

## II.6. THE DETERMINATION OF THE RYDBERG CONSTANT

### 1. Work purpose

The determination of the constant involved in the spectral series of the hydrogenoid atoms / ions.

### 2. Theory

The atoms of each element emit, when they are excited (for instance in an electrical discharge in a gas), an optical discrete spectrum on the basis of which the element can be identified. The spectra of chemical elements are as complicated as their atomic number  $Z$  is greater. The optical spectra of the atoms are due to the optical electrons, that is the electrons situated on the peripheral orbitals.

The spectroscopists established that all the lines of different spectral lines of the hydrogenoid atom / ion (a hydrogenoid ion is formed by a nucleus and a single electron) could be described by a general relation, which gives us the wavelength of the spectral lines:

$$\tilde{\nu}_{n,m} \equiv \frac{1}{\lambda_{n,m}} = T(m) - T(n) = \frac{R}{m^2} - \frac{R}{n^2} = R \cdot \left( \frac{1}{m^2} - \frac{1}{n^2} \right). \quad (1)$$

In the above relation  $n$  and  $m$  are integer numbers,  $T(m)$  and  $T(n)$  are spectral terms, and

$$R = \frac{Z^2 R_\infty}{1 + \frac{m_e}{M}} \cong Z^2 R_\infty, \quad (2)$$

where  $m_e$  is the electron mass,  $M$  is the nucleus mass and  $R_\infty$  is Rydberg constant. For hydrogen, this constant becomes the hydrogen Rydberg constant:

$$R_H = \frac{R_\infty}{1 + \frac{m_e}{M_{H^+}}} \cong R_\infty. \quad (3)$$

The explanation of the spectral series of the hydrogen atom represented a successful verification of the hydrogen atom theory given by Niels Bohr. Bohr sustains that there are only certain orbits allowed for the electron, corresponding to certain stationary states. He formulated the following postulates:

I. The atom can exist in a discrete series of stationary states determined by the discrete series  $E_1, E_2, \dots, E_n, \dots$  of the total energy. In these states the atom does not emit or absorb energy.

II. The energy of the atom can change discontinuously, by the transition from one stationary state of total energy  $E_m$  to another stationary state of total energy  $E_n$ , with the absorption or emission of a photon. The frequency of the absorbed or emitted photon is given by the relation:

$$\nu_{n,m} = \frac{E_n - E_m}{h} \quad (4)$$

( $h$  being the Planck constant), the process of absorption taking place in the case when the electron passes from a closer orbit to nucleus to a more distant one, and the emission taking place in the opposite case.

The specification of the allowed orbits is obtained by introducing the quantification condition stated by Bohr, who found that the angular momentum of the electron on the allowed orbits must be an integer multiple of  $\hbar$ :

$$L = m_e v r = n \hbar, \quad (5)$$

where  $\hbar = \frac{h}{2\pi}$  is the rationalised Planck constant and  $n = 1, 2, 3, \dots$  is called the principal quantum number. The total energy  $E_n$ , on the  $n$ -th orbit is quantized by the expression:

$$E_n = -\frac{\mu e^4}{8\varepsilon_0^2 \hbar^2} \cdot \frac{1}{n^2} \cong \frac{m_e e_0^2}{2\hbar^2} \cdot \frac{1}{n^2}, \quad (6)$$

where

$$\mu = \frac{m_e}{1 + \frac{m_e}{M_{H^+}}} \cong m_e \quad (7)$$

is the reduced mass and

$$e_0^2 = \frac{e^2}{4\pi \varepsilon_0} \quad (8)$$

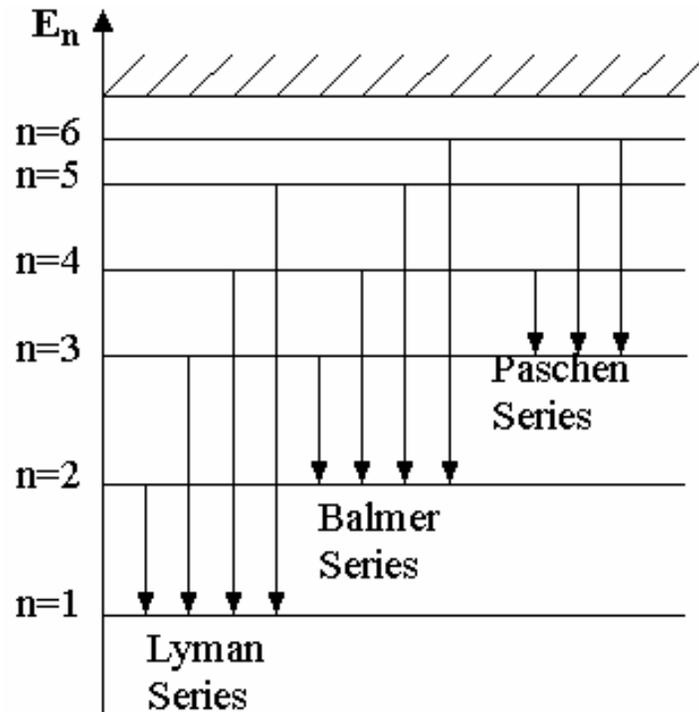
is the rationalised elementary charge ( $\varepsilon_0$  being the vacuum permittivity). In the quantum mechanics, the electron energy for the hydrogen atom (Eq. (6)) is found by integrating the Schrödinger equation. The total electron energy on different stationary orbits is negative, which means that the electron is bound by the electromagnetic field of the nucleus. Using the relations (4) and (6), one can obtain:

$$\frac{1}{\lambda_{n,m}} = \frac{\mu e_0^4}{4\pi \hbar^3 c} \left( \frac{1}{m^2} - \frac{1}{n^2} \right), \quad m, n = 1, 2, 3, \dots, \quad m < n \quad (9)$$

( $c$  being the speed of light in vacuum) and, comparing this with (1), (3) and (7), it results that:

$$R_\infty = \frac{m_e e_0^4}{4\pi \hbar^3 c}. \quad (10)$$

Using Eq. (4), every wavelength of the lines from different spectral series for hydrogen can be found. A spectral series represents the sum of spectral lines that have a common desexcited energetic level (see Figure 1).



**Figure 1.**

So, there is the Lyman series, which has the common energetic level corresponding to  $m = 1$  (in Eq. (9)), and  $n \geq 2$  and is situated in the ultraviolet range; Balmer series, for which  $m = 2$  and  $n \geq 3$ , in the visible range; Paschen series, for which  $m = 3$  and  $n \geq 4$  and the following series, all in the infrared range.

In this experiment we will study Balmer spectral series and determine the wavelengths for the lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , and  $H_\epsilon$  presented in Figure 2. In the case of Balmer series, the relation (1) becomes:

$$\tilde{\nu}_{n,2} = \frac{1}{\lambda_{n,2}} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, 6, 7, \quad (11)$$

from which the Rydberg constant results:

$$R_H = \frac{4n^2}{(n^2 - 4) \cdot \lambda_{n,2}} \quad (12)$$

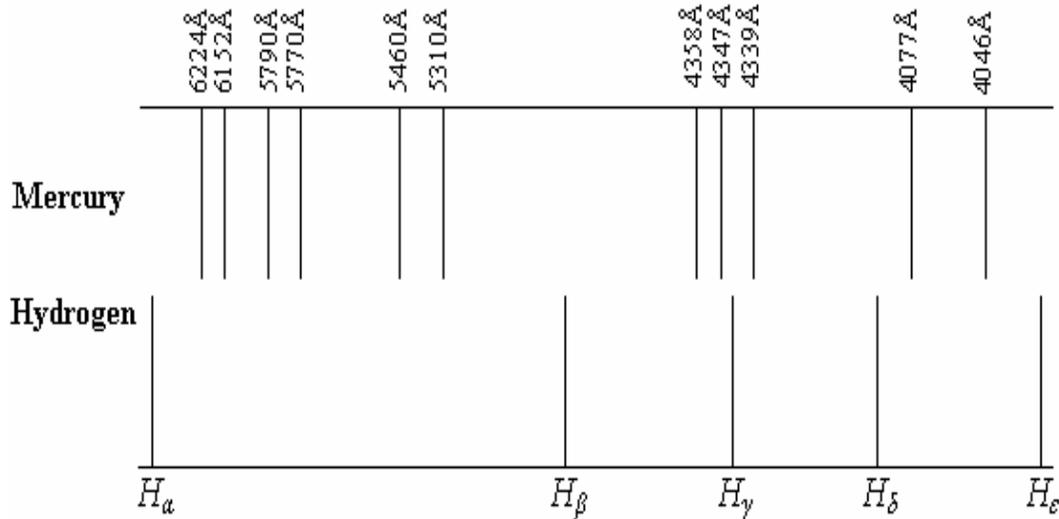


Figure 2.

### 3. Experimental set-up

The hydrogen spectrum in the visible band is recorded on a photographic plate (spectrogram), which is set between two plexiglas plates. On the same photographic plate, it appears, parallel to the hydrogen spectrum, the mercury spectrum, used as a comparison spectrum, being recorded at the same spectrograph and in identical conditions.

The mercury spectrum presents a number of lines, their configuration appearing in Figure 2, on which there are also indicated the wavelengths corresponding to each spectral line. The lines of the atomic hydrogen belonging to Balmer series ( $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , and  $H_\epsilon$ ) whose wavelength we are going to determine, also appear in Figure 2, in their relative positions with respect to the lines of the mercury spectrum.

We study the spectrogram with a microscope. The microscope bed can be moved horizontally, along two perpendicular directions, using two screws. The movement along the spectrum allows us to measure the

position of a spectrum line on a ruler, graduated in mm and with a vernier, the precision being 0.1 mm. To fix the position of desired line the ocular of the microscope has a reticular wire.

To accomplish the work, there are necessary the spectrogram with the visible atomic hydrogen spectrum (Balmer series) and the mercury spectrum, and a microscope.

#### 4. Working Procedure

Looking through the ocular, adjust the microscope mirror to have the best illumination. If the microscope has a lamp, plug in its transformer. In order not to break the spectrogram, the initial position of the microscope must have the object lens stuck to the spectrogram and then gradually lift, until the spectral lines are clearly visible. Verify the parallelism between the spectral lines and the reticular wire, the parallel setting of the reticular wire being made by rotating the ocular.

Identify the mercury and hydrogen spectra, looking first at the spectrogram with the naked eye and then at the microscope. Read on the ruler (after superposing the reticular wire on each line) the positions  $x_i$  of the mercury lines (the wavelengths being given for each of them). Read also on the ruler the positions  $x_j$  of the lines from the hydrogen series ( $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , and  $H_\epsilon$ ).

Draw on a millimetric paper the calibration curve for the mercury  $\lambda = \lambda(x)$ . Having the positions  $x_j$  of the hydrogen lines, the wavelengths of the lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , and  $H_\epsilon$ , necessary to compute the Rydberg constant, result from the calibration curve.

#### 5. Experimental data processing

The data measured for mercury are written in Table 1.

**Table 1.**

$\lambda$ (Å)	$x$ (mm)
...	

The measured data for the lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ,  $H_\delta$ , and  $H_\varepsilon$  are written in Table 2.

**Table 2.**

Line	$x$ (mm)	$\lambda$ (Å)	$n$	$R_H$ (m <sup>-1</sup> )
$H_\alpha$			3	
...			...	

Compute the Rydberg constant according to the relation (12); the obtained value are written in Table 2.

Compute the mean value

$$\langle R_H \rangle = \frac{1}{5} \sum_{j=1}^5 R_{Hj} \quad (13)$$

and the standard error

$$\sigma_{R_H} = \sqrt{\frac{1}{20} \sum_{j=1}^5 (R_{Hj} - \langle R_H \rangle)^2}. \quad (14)$$

The final result is presented in the form

$$R_H = \langle R_H \rangle \pm \sigma_{R_H} \quad (\text{m}^{-1}). \quad (15)$$

## 6. Questions

1. What is a spectral series?
2. What is a spectral term?
3. What postulates lay at the basis of Bohr's formula for the energy levels of the hydrogenoid atoms / ions?