

# Spectroscopy

An Introduction to the Theoretical  
and Experimental Fundamentals

## 1 Introduction

In the year 1666 at Cambridge, Isaac Newton procured a triangular glass prism and let a ray of sunlight from a small round hole in the window illuminate it. He observed the image created thereby on a paper screen. The white light from the window dissociated into red, yellow, green, blue, and violet. He called the invisible colors in the white sunlight the “spectrum” (lat *spectrum* = image in the soul) [1]. It was at the end of the 19<sup>th</sup> century that the observation of spectra was first christened “Spectroscopy”. This word has both a Latin and Greek root (Greek *skopein* = to look). Arthur Schuster first used the term *spectroscopy* in 1882 during a lecture at the Royal Institution [2].



Newton led the way from speculation to spectral analysis by making exact measurement and having clear insights. The oldest observation of nature dealing with the properties of invisible light comes to us from the Roman scholar and philosopher Titus Carus Lucretius. Infrared spectroscopists therefore consider him to be their intellectual father. Around 60 B.C. he hypothesized the existence of infrared radiation: [3]: »Forsitan et rosea sol alte lampade lucens possideat multum caecis fervoribus ignem circum se, nullo qui sit fulgore notatus, aestifer ut tantum radorum exaugeat ictum.« (original Latin) or freely translated into English: »Perhaps the sun, shining above with rosy lamp is surrounded by much fire and invisible heat. Thus the fire may be accompanied by radiance which increases the power of rays.« or translated by Knebel [3] into German: »Mag es auch sein, dass hoch die rosige Fackel der Sonne ringsum Feuer verbirgt in düsteren unscheinbaren Gluten, die beitragen, die Macht so heftiger Strahlen zu mehren«.

The names of other famous natural scientists appear in the history of spectroscopy after Newton: Edmé Mariotte [4] experimentally demonstrated in 1686 the hypothesis of Lucretius concerning light and radiative heat. He observed that the heat image of a candle focused by a concave metal mirror cooled when a glass plate was placed in the ray trajectory. Frederick William Herschel [4] performed an important experiment in 1800 which can be considered as the year of birth for infrared spectroscopy. In a darkened room, he projected sunlight through a glass prism behind a horizontal slit onto a table. With two blackened mercury thermometers placed on the table in the plane of projection, the difference between the temperature in the spectrum and the temperature to the side out of range of the colored bands could be measured. He observed an increase in the difference as he moved the thermometer from violet to red and found that the difference continued to increase for a distance as he moved the thermometer out of the visible red area. Shortly thereafter, Johann Wilhelm Ritter [6] discovered that the darkening effect of light on silver chloride did not end at the violet end of the spectrum, but continued into the ultraviolet range of the sun’s radiation and even increased. Thomas Johann Seebeck [7] discovered the thermoelectric effect in 1822. It was subsequently used by Leopoldo Nobili [8] and Macedonio Melloni [9] to improve the detection of heat radiation.

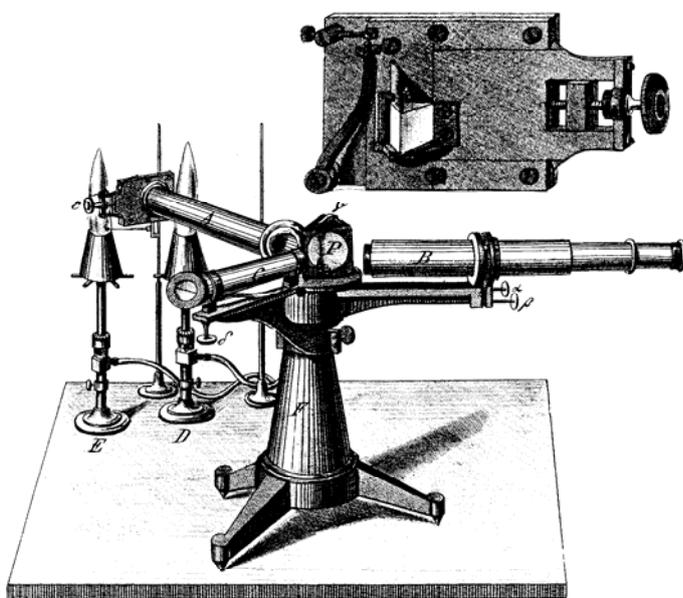
In the visual spectral range, the observation of the continuous spectrum of the sun by Newton was followed by the recognition of the black lines in this spectrum by William Hyde Wollaston in 1802 [10]. Joseph von Fraunhofer [11] examined the lines caused by selective absorption in the photosphere or atmosphere and labeled the most important dark lines with the letters A, B, C, D, E, F, G, H. He noticed that the D line, which is still commonly referenced today (later called the Na-D line [12]), has the same refractibility as the intensive yellow line of a candlelight (candle made from tallow). Approximately 1000 black lines were found by Anders Jonas Ångström [13], who also introduced the unit length  $10^{-10}$  m into spectroscopy. The unit was later named after him (proposal of H. Kayser, cf. [14] page XVIII) and is still in use today, not having been entirely replaced by the SI unit  $1 \text{ nm} = 10 \text{ \AA}$ .



In the second half of the 19<sup>th</sup> century, spectroscopy experienced a period of great advance due to its successful application to the analysis of substances. The physicist Gustav Robert Kirchhoff (left), the chemist Robert Wilhelm Bunsen (right) and the optician Carl August von Steinheil, who manufactured the spectroscope shown in Fig. 1.1 in his Munich workshop, set the



groundwork for the wide application of spectroscopy in science and technology through their works “Chemical Analysis through Spectral Observations” [12] and the construction of an excellent spectroscope. Spectroscopes of that sort were in use until the end of the 19<sup>th</sup> century. Today’s spectrometers have greatly improved in sensitivity and resolution, but have lost much in simplicity of use and ease of understanding.



**Fig. 1.1** The spectroscope of Kirchhoff, Bunsen and Steinheil from the year 1861 [12]. The collimator tube *A* is solidly connected to the frame and contains a plate with a vertical entrance slit and converging lens at the opposite end. The flint glass prism *P* is solidly mounted, but the observation tube *B* can be rotated. The scale tube *C* has an externally illuminated scale *S* on a black background. It is added to the spectrum with the aid of a lens in *C* and a mirrored surface of *P*. The lower portion of the entrance slit is covered by a prism which adds the light of the control light source *D* into the ray trajectory. The substance in question is heated by the flame *E* and its light, together with the light of the flame, enters the upper portion of the entrance slit. The upper part of the observed spectrum is therefore a combination of substance and flame, the lower part only the spectrum of the flame.

At the end of the 19<sup>th</sup> century, the close relationship between theory and spectroscopy was established. Experimental results of spectroscopic studies are an important input for the development of theoretical models of the structure of matter, and the theoretical models are necessary for the interpretation of results also in the modern spectroscopy. Ångström measured accurately the lines of atomic hydrogen in the visible range. Johann Jakob Balmer in 1885 [15] was the first to find an (empirical) formula for the lines between 656 and 377 nm with  $m = 3, 4, \dots, 11$ :

$$\lambda = H \frac{m^2}{m^2 - 4}, \quad (1.1)$$

in which the constant  $H = 364,56$  nm. The difference between the predictions of this formula and the measurements of Ångström is less than 25 ppm in wavelength.

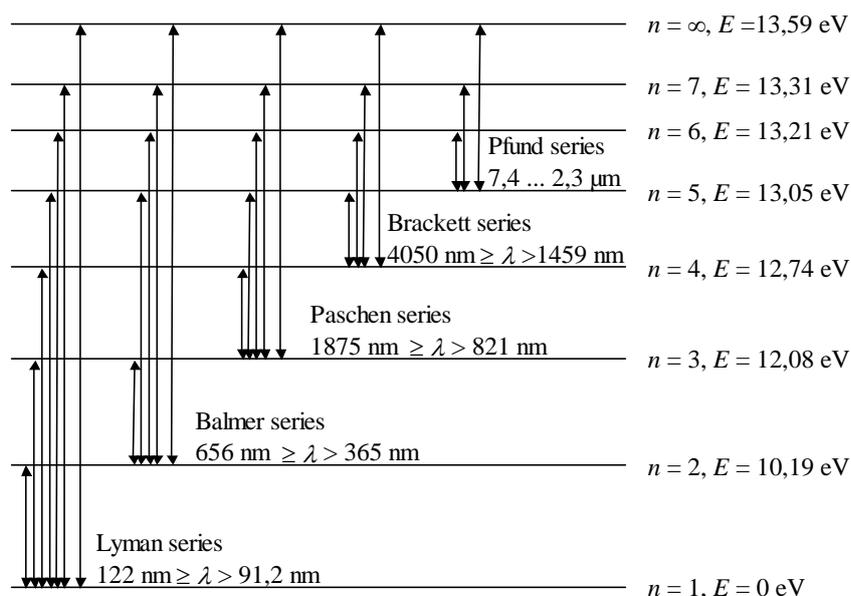
Janne Robert Rydberg [16] noticed a few years later that the wave number (reciprocal wavelength, symbolized with  $\tilde{\nu}$  and given in units of  $\text{cm}^{-1}$ ) can be given as a difference of terms. A common representation is, for example:

$$\tilde{\nu} = \frac{1}{\lambda} = R_{\text{H}} \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right), \quad (1.2)$$

where  $R_{\text{H}} = 109677,58 \text{ cm}^{-1}$  is the Rydberg constant for the hydrogen atom. In the Balmer series,  $n' = m > 2$  and  $n'' = 2$ . The convention will be used that single and double marks on state numbers indicate states with higher and lower energies respectively. In later years, the series for the ultraviolet and infrared spectral ranges were found: Lyman Series 1906 ( $n' > n'' = 1$ ), Paschen series 1908 ( $n' > n'' = 3$ ), Brackett series 1922 ( $n' > n'' = 4$ ) and Pfund series 1924 ( $n' > n'' = 5$ ), compare Fig. 1.2. With these it was possible to find the lines predicted with equ. (1.2). The Pfund series does not end the hydrogen spectrum presented in diagram 1.2. Radio astronomers have succeeded in observing the transition  $n'=167 \leftrightarrow n''=166$  at  $\nu = 1,425$  GHz or  $\lambda = 21,04$  cm in the interstellar medium.

Bohr, Heisenberg, Schrödinger and Dirac tested their theories on the spectrum of the hydrogen atom and discovered principles upon which modern spectroscopy is based.

At the end of the 19<sup>th</sup> century, Heinrich Kayser began to collect the knowledge of the day into his multiple volume work "Handbook of Spectroscopy" [14]. He used the first 128 pages to write a detailed historical portrayal. When the final volume of the work appeared in the year 1928, it was no longer possible to write an overview of the advances in the many disciplines of spectroscopy. Since then, many new methods have been introduced and old methods have changed. The number of acronyms for spectroscopic methods became immense. An examination of the "Current Contents<sup>®</sup>/Physical, Chemical & Earth Sciences and Life Sciences" in the year 2000 showed that from about 300 000 publications per year in these areas (Physics, Chemistry, Earth Sciences, Biology, Medicine), approximately 50 000 used spectroscopic examination methods. The most commonly applied method was NMR (*nuclear magnetic resonance*), used in approximately 14000 publications per year. Around the world about 20 books per year appear that have the word "Spectroscopy" in the title.



**Fig. 1.2** Energy level diagram and spectral series of the H atom. The levels corresponding to the principal quantum numbers  $7 < n < \infty$  have been left out. The energies given are relative to the ground level  $n = 1$ . The ionization energy corresponds to  $n = \infty$ . It should be noted that the distances between the energy levels is not shown to scale.

The electromagnetic spectrum ranges from radio frequencies over the visible and X-ray ranges all the way to nuclear radiation. The realization that light as well as particle radiation can be described by electromagnetic waves allows the following definition: *Spectroscopy is a branch of science studying the interaction of electromagnetic radiation with matter, with the object of determining the nature of the matter in question. The intensity (power) of this radiation as a function of wavelength, frequency, or energy is called the "spectrum".*

By referring to spectroscopy as a branch of science, the question of where it belongs presents itself. The methodology and experimental foundations are part of physics. In the construction of the tools and machines used by spectroscopists, engineers work together with physicists. The applications are chemical, physical, and biological. The word "matter" used in the definition above includes elementary particles, nuclei, atoms, molecules, solids, and living substances. In magnetic resonance tomography, a living human is in the sample chamber of the spectrometer.

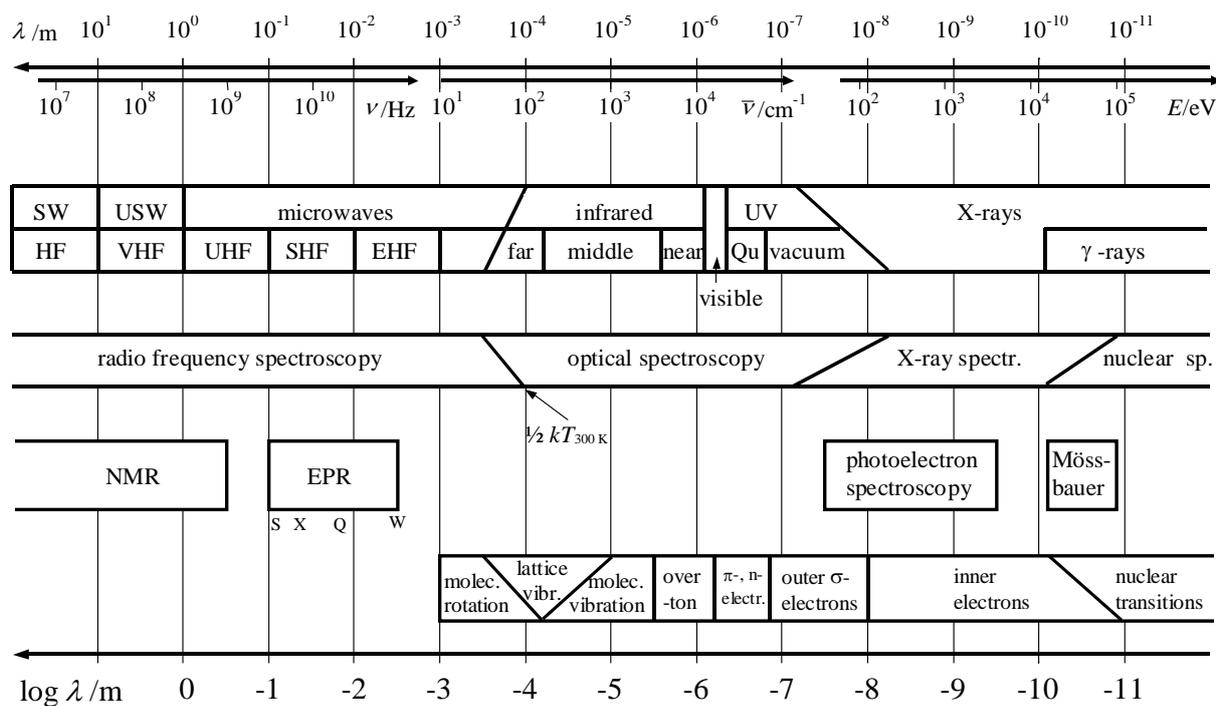
The wavelength and frequency are related by the speed of light  $c$  through the equation:

$$\lambda \nu = c \quad (1.3)$$

The energy  $E$  of a quantum of light is given, with the Planck constant  $h$ , through the equation:

$$E = h \nu. \quad (1.4)$$

Over a large range of the spectrum, the wavelength is used as a unit. In high frequency spectroscopy, the use of frequency is more common, and in optical spectroscopy wave numbers in  $\text{cm}^{-1}$  are used. For X-rays and nuclear radiation, the unit of energy is the electron volt, where 1 keV has the wavelength 1,23985 nm.



**Fig. 1.3** Spectroscopy and electromagnetic spectrum over 14 orders of magnitude of the wave length.

In Fig. 1.3 an attempt is made to portray spectroscopy over a range of 14 orders of magnitude in the electromagnetic spectrum. In the decimal scales, a classification of the spectrums is given. The radio frequencies (rf) found in this spectral range are referred to as decimeter waves (high frequencies HF in English and short wave, *Kurzwelle*, in German), meter waves (very high frequencies VHF in English and ultra short wave, *Ultrakurzwelle*, in German), decimeter waves (ultra high frequencies = UHF), centimeter waves (super high frequencies SHF), and millimeter waves (extremely high frequencies EHF). In the microwave range, the use of wave guides is common. A few neighboring microwave bands are referred to by P, L, S, X, K, Q, V and W. The overlap between the radio frequency range, optical range, and X-ray ranges show that radiation of some wavelengths can be created electronically and optically or optically and with X-ray tubes. Across the entire optical range, radiation can be created by both thermal emitters as well as lasers (Light Amplification by Stimulated Emission of Radiation). Spectroscopy can be separated into rf spectroscopy, optical spectroscopy, X-ray spectroscopy and nuclear spectroscopy. In Fig 1.3, a few spectroscopic methods are also named along with the spectral ranges that they cover. The figure ends with the presentation of the transitions that absorb or emit electromagnetic radiation.

According to the definition above, not all methods of analysis which produce a “spectrum” of the substance in question can be classified under spectroscopy. This is true, for example, of gas and liquid chromatographic separation methods. Mass spectroscopy is also a separation method and is therefore not included in Fig. 1.3. If, however, we look at the method of operation of a modern Fourier mass spectrometer, the ions move in circular paths in a homogenous magnetic field. They are not separated in space but absorb or emit high frequency electromagnetic radiation. Since there are also many other similarities between mass spectroscopy and other spectroscopic methods, we have dedicated a chapter to mass spectroscopy.

For the treatment of spectroscopic methods and branches there is no necessary order. We begin with two chapters that deal with the absorption and emission of radiation (chapter 2) and a few useful fundamentals of electron levels, electron orbitals, and symmetries in molecules and crystals (chapter 3). In the following chapters, a few important spectroscopic methods and branches (excluding mass spectrometry) are arranged according to frequency.

An overview of the areas of application of the methods discussed is not given in this book. In the application examples and exercises, references will only be made to the listed books and articles. The principle shortcoming of this introduction to spectroscopy is the lack of a possibility for *practical* exercises. For this reason, the lectures should be complemented by demonstrations on real spectrometers. Spectroscopy has remained an experimental branch of science despite theoretical aids and the use of computers. The inspiration for many spectroscopic experiments today is still that pronounced by Newton in the Philosophical Transactions of the Royal Society [1]: "I procured me a triangular glass-prisme, to try therewith the celebrated phenomena of colours".

### Literature for Chapter 1

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