Electromagnetic Radiation and the Spectrum of Atomic Hydrogen

To make sense of the chemistry of the elements we need to understand the electronic structure of atoms. It is the atom's electronic structure which governs everything from molecular geometry to chemical reactivity. Electromagnetic radiation is the probe we use to obtain knowledge of electronic structure, so we begin by looking at some of its properties.

Light has a *dual nature* – it is both wave-like and particle-like. Thus light and all other forms of electromagnetic radiation obey two equations, one of which shows the inverse relation between wavelength λ and frequency ν (both properties of waves) and the other which relates the energy of light photons ("particles") to their frequency ν:

$$\textit{Wave model} \qquad \lambda(\text{m}) \times \nu(\text{s}^{-1}) = c(\text{m/s}) \tag{1}$$

$$\textit{Particle model} \qquad E_{photon}(\text{J}) = h(\text{J s}) \times \nu(\text{s}^{-1}) \tag{2}$$

The constants and variables in these equations are

Speed of light = c = 3.00 x 10^8 m/s = 3.00 x 10^8 m s^{-1}
Planck's constant = h = 6.626 x 10^{-34} J s
Wavelength = λ = Greek lower case *lambda*
Frequency = ν = Greek lower case *nu*
Photon Energy = E_{photon}

Common units include

Wavelength λ : 1 nm = 10^{-9} m = 10 Å
Frequency ν: 1 s^{-1} = 1 Hz

The H Atom Emission Spectrum

Our modern theory of the electronic structure of atoms began with attempts to understand the emission spectrum of the simplest atom – hydrogen. By the end of the nineteenth century it was established that the frequencies ν of the spectral lines in the H atom emission spectrum all fit a very simple formula (see Eq (6) ahead). The famous *Bohr model of the H atom* proposed by Bohr in 1914 was an attempt to understand where this formula came from. Bohr recognized that the frequencies would be predicted correctly if the H atom energy levels obeyed the equation

$$E_n = -\ R_H\left(\frac{1}{n^2}\right) \quad \text{for n = 1, 2, 3, ...} \qquad \textit{(Applies only to H atom!!)} \tag{3}$$

where

R_H = Rydberg constant = 2.18 x 10^{-18} J

While the Bohr model was *incorrect in assuming that the electrons orbit the nucleus like planets orbit the sun, it was correct in predicting the energies of the H atom energy levels*.

Absorption and Emission

Absorption of electromagnetic radiation occurs when electrons make transitions from *lower* to *higher* energy levels. Photons provide the energy required for the jumps. Similarly, when