LOWRY, L. NATANSON, AND L. TSCHUGAEV

It is a moot question how far a treatise on the history of natural sciences ought to be supplemented by a personalized account. It is the present author's contention that such an approach is helpful to provide a balanced background for the scientific results

TABLE 1.3. From RD to ORD (but not from CD to OCD)

1960	C. Djerassi,[a] *Optical Rotatory Dispersion*: "abbreviated **RD** (curves)"
1960	W. Klyne, *Adv. Org. Chem. 1*, 239–348: "abbreviated **R.D**. curves"
1965	P. Crabbé,[b] *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*: "circular dichroism, abbreviated **CD**; rotatory dispersion curves, abbreviated **RD**"
1965	L. Velluz, M. Legrand, M. Grosjean,[c] *Optical Circular Dichroism*: "**CD**-curves"
1963	D. Lightner,[d] *PhD Thesis*: **ORD**
1966	K. Mislow,[e] *Introduction to Stereochemistry*: **ORD, CD** [preface September 1964, © 1965, published 1966]
1967	G. Snatzke,[f] ed., *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* [Summer School, Bonn, 24 September–1 Oct., 1965]: **ORD, CD**; "**MORD**", **MCD**
1972	P. Crabbé[g], **ORD** *and* **CD** *in Chemistry and Biochemistry*

[a] McGraw-Hill, New York.
[b] Holden-Day, San Francisco.
[c] Verlag Chemie, Weinheim/Academic Press, New York.
[d] Stanford, CA.
[e] W. A. Benjamin, New York.
[f] Heyden & Son, London.
[g] Academic Press, New York.

TABLE 1.4. 'CD'' and ''ORD'' [and ''CE''] in English, French, German, and Russian

CD	circular dichroism, Circulardichroismus	DC	dichroïsme circulaire
RD	rotatory dispersion, Rotationsdispersion	DR	dispersion rotatoire
ORD	optical rotatory dispersion, optische Rotationsdispersion	DRO	dispersion rotatoire optique
КД	Круговой дихроизм	ДОВ	Дисперсия оптического вращения
[CE	Cotton effect, Cotton-Effekt]	[EC	effet Cotton]

discussed in the foregoing sections. After all, the common expression "it was found that" is deceptive insofar as it tends to obscure the fact that these results were not "found" by anonymous agencies, but earned by individual scientists, working at a specific time and under specific circumstances that pertain to both their professional and their private lives.

Among the many actors in the first decades after the discovery of the Cotton effect, who could be considered for some biographical notices, here seven scientists are selected, as listed in the section title in alphabetical order. These names may reflect some personal predilection, but it is not too difficult to defend these choices impartially: Cotton is, of course, of outstanding importance. Natanson opened the route to an understanding of the interconnection of CD, ORD, and absorption generally. Tschugaev pioneered the investigation of chiroptical properties of organic molecules, while Lifschitz did the same with coordination compounds and has, moreover, coined the technical term "Cotton effect." Bruhat was of particular importance for the development of instruments for chiroptical studies, together with Lowry and Kuhn, while the two latter scientists (both of them chemists, by the way) were instrumental also for the progress in the application of the theory of optical activity to chemical problems. All of these persons earned universal recognition, and even fame, also in other fields of chemistry or physics. All of them would merit attention, even if their part in the progress of chiroptics were to be neglected. Actually, for some among them, their activity in this field was rather incidental, if seen against their lifetime achievements. In the following, summary biographies of these scholars will be related in sequence according to their date of birth, with Cotton's biography at the end, however.

The theoretical physicist **Ladisla(u)s [Władysław] Natanson** (1864–1937) was born in Warszawa (Warsaw), Poland, the son of a medical doctor. Warsaw was under Russian rule at the time, and Natanson was a Russian subject. After graduation from a classical school in 1882, he enrolled as a student at the Faculty of Sciences of the University of St. Petersburg, where he became a "*Candidate*" (Licentiate) in 1886. After a few months at the Cavendish Laboratory at Cambridge, U.K., he returned to Imperial Russia in order to fulfil the requirements necessary for Russian subjects who wanted to embark on an academic career. Therefore, in 1887 he moved to Dorpat, Livonia (now Tartu, Estonia), to work for his doctorate with the physicist Professor A. von Oettingen, which he obtained in 1888. Incidentally, the official language at the University of Dorpat was German. After some postdoctoral studies with L. Boltzmann at the University of Graz, Austria, he returned to Warsaw to write an "Introduction to Theoretical Physics" [97]. This book was met with much acclaim, which helped him to be granted a position at the Jagiellonian University Kraków (Cracow), Poland (then under Austrian rule). There he moved up through the academic ranks: 1894 Titular Professor, 1899 Extraordinary Professor, and finally 1902 Professor of Theoretical Physics. Later he was also appointed Dean of the Faculty, and in 1922/23 he became Rector of the University. Elected to the Academy of Sciences in 1893, he became President of the Section of Mathematical and Natural Sciences in 1926, until he resigned from both the Academy and the University in 1935 for health reasons. His professional achievements are expanded upon in the obituary notice by Léon Klecki, which includes a bibliography [98].

The chemist **Lev Aleksandrovi(ts)ch Tschugaev (Chugaev)** (1873–1922) was born in Moscow, Russia. After completing his studies at the University of Moscow in 1894, he became Assistant at the Bacteriological Institute of the University, where he started his research on the optical activity of organic compounds. From the beginning, Tschugaev strove to be competent in organic as well as inorganic chemistry. His master's thesis in 1903 dealt with studies in the terpene and camphor series, while in his doctoral thesis (habilitation) of 1906 he presented results from coordination chemistry. Throughout his life, he successfully followed this dichotomy in his research, with some excursions into physical chemistry. In 1906 he was appointed Professor at the Technical University in Moscow, and in 1908 he was called to the Chair of Inorganic Chemistry at the Imperial University of St. Petersburg (later: University of Petrograd). He held this position at the time of his death. During World War I and the Russian Revolution he was mainly active in the field of technical and applied chemistry. He was one of the founders of the Institute of Applied Chemistry in Petrograd and became its director. In the aftermath of the revolution, he died of typhoid fever at Wologda, Russia, at the age of not yet 50. Obituary notices have appeared in England [62] and in Germany [99], acknowledging his abundant contributions to chemistry. Attention should also be paid to his "Selected Works" [95].

The physical chemist **Thomas Martin Lowry** (1874–1936) was born at Low Moor, Bradford, Yorks., U.K., the son of a Wesleyan Chaplain. He studied at the Central Technical College, South Kensington, London. From 1896 to 1913 he was assistant to Professor

H. E. Armstrong and from 1904–1913 he was Lecturer in Chemistry at the Westminster Training College. In 1913 he became Head of the Chemical Department in Guy's Hospital Medical School and Professor of the University of London. In 1920, finally, he was appointed to the newly created Chair of Physical Chemistry at Cambridge University. He continued at Cambridge for the rest of his life. In his extensive obituary notice, W. J. Pope wrote [100]: "[The book] on "Optical Rotatory Power" was issued in 1935 and will long remain a standard work on the subject. The immense amount of accurate experimental work which Lowry has left on record secures him a permanent place in the history of the science to which he was devoted." But, although chiroptical methods are central to this overview, Lowry's important contributions to other areas should not be forgotten. Mention may be made of his studies of the polymorphism of inorganic salts, his "Studies of Valency" and of the nitrogen oxide/water system, the nature of the sulfur halides, and the stereochemistry of tellurium compounds. In all cases he tried to apply modern physical concepts to chemical problems. Lowry was a member of the Faraday Society from its beginnings in 1903 and acted as its president in 1928–1930. He became a Fellow of the Royal Society in 1914.

The physicist **Georges Bruhat** (1887–1945) was born in Besançon, France, the son of a civil servant. He was admitted with honors into the renowned École Normale Supérieure (ENS) in Paris in 1906. After having obtained his B.Sc. ("*licence ès sciences physiques*") at the University of Paris, he acquired the qualification to teach at secondary schools (as "*Professeur agrégé*") and taught at a high school in Paris for one year. Perhaps this interval in his scientific career awakened his interest in teaching and in writing textbooks for this purpose. He then got a position as laboratory assistant ("*préparateur*") at the ENS, which enabled him to work under the guidance of A. Cotton on his doctoral dissertation: "*La dispersion anormale du pouvoir rotatoire moléculaire*" (the anomalous dispersion of the molecular rotatory power). After an interruption by his military service during the First World War, he could continue his academic career in 1919 in Lille, France, where he was Professor of General Physics from 1921 to 1927. His successor was Marcel Pauthenier, by the way, who had been his partner in the construction of UV spectropolarimeters [79]. Bruhat returned to the University of Paris in 1929 as Lecturer and Professor Extraordinary. In 1938 he was promoted to the Chair of Theoretical and Celestial Physics. During this time he published four compendious textbooks on general physics: *Electricity* (1924), *Thermodynamics* (1926), *Optics* (1930), and *Mechanics* (1934). These books have become standard texts in French universities, with many editions; *Optics*, for example, has been reedited as recently as 2004. Bruhat also continued his association with the ENS, serving as "Sub-Director" from 1935, and as acting director during World War II. In the beginning of August 1944, he was arrested by the political police ("Gestapo") of the German occupation powers and held prisoner in lieu of a student accused of activities in the French Resistance Movement. He was taken to Germany into a concentration camp and died there on January 1, 1945, of pneumonia and exhaustion.

The chemist **Israel Lifschitz** (1888–1951) was born in Shklov, Russia (now Belarus) (see Figure 1.4). His family was German and lived in Leipzig, Germany. His mother had moved to Shklov just for her confinement, motivated by family regards. He studied chemistry at the University of Leipzig and worked there for his doctoral degree under the guidance of A. Hantzsch. His dissertation of 1911 dealt with the spectroscopic properties of various organic nitrogen compounds. Faithful to the ideas already developed in this dissertation, his main interest became the correlation of chemical constitution and bonding with electronic absorption. Although by training he was an organic chemist, his research

Figure 1.4. Israel Lifschitz. (Photograph provided by Ms. E. H. Lifschitz, Haifa, and reproduced with her permission.)

led him far into physical chemistry and, later, also inorganic chemistry. Leaving Leipzig in 1911, he moved to the University of Zurich, Switzerland, for his habilitation. To this end, he submitted a second dissertation on the changes of light absorption by organic acids on salt formation. As a result, the title of "Private Docent of Chemistry" was conferred on him in 1914, allowing him to do independent research, but not connected with any paid position. The life of a Private Docent was difficult, unless one was privately affluent. The economic troubles after World War I also forced Lifschitz to interrupt his work at the university in 1920, in order to look for a source of income outside of Academia, to support his growing family.

Lifschitz extended his investigations to include the optical rotatory dispersion of transition metal coordination compounds (see, *e.g.*, paper V of a series on the function of chromophores [101]); after 1920 this became his central area of research. From these papers it can be deduced that he had established a cooperative arrangement with the Dutch inorganic stereochemist F. M. Jaeger at the Rijksuniversiteit Groningen (RUG) in the Netherlands, by 1919 at the latest. Jaeger invited Lifschitz to join his laboratory and offered him a tenured staff position as "*Conservator*". This induced Lifschitz to move to Groningen, although he had become a Swiss citizen and probably had intended to stay in that country. As a result, in the summer of 1921, Lifschitz became Private Docent of Electrochemistry and Photochemistry, as well as Conservator at the Laboratory of Inorganic and Physical Chemistry at RUG. He helped to develop the department into a center of chiroptical spectroscopy. RUG became the birthplace of the "Cotton effect," since Lifschitz coined this technical term there. The relevance of his research was readily acknowledged by stereochemists and physical chemists at other institutions. Already in 1935, J.-P. Mathieu in Paris had pointed out that Lifschitz was the first to systematically investigate the relations between the experimental data on the Cotton effect and the chemical bonds in optically active compounds [83].

Lifschitz held his position at RUG until he was dismissed in November 1940 for political reasons. Under the German occupation of the Netherlands in World War II, the situation of Jewish people deteriorated continually. Since Lifschitz was unable to continue his research at RUG, he turned again to his private studies of the mystical movements in Judaism, of which he was a dedicated and competent scholar. He was a deeply religious person, who had also published on related subjects. Now he became absorbed again in his studies of Chassidism, and he gave even private lessons on the Zohar. All this ended, when he, his wife, and their five children were detained in February 1943. He was eventually deported to the Theresienstadt Concentration Camp in Bohemia in September 1944, separated from his three sons, two of whom did not survive the ordeal. Liberated at the end of the war, he, his wife, and the three children left returned to Groningen, where he was reinstalled at RUG. He died in the Netherlands in 1953 and was buried in Haifa, Israel. The dire story of the family's fate has been reported by his elder daughter Esther Hadassa Lifschitz [102]. It had proved to be fatal that the Dutch authorities had insisted, shortly before the war, that the family accept Dutch citizenship while relinquishing their Swiss citizenship. An attempt to regain Swiss nationality during World War II failed. It is likely that they could have otherwise left for Switzerland. The present paper may perhaps draw some attention to Lifschitz, who has been undeservedly forgotten.

The physical chemist **Werner Kuhn** (1899–1963) was born at Maur am Greifensee, Switzerland, the son of a pastor. He studied chemistry at the ETH Zürich and obtained his doctorate at the University of Zurich in 1923, with a dissertation on a photochemical topic. After working with Niels Bohr in Copenhagen, Denmark, for two years, he returned to Zurich for his habilitation in physical chemistry in 1927. He moved to Germany thereafter. For three years he worked at the University of Heidelberg, where he started his research on optical activity; in 1930–1936 he worked at the Technische Hochschule Karlsruhe, and in 1936 he occupied the Chair of Physical Chemistry at the University of Kiel. In the year 1939 he returned to his home country, when he was called to the Chair of Physical Chemistry at the University of Basel. Later he was also elected rector of the University. He remained there until the end of his life. A report on "*Leben und Werk von Werner Kuhn*" (life and work of W. K.), including a bibliography, appeared in 1984 in connection with a "Werner Kuhn Symposium" of the Swiss Chemical Society [103].

The physicist **Aimé Auguste Cotton** (1869–1951) was born in the French provincial town of Bourg-en-Bresse, where his father taught mathematics (see Figure 1.5). He was a student of physics at the École Normale Supérieure (ENS) in Paris from 1890 to 1893. He completed his doctoral studies, in the course of which he discovered the "Cotton effect" at the Laboratory of Physics with M. Brillouin and J. Violle and earned the title "*Docteur ès-sciences physiques*" in 1896. It is noteworthy that he included in his thesis his first attempts at measuring magnetic optical activity, since his future scientific career was to be centered on the physics of magnetism and magneto-optics. It would be in these fields, rather than in research on natural optical activity, that he would rise to eminence.

Figure 1.5. Aimé Auguste Cotton. (From L. de Broglie, *Notice sur la vie et l'œvre de Aimé Cotton*, Académie des sciences—Institut de France, Paris, 1953; reproduced with permission.)

After a few years at the Faculty of Sciences of the University of Toulouse as Assistant/Associate Professor (*Maître de Conférences, Professeur adjoint*), he returned to the ENS in Paris, entrusted with the substitution of the Academician J. Violle, his teacher, for the period of 1900–1904. From 1904 to 1922 he served as Lecturer (*Chargé de cours*) at the Faculty of Sciences of the University of Paris, delegated to the ENS. He was promoted to Professeur-adjoint in 1910 and became Professor of Theoretical and Celestial Physics at the Sorbonne in 1920. Finally, he was called to the Chair of General Physics there in 1922, succeeding G. Lippmann (Nobel Prize 1908). In 1923 he was elected a member of the illustrious Academy of Sciences as successor to J. Violle. He even became President of the Academy in 1938. Cotton retired from the Sorbonne in 1941, but continued until his death as Director of the Laboratory for Magneto-Optical Studies that he had founded in 1927.

In France, A. Cotton is considered to be one of the eminent physicists of the twentieth century. He himself described his scientific aims and accomplishments in a 1923 pamphlet on the occasion of his election to the Academy [104]. As he pointed out, he had worked extensively on the Zeeman effect, but even more on the magneto-optical properties of colloids and molecular solutions. Many of the latter investigations were performed in cooperation with the biologist Henri Mouton (1869–1935) of the Institute Pasteur (later Professor of Physical Chemistry at the University of Paris). Together they discovered in 1907 the important "Cotton-Mouton-Effect" (magnetic field induced linear birefringence) [105]. Cotton's fame in physics rests, arguably, more on this discovery than on the "Cotton effect" in natural optical activity.

Detailed information on his life and work is easily available thanks to various obituaries [106] and to a notice published on the occasion of the centenary of his birth [107].

Cotton received many honors and was awarded many prizes. He was nominated for the Physics Nobel Prize in the years 1915, 1916, 1920, 1922, 1925, 1927, 1928, 1929, 1930, 1931, 1932, 1933, 1934, 1944, and 1949, but without success [108]. His memory is kept alive in France with the "Laboratoire Aimé Cotton," as his former Laboratory for Magneto-Optical Studies has been renamed. It is now the Atomic and Molecular Physics Laboratory of CNRS, associated with the University Paris XI and situated on its campus in Orsay. Also the "Prix Aimé Cotton" should be mentioned, which was established by the French Physical Society in 1953 in memory of A. Cotton and is awarded annually. In what esteem he is held by the French physicists is also apparent by the fact that he is one of the twelve "most eminent" physicists chosen by the Academy on the occasion of the World Year of Physics 2005 (WYP2005/UNESCO).

Among chemists of countries other than France, and especially among the younger fold, the name "Cotton" rarely brings to their minds memories of a specific person, unfortunately, unless they mistake it for the name of the distinguished American inorganic chemist A. Albert Cotton (1930–2007) of textbook fame. However, whether they know anything about the person or not, for the chemists working in chiroptics or stereochemistry, T. M. Lowry's words of 1935 still hold true [21]:

> Cotton's discovery in absorbing optically-active media of the twin phenomena of circular dichroism and of anomalous rotatory dispersion, which are indissolubly associated with his name, is [. . .] amongst the "classics."

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