

The Quantum Chemistry Experiment: Measuring the Balmer series of lines for the Hydrogen atom.

OBJECTIVES

- 1) To observe and measure the Balmer series in the emission spectrum of hydrogen.
- 2) To understand the importance of the nature of the spectrum in terms of our modern day understanding of the structure of the atom.
- 3) To use the measurement of the emission spectrum of hydrogen to calculate the Rydberg constant for hydrogen and the ionization potential of hydrogen.

THEORY

The full theory behind this experiment is given in the video presentations. Here a brief background synopsis is given.

The presence of discrete lines in the emission spectrum of electronically excited atoms provides some of the most compelling evidence for quantum theory. In this experiment and simulation, the different energy levels accessible to the electron in a hydrogen atom are examined directly through spectroscopic measurement of the wavelengths of emissions from a hydrogen discharge lamp. From these, the values of the electronic energy levels, and by extrapolation, the ionisation energy of the hydrogen atom may be determined.

Electromagnetic radiation is characterised by its frequency ν and its wavelength λ . The frequency ν is expressed in the International System of Units (SI) as s^{-1} or Hz. The wavelength λ is expressed in the SI unit m. The two quantities are related to the speed of propagation of light *in vacuo* c by the equation:

$$c = \nu \lambda. \quad [1]$$

The energy ε possessed by one quantum of radiation (a photon) of frequency ν is given by the Planck equation

$$E = h \nu \quad [2]$$

where h is the Planck constant and has a value of $6.62607 \times 10^{-34} \text{ J s}$. This equation yields the energy in J. The energy of one mole of photons E may be calculated from an adaptation of the Planck equation

$$E = N_A h \nu \quad [3]$$

where N_A is the Avogadro constant and has a value of $6.02214 \times 10^{23} \text{ mol}^{-1}$. This equation yields molar energy in J mol^{-1} . Spectroscopists often characterise radiation by its wavenumber

$$\bar{\nu} = 1 / \lambda. \quad [4]$$

The wavenumber is expressed in the SI unit m^{-1} , but is invariably quoted in cm^{-1} . [$1 \text{ cm}^{-1} = 100 \text{ m}^{-1}$]

The emission spectrum of electronically excited hydrogen arises as a consequence of electronic transitions between energy levels in the atom. The existence of discrete lines in the spectrum implies

that only certain transitions are possible, which further implies the existence of quantised energy levels.

The solution of the Schrödinger equation for the hydrogen atom, see video presentation xx gives:

$$E_n = -R \frac{1}{n^2} \quad [5]$$

Here n is the principal quantum number and must be an integer. E is the electron's energy in quantum level n . R is called the Rydberg constant. The energy of a given level is referenced to an energy zero, with $n = \infty$, corresponding to a free electron and the ionised atom. When $n = 1$ the electron is in the 1s orbital, when $n = 2$ the electron is in either the 2s or 2p orbital and when $n = 3$ the electron is in either the 3s, 3p or 3d orbital etc... Emission of a photon occurs as an electron undergoes a transition from some energy level with a quantum number n_2 down to a lower energy level with a quantum number n_1 . The energy of the photon will be determined by the energy difference $\Delta E = E_2 - E_1$ between the levels and may be expressed by the relationship

$$\Delta E = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad [6]$$

The spectrum consists of a number of series of lines. All the lines may be identified in terms of transitions from an excited state to a lower energy level. Different lines within the same series correspond to starting in different excited states but falling to the same lower state. The lowest energy line in the Balmer series corresponds to an electronic transition from $n_2 = 3$ to $n_1 = 2$. Using equation [6] this emission has an energy given by:

$$\Delta E = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R$$

EXPERIMENTAL PROCEDURE (SEE ACCOMPANYING VIDEO)

This spectroscopic method involves exciting electrons within H atoms by means of electrical discharge. Electrons are promoted to excited states and then emit a photon as they fall back to lower states. When large numbers of atoms undergo such transitions, the emission is of sufficient intensity for spectral lines to be observed by eye. The wavelengths of the spectral lines are measured using a spectrometer.

DATA TREATMENT

- Using the spectrometer simulator, obtain the wavelengths in nanometres (nm) of four lines in the Balmer series and then convert these to eV.
- Identify the transitions. In each case, you know that the lower energy level has a principal quantum number $n_1 = 2$. The lines must therefore correspond to transitions from higher levels, with $n_2 = 3, 4$ etc...
- To help with the assignment, consider the following questions:

Which transition in the Balmer series has the lowest energy change?

Which of the observed lines corresponds to the lowest energy?

Which is the next lowest transition and which line corresponds to the next lowest energy?

- In this way, assign the principal quantum number n_2 of the excited state to each of the observed lines.
- Plot a graph of the energy of each transition in eV against $1/n_2^2$ using Excel or another spreadsheet and obtain the gradient and intercept. Think very carefully about the units of these quantities.
- Adapt equation [6] to the Balmer series and express it in the form $y = mx + c$ and use it to evaluate the Rydberg constant, R , separately, both from your calculated gradient and your intercept.
- Use your value of R to estimate the ionisation energy for the hydrogen atom in kJ mol^{-1} , and cm^{-1} given that $1 \text{ eV} = 96.487 \text{ kJ mol}^{-1}$ or 8065.6 cm^{-1} .
- Compare your result with the literature value.

NOTES

- (1) Energy units: The energy of a spectroscopic transition may be conveyed by stating the corresponding wavenumber (or reciprocal wavelength), where

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc},$$

$\bar{\nu}$ should however NOT actually be called the energy – despite this being common practice. Typically the actual energy change per molecule is correctly quoted in units of eV or as a molar quantity in units of kJ mol^{-1} ($1 \text{ eV} \equiv 1.60210 \times 10^{-19} \text{ J}$). The quantity 1 eV represents the same amount of energy / molecule as $96.487 \text{ kJ mol}^{-1}$ and corresponds to wavenumber 8065.6 cm^{-1} .

- (2) Slightly different theoretical values for the Rydberg constant are to be found in the literature. This stems from two definitions of the reduced mass of the electron. Quantum theory calculates the Rydberg constant as:

$$R = \frac{2\pi^2 \mu e^4}{ch^3} \times \frac{1}{(4\pi\epsilon_0)^2} \text{ cm}^{-1}$$

where the reduced mass is $\mu = \frac{m_p m_e}{m_p + m_e}$ kg where m_p is the mass of the proton and m_e that of

the electron, both in kg. If one assumes that the mass of the proton is infinite compared to that of the electron then $\mu = m_e$ and this generates R_∞ , but if one uses the real mass of the proton relative to that of the electron then $\mu \approx \frac{1864 m_e}{1865}$. R_∞ and R_H are thus only slightly different.