

2.5: Hydrogen Luminescence

The luminescence spectrum of the hydrogen atom reveals light being emitted at discrete frequencies. These spectral features appear so sharp that they are called lines. These lines, occurring in groups, are found in different regions of the spectrum; some are in the visible, some in the infrared, and some in the vacuum ultraviolet. The occurrence of these lines was very puzzling in the late 1800's. Spectroscopists approach this type of problem by looking for some regularity or pattern in the observations. Johannes Rydberg recognized a pattern and expressed it in terms of the following formula,

$$\bar{\nu} = R_H \left(\frac{1}{f^2} - \frac{1}{i^2} \right) \quad (2.5.1)$$

Here $\bar{\nu}$ is the “frequency” of the line in wavenumber units

$$\bar{\nu} = \frac{\nu}{c} \quad (2.5.2)$$

R_H is a constant equal to $109,677.581 \text{ cm}^{-1}$, now called the Rydberg constant, and f and i are positive integers with $i > f$. Different groups of lines, called Rydberg series, are obtained for different values of f . The lines in each series arise from a range of values for i . This analysis by Rydberg was pretty amazing. It pictured the hydrogen atom as some sort of counting machine that utilized integer numbers for some unknown reason.

Example 2.5.1

Calculate the wavelength of a line in the hydrogen atom luminescence spectrum corresponding to $f = 7$ and $i = 8$. In which region of the electromagnetic spectrum will this line appear?

Since the Rydberg equation was derived empirically (i.e., invented to describe experimental data), the next question was, “Can the Rydberg equation and the origin of the integer values for f and i be obtained from theoretical considerations?” This question was enormously difficult for scientists at the time because the nature of the spectrum, discrete lines rather than a continuous frequency distribution, and the very existence of atoms, was not consistent with existing physical theories.

Example 2.5.2

Explain what it means to say a constant or an equation is empirical. Give an example of a value that is determined empirically.

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