Experiment No. 61

Atomic spectra (Bohr atomic model)

Keywords:
Emission spectra, line spectra, spectral series, Balmer series, Bohr's postulates, Bohr's hydrogen atom, Rydberg constant, term values, quantum numbers, visible wavelength range

Literature:

Christen “Fundamentals of general and organic chemistry”
Textbooks on physical chemistry:
Atkins, “Physical Chemistry”
Gerthsen, Kneser, Vogel: Physics
Textbooks on experimental physics, e.g:
Demtröder: Experimental Physics 2
Bergmann, Schäfer: Textbook of Experimental Physics 3, Optics
Haken, Wolf: Atomic and quantum physics

Fundamentals:
All matter emits electromagnetic waves, which can often be perceived as visible light (e.g. sun, light bulb, fluorescent tube, natural gas flame). It has been observed that the wavelengths of the emitted light are characteristic of the type of emitting matter, and the spectra that occur are divided into line spectra, band spectra and continuous spectra according to their external appearance.

Line spectra are characteristic of atoms. To explain this empirically found fact, one must consider the atomic structure of matter. The simplest spectrum is emitted by excited hydrogen atoms. The hydrogen atom consists of a positively charged proton as the atomic nucleus (diameter approx. 10^{-14} m) and a negatively charged electron orbiting around the nucleus, which forms the atomic shell (diameter approx. 10^{-10} m). From his spectrum of lines in the visible wavelength range (approx. 400 to 700 nm), which is particularly simple because of this one electron only, the Basel secondary school teacher Balmer recognized that the position of the visible hydrogen lines obeys a simple law.

Such a regular sequence of lines is called a series and the lines are assigned to certain energy levels of the atomic shell. In 1889, J. Rydberg found that not only the position of the lines in the spectrum of the hydrogen atom can be described by a formula, but that it is also possible to calculate the line spectra of alkali metals, for example, using a similar formula. The constant appearing in these equations was named the Rydberg constant in his honor.

The following applies to the Balmer series of the hydrogen atom:

(1) $$\tilde{\nu} = R * \left(\frac{1}{2^2} - \frac{1}{n_2{}^2} \right)$$ with n_2 = 3, 4, 5, ...

and = $1/\lambda$ = wavenumber

The wavenumber indicates the number of wavelengths falling on 1 cm of light path in a vacuum (unit: cm^{-1}). The Rydberg constant here also has the dimension cm^{-1}. R/4 is the fundamental term, $R/n2^2$ is the running term of the Balmer series. The hydrogen atom has even more series whose lines can be combined from two terms according to Eq. (1):

(2) $$\tilde{\nu} = R * \left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2} \right)$$ with n1 = 1, 2, 3, 4,... n2 > n1

A series is created by holding n_1 fixed and letting n_2 run through the integers from $n_1 + 1$ upwards. As the $1/n_2$ become smaller and smaller, the lines become closer and closer together and converge towards the series limit $R/n_1{}^2$. An interpretation of the relationships shown in equations (1) and (2) is given by Niels Bohr in his atomic theory.

It is based on the following postulates:

a) Because of the existence of stable atoms, there must be stable electron orbits on which electrons can orbit without radiation. For these orbits there is equilibrium between Coulomb force and centrifugal force. They therefore correspond to certain stationary energy conditions E.

(3) $$\frac{e^2}{4 * \pi * \varepsilon_0 * r^2} = \frac{m * v^2}{r} \Rightarrow E_{kin} = \frac{1}{2} mv^2 = \frac{e^2}{8 * \pi * \varepsilon_0 * r}$$

b) Radiation is only emitted or absorbed during the transition between two stationary states. The frequency v of the spectral lines results from the energy difference between the stationary states:

(4) $\Delta E = h*v = E(n_2) - E(n_1)$, where $E(n_2) \rightarrow E(n_1)$ = emission

$E(n_1) \rightarrow E(n_2)$ = absorption

c) Not every arbitrary orbital radius is allowed, but only those on which the angular momentum of the electron is an integer multiple of :

(5) $m * v * r = n * \hbar$ where $\hbar = h/2\pi$

n is the principal quantum number and can assume the values 1, 2, 3, …

From eqs. (3) and (5) one obtains for the permitted radii:

$$(6) \qquad r = n^2 * \frac{4\pi * \varepsilon_0 * \hbar^2}{m * e^2} = n^2 * r_B$$

The constants of the fraction can be summarized to a constant r_B, the Bohr radius.

On the nth orbit, the electron has the potential energy

$$(7) \qquad E_{pot} = -\frac{e^2}{4 * \pi * \varepsilon_0 * r} = -\frac{m * e^4}{4 * \varepsilon_0^2 * n^2 * h^2}$$

Since the kinetic energy of the electron is exactly half as large as E_{pot} except for the sign (see Eq. (3)), the total energy on the nth orbit becomes

$$(8) \qquad E_{ges} = E_{pot} + E_{kin} = -\frac{m * e^4}{8 * \varepsilon_0^2 * h^2} * \frac{1}{n^2}$$

The wavenumbers of the spectral lines emitted at the transition from orbit n_2 to orbit n_1 are given by

$$(9) \qquad \bar{\nu}_{21} = \frac{E(n_2) - E(n_1)}{h * c} = \frac{m * e^4}{8 * \varepsilon_0^2 * c * h^3} * \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The natural constants are combined to give the Rydberg constant in cm^{-1}:

$$(10) \qquad R_H = \frac{m * e^4}{8 * \varepsilon_0^2 * c * h^3}$$

In the emission spectra of other atoms, the individual series overlap more than in the hydrogen atom, which makes it very difficult to interpret the spectra. The emission of alkali and alkaline earth elements in the visible wavelength range is often used for qualitative and quantitative analysis (e.g. in flame photometers). Heavy metals (e.g. Hg) have particularly line-rich emission spectra, which are often used for photochemical experiments and for calibration purposes.

Task:

The Rydberg constant is determined from the spectral position of the Balmer lines of the hydrogen atom spectrum.

Experimental setup:

The emission spectrum of the hydrogen atom is generated using an H_2 discharge lamp.

Emission lines of the mercury (in nm) are:

253, 6	365, 0	546,1	626,4 *
296,7	404,7	577,0	730,0 *
302,2	407,8	579,1	760,8 **
313,2	435,8	593,5 *	
334,1	507,3 *	604,3 *	

* 2nd order
** 3rd order

The same arrangement of grating monochromator, photomultiplier and compensation recorder as in experiment 54 is used for spectral decomposition of the emission and detection of the spectra obtained.

Procedure:

1) Set the device parameters as in experiment 54. Observe the precautionary measures!

2) The wavelength scale of the monochromator is calibrated using known lines of the mercury spectrum (see table).

The following spectra are required:

a) an overview spectrum between 200 and 700 nm.

b) a spectrum between 500 and 700 nm with greater sensitivity than a).

The two emissions between 577 and 580 nm are set to about 3/4 of the recorder deflection.

3) First view the emission spectra through the hand spectroscope.

4) Record the discharge spectrum of the hydrogen tube (do not let the lamp burn longer than necessary):

a) between 350 and 700 nm

b) between 350 and 450 nm with greater sensitivity than a).

Evaluation:

1) The wavelengths obtained from the mercury spectra are entered in the spectrum, compared with the literature values in a table and plotted on graph paper as a function of the known (tabulated) emission lines.

2) Using linear regression, obtain a calibration curve for the monochromator and use this to determine the exact wavelengths of the lines of the Balmer series.

Assign the observed lines to the corresponding transitions in the atom in a table.

3) Convert the wavelengths into frequencies or wave numbers and calculate the Rydberg constant [cm^{-1}] according to Eq. (1).
To do this, enter the run number n_2 in Eq. (1) (starting with $n = 3$).

4) Draw a true-to-scale term diagram of the hydrogen atom (energy in cm^{-1}) on graph paper.

5) What is the physical significance of the Rydberg constant?

Estimate the accuracy of the value for the Rydberg constant.

Accessories:

Grating monochromator, photomultiplier with power supply, flat recorder, hydrogen discharge lamp, mercury vapor lamp, hand-held spectroscope.