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Part I

Instruments, Messengers, and Cosmic Messages

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1

Instruments, Messengers, Astrophysics, and Cosmochemistry

Well before the start of the twentieth century two major classes of instruments revolutionized our understanding of the Universe – the telescope and the spectroscope. A third, the photographic plate, the first means to establish a permanent record which any astronomer could independently examine, became fully embraced only as the twentieth century was about to dawn.

Historians have long celebrated Galileo's contributions to science through his introduction of the improved telescopes he constructed to study the Moon, the planets, and the stars. The revolution introduced by the spectrometer has not been publicized as widely but was of comparable significance. It led to the startling realization that many of the chemical elements that abound on Earth also exist in the outer layers of the Sun and stars.[2] [a; b]

1.1 Fraunhofer's Prisms

To understand the origins of astronomical spectroscopy we need to recall the craftsmanship of Joseph Fraunhofer. In 1815 this 28-year-old, largely self-taught optician was trying to perfect an achromatic lens – a lens to sharply

[a] This chapter could not have been written without extensive reference, throughout, to Klaus Hübner's insightful biography *Gustav Robert Kirchhoff: Das Gewöhnliche Leben eines außergewöhnlichen Mannes*, loosely translated as "Gustav Robert Kirchhoff: the ordinary life of an extraordinary man." Surprisingly, as Hübner himself points out, no other comparably complete biography of Kirchhoff surfaced until Hübner's own work appeared in 2010, 123 years after Kirchhoff's death in 1887.[1]

[b] Translations of German passages appearing as footnotes in this chapter are my own (MH).

Fig. 1.1 Portrait of Joseph Fraunhofer. (From Deutsches Museum München: Bild-Nr. 43952, with permission of the Deutsches Museum.)

focus all colors of light onto a single point. This wasn't easy, but for Fraunhofer nothing had ever been.

Born on March 6, 1787, and orphaned at age 11 with no means of support, the young Joseph was bonded through a six-year apprenticeship to a Munich glass grinder and mirror maker. Denied further schooling he remained weak in writing and arithmetic. In 1801, the second year of his apprenticeship, two houses in Munich suddenly collapsed. After four hours of strenuous efforts, Joseph was pulled out of the rubble as sole survivor. The Crown Prince of Bavaria, Maximilian Joseph, who had come to inspect the disaster was impressed by the youngster's intelligence and awarded him 18 Dukats, also promising him further support if needed.

This gesture enabled Fraunhofer to extricate himself from bondage, acquire his own glass grinding and polishing machinery, and buy several books to make up for lost schooling.

Years later, at a newly established institute for mathematical optics in Bavaria, Fraunhofer, shown in Figure 1.1, realized his most ambitious optical achievements, among them the design and construction of achromats fabricated from two mutually compensating types of glass, neither of which by itself could bring all the colors of light to a single focus.[3]

While testing one of these achromats, he hit on the idea of first testing its performance in several narrower monochromatic ranges. To obtain sufficiently bright beams Fraunhofer used sunlight and a prism to isolate the various colors the Sun emits. On closer examination he was surprised to discover that sunlight, ranging from blue at one end of the spectrum to red at the other, was interrupted by hundreds of narrow dark streaks interspersed along his prism's display.[4]

He carefully mapped 324 of these streaks, designating the most prominent among them by the letters of the alphabet by which we still know them today.[5] The dark streak designated D was double. He found it present not only in the spectrum of the Sun, but also in the spectra of the stars Betelgeuse, Capella, Pollux, and Procyon; and its position in the Sun's spectrum coincided precisely with that of a bright yellow feature he had already identified in the light emitted by terrestrial flames.[6]

There, Fraunhofer needed to cease this pursuit and return to his primary goal of designing and fabricating superior achromats. He wrote:

> In these experiments lack of time permitted me to consider solely matters of optical consequence, leaving the rest untouched or insufficiently pursued. Since the path set by these physical-optical experiments appears to promise interesting results, it would be highly desirable for trained scientists to award them attention.[7] [c]

Fraunhofer's contemporaries did not follow this advice. Prisms had long been known to divide light into the colors of the rainbow but appeared to serve no other recognized purposes.

Fraunhofer died in 1826 at age 39. Thirty-three years would have to pass before his efforts once again bore fruit.

1.2 Bunsen's Burner and Kirchhoff's Spectroscope

In the fall of 1859, two colleagues at the University of Heidelberg, the 48-year-old professor of chemistry Robert Wilhelm Bunsen, and his younger colleague, the 35-year-old professor of physics Gustav Robert Kirchhoff, both shown in Figure 1.4, embarked on a collaboration that was to change forever our understanding of the chemical composition and elemental transformation of the Universe![8]

[c] Bei allen meinen Versuchen durfte ich, aus Mangel der Zeit, hauptsächlich nur auf das Rücksicht nehmen, was auf praktische Optik Bezug zu haben schien, und das übrige entweder gar nicht berühren oder nicht weit verfolgen. Da der hier mit physisch-optischen Versuchen eingeschlagene Weg zu interessanten Resultaten führen zu können scheint, so wäre sehr zu wünschen daß ihm geübte Naturforscher Aufmerksamkeit schenken möchten.

Four years earlier, Bunsen had invented a burner that now bears his name. It burnt an adjustable mix of air and lighting gas – a mixture of methane, hydrogen, and carbon monoxide extracted from coal.

Bunsen found that, by throttling back the air fed to the burner, he could obtain a low-luminosity flame that exhibited strikingly bright colors when heating the salts of different metals. He wondered whether the colors of these flames, by themselves, might reliably identify the chemical composition of the various salts he was heating. Although his attempts were partly successful, the bright yellow emission of sodium present even in the slightest traces of airborne dust was a major nuisance. Seeking to eliminate this shortcoming, Bunsen considered various ways to filter out the yellow sodium light.

That same year, 1859, Kirchhoff had just constructed a spectroscope for determining the refractive indices of the birefringent crystal aragonite.[9] To help out Bunsen, he used this apparatus to examine substances that strongly absorbed yellow light. Two possibilities appeared suitable. Both cobalt glass and the dye indigo proved opaque to sodium's yellow flame emission and transmitted light at both shorter and longer wavelengths.

Using these findings, Bunsen was able to enhance his method of chemical analysis by flame color, by viewing the flames through a glass-walled prism filled with indigo dye. With this he could filter out sodium's yellow emission by viewing a flame through shorter or longer light paths through the prism, depending on the strength of the yellow emission he needed to suppress. Bunsen published these findings in September 1859.[10]

As Bunsen later recalled, he and Kirchhoff were discussing their respective findings, that September, when Kirchhoff proposed that Bunsen's chemical analyses by color might prove more incisive if he were to obtain the flames' spectra rather than merely their color judged by eye. He thought it would not take too much added effort to modify the spectroscope with which he had been studying the refraction of aragonite: To denote the wavelengths at which he was conducting his measurements Kirchhoff had been passing sunlight through the crystal, using Fraunhofer's dark sunlight features as fiducial wavelength markers.

The two friends agreed to give this method a try.[11]

1.3 Curiosity's Drive

Later, Kirchhoff would write a colleague, "The apparatus we used was assembled in haste from parts, a majority of which we already possessed; it is thence incomplete in some aspects."[12] [d]

[d] "Der von uns benutzte Apparat ist in aller Eile aus Theilen, die wir zum größten Theile besaßen, zusammengesetzt; er ist daher in mancher Beziehung unvollkommen."

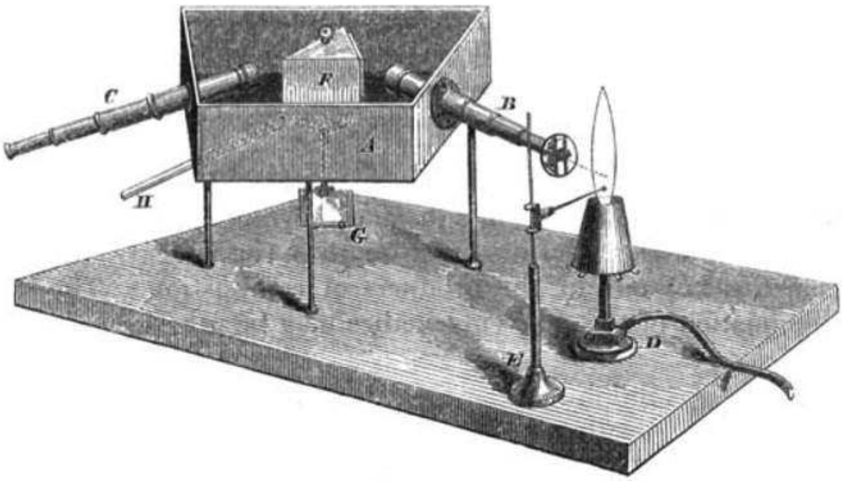

Fig. 1.2 Woodcut of the Spectroscopic Apparatus of Gustav Kirchhoff and Robert Bunsen. A trapezoidal box A, blackened on the inside, houses a prism F. Mounted on the sides of the box are two small telescopes B and C. The ocular lenses of telescope B have been removed and replaced by a plate in which a slit formed by two knife edges is placed in the focal plane of the telescope's objective. The flame of Bunsen's burner D is aligned with the axis of telescope B. The end of a fine platinum wire supported by a small stand E is bent into a hook and placed near the bottom of the flame. On this hook is a melted globule of metal chloride to be inserted in the flame. Between the objective lenses of B and C, a hollow prism F, having a refracting angle of 60°, is filled with carbon disulfide. The prism can be rotated about a vertical axle carrying a mirror G, above which a handle H simultaneously turns both the prism and the mirror. A small auxiliary telescope, not shown but placed at some distance, views the mirror and, through it, the reflection of a horizontal scale indicating the prism's rotational angle. The telescope C has a fine vertical wire, the wavelength of light falling on which is indicated by the scale viewed by the auxiliary telescope. A small light placed near the wire can illuminate it to make it more visible. (This figure was published in the *Philosophical Magazine* series 4, 20, 88–109, August 1860 with an English translation of Kirchhoff and Bunsen's original paper. The figure caption presented here is somewhat shorter than that reproduced in the translated article.)

Complete or not, the insights Kirchhoff and Bunsen gained by means of this apparatus shown in Figure 1.2 were momentous!

Whereas before 1859 nothing was known about the composition of the Sun or the myriad stars populating the Galaxy, a year later in 1860 it was clear that the Sun, and most likely also the stars, contained many if not all of the same elements known on Earth – and possibly consisted entirely of these elements. The way to find out was now open!

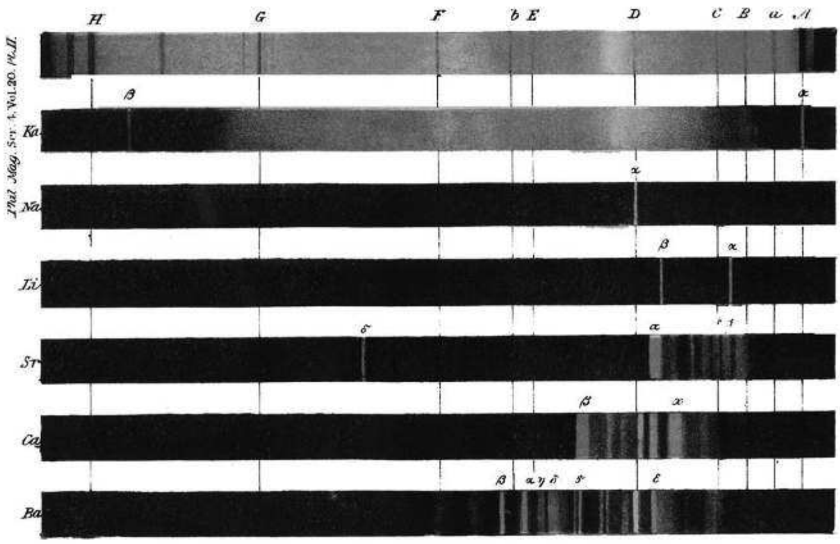

Fig. 1.3 This set of spectra of different elements purified in the laboratory, with their wavelengths calibrated against the Solar spectrum shown at top, was published in the English translation of Kirchhoff and Bunsen's original paper by Henry Enfield Roscoe. At the time the authors identified potassium by the letters *Ka* for *Kalium*, at left, in place of today's accepted abbreviation *K*. The laboratory emission lines for potassium and sodium clearly match the corresponding absorption lines marked *A* and *D* in the Sun. For the remaining elements the correspondences are not as apparent in this reproduction; but the distinct spectrum of every highly purified element does appear to uniquely identify each. (This plate was reproduced in the *Philosophical Magazine* series 4, 20, 88–109, August 1860.)

Kirchhoff and Bunsen first wanted to make sure that the characterizing flame spectra their alkali salts emitted when heated in their flames were due entirely to the alkali component of the salt, and remained constant, whether the alkali salt in question happened to be a chloride, bromide, nitrate, sulfate, etc. After exhaustive tests of hundreds of such highly purified salts, they found each alkali salt's flame spectrum to invariably emit the alkali's characteristic spectrum regardless of the salt the alkali had formed. This assured them that the salts of sodium, potassium, lithium, etc. in their laboratory spectra also implied the existence of these same sodium, potassium, lithium, etc. metals in the Sun.[13] In a second paper, published a year later, Kirchhoff and Bunsen conjectured that this unique spectral identification of the alkali metals their salts contained might be that, at the extreme temperatures of their flames, the salts dissociated to expose the free alkalis.[14]

Although Bunsen and Kirchhoff often mentioned the possibility of determining the chemical composition of the stars by these means, neither of them ever undertook these astronomical measurements.

For another year, Kirchhoff continued his studies of the Solar spectrum and the physical identification of many of its spectral features. The prolonged exposure to the bright sunlight entering his spectroscope's slits began taking its toll on his eyes. To save his eyesight, he eventually abandoned this line of research altogether. With the significance of Kirchhoff and Bunsen's work quickly sinking in, a number of other astronomers began to follow their lead. By 1864, Lewis Morris Rutherford in the United States, Angelo Secchi in Italy, and William Huggins and William Allen Miller in England, respectively, had published their observations on the spectra of Jupiter, Mars, the Moon, and various stars.[15]

1.4 The Discovery of Two New Chemical Elements

In the meantime, Kirchhoff and Bunsen began to concentrate on even more challenging matters. The first was a physical explanation for a ubiquitous reversal of the spectral emission features they found in their laboratory flames into corresponding absorption features in the Sun's spectrum. The second was the discovery and identification of two previously unknown chemical elements giving rise to absorption features they had detected in their spectra of the Sun and in faint emission features they had occasionally encountered in laboratory flames.

To this end, it is worth identifying the distinct roles that Kirchhoff and Bunsen played in reaching their conclusions about the chemical composition of the Sun. On November 13, 1859, Bunsen wrote Henry Roscoe, shown with Kirchhoff and Bunsen in Figure 1.4:

> At the moment I and Kirchhoff are collaborating on work leaving us sleepless. Kirchhoff has made a beautiful, totally unexpected discovery, in determining the origin of the dark lines in the Solar spectrum, and in artificially amplifying these in line-less flame spectra, specifically at the identical position as the Fraunhofer lines. Thereby the way is now clear for determining the chemical composition of the Sun and stars with the same assurance as we can determine strontium chloride, etc., in our chemical reagents. On Earth one can differentiate by this method between materials with the same assurance as on the Sun … If you have a mix of lithium, potassium, sodium, barium, strontium, calcium, you need only to bring a milligram of this into our apparatus in order to immediately read off all these constituents simply by observing them through a telescope.[16] [e]

[e] Im Augenblick bin ich und Kirchhoff mit einer gemeinschaftlichen Arbeit beschäftigt, die us nicht schlafen läßt. Kirchhoff hat nämlich eine wunderschöne, unerwartete Entdeckung gemacht, indem er die Ursache der dunklen Linien im Sonnenspektrum

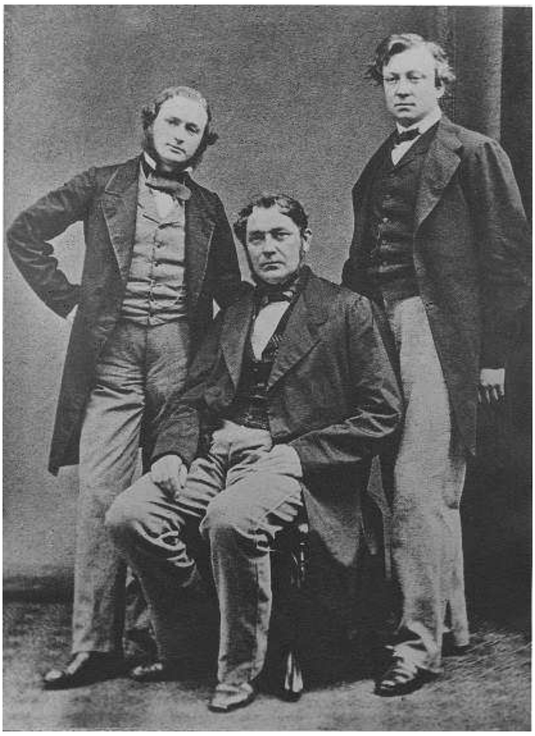

Fig. 1.4 Photograph of Gustav Robert Kirchhoff at left and Robert Wilhelm Bunsen seated, taken during a joint visit to England in 1862. Their host, Henry Enfield Roscoe at right, a former student of Bunsen and by then professor of chemistry at Owens College in Manchester, had regularly spent his summers in Heidelberg working with Bunsen. By March 1861 Roscoe had lectured on the work of Kirchhoff and Bunsen at the Royal Society in London, and was working on an English translation of their entire first paper on chemical spectroscopy and the nature of the Solar atmosphere, later published in the *Philosophical Magazine*. Through the near-simultaneous publication of their series of papers, in Germany as well as in England, Kirchhoff and Bunsen's astounding spectroscopic work found rapid and enthusiastic reception throughout science. (This photograph taken in1862 is reproduced here with the kind permission of the Heidelberg University Archives, where it is identified by shelf-mark: Universitätsarchiv Heidelberg, BA Pos I 388.)

Bunsen's words "read off" indicate that he and Kirchhoff already were audaciously interpreting the Solar spectrum's dark Fraunhofer features as a

aufgefunden und diese Linien künstlich im Sonnenspektrum ferstärkt und in Linienlosen Flammenspektren hervorgebracht hat, und zwar der Lage nach mit den Fraunhoferschen identische Linien. Dadurch ist der Weg gegeben, die stoffliche Zusammensetzung der Sonne und der Fixsterne mit der selben Sicherheit