The Electronic Structures of Atoms
Electromagnetic Radiation

- The **wavelength** of electromagnetic radiation has the symbol λ .
- Wavelength is the distance from the top (crest) of one wave to the top of the next wave.
  - Measured in units of distance such as m,cm, Å.
  - 1 Å = 1×10^{-10} m = 1×10^{-8} cm
- The **frequency** of electromagnetic radiation has the symbol υ.
- Frequency is the number of crests or troughs that pass a given point per second.
  - Measured in units of 1/time - s^{-1}

Electromagnetic Radiation

- The relationship between wavelength and frequency for any wave is **velocity = λ υ**.
- For electromagnetic radiation the velocity is 3.00 x 10^8 m/s and has the symbol c.
- Thus **c = λ υ** for electromagnetic radiation.

Electromagnetic Radiation

- Molecules interact with electromagnetic radiation.
  - Molecules can absorb and emit light.
- Once a molecule has absorbed light (energy), the molecule can:
  1. Rotate
  2. Translate
  3. Vibrate
  4. Electronic transition

Electromagnetic Radiation

- What is the frequency of green light of wavelength 5200 Å?

$$c = \lambda \nu \quad \therefore \quad \nu = \frac{c}{\lambda}$$

$$(5200\ \text{Å}) \left(\frac{1\,\text{x}\,10^{-10}\ \text{m}}{1\ \text{Å}} \right) = 5.200 \times 10^{-7}\,\text{m}$$

$$\nu = \frac{3.00 \times 10^{8}\ \text{m/s}}{5.200 \times 10^{-7}\,\text{m}}$$

$$\nu = 5.77 \times 10^{14}\ \text{s}^{-1}$$

Electromagnetic Radiation

- In 1900 Max Planck studied black body radiation and realized that to explain the energy spectrum he had to assume that:
  1. Energy is quantized
  2. Light has particle character
- Planck's equation is

$$E = h\,\nu \quad \text{or } E = \frac{hc}{\lambda}$$

$$h = \text{Planck's constant} = 6.626 \text{ x } 10^{-34} \text{ J} \cdot \text{s}$$

Electromagnetic Radiation

- What is the energy of a photon of green light with wavelength 5200 Å? What is the energy of 1.00 mol of these photons?

$$\text{We know that } \nu = 5.77 \text{ x } 10^{14} \text{ s}^{-1}$$

$$E = h\,\nu$$

$$E = (6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(5.77 \times 10^{14}\ \text{s}^{-1})$$

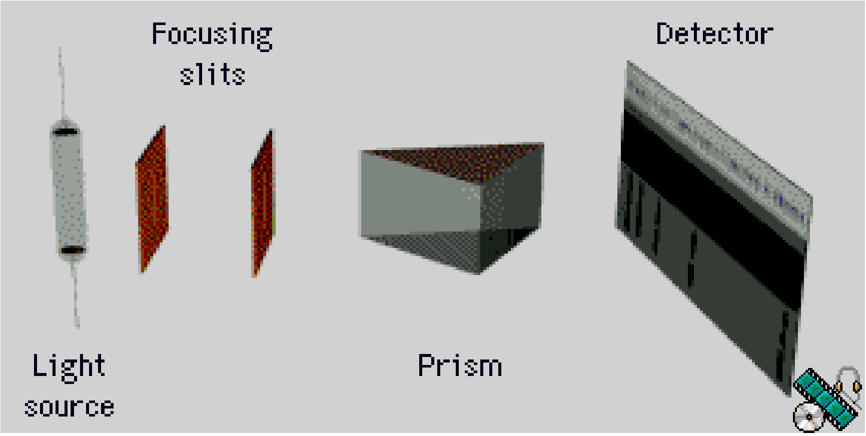
$$E = 3.83 \times 10^{-19}\ \text{J per photon}$$

$$\text{For } 1.00 \text{ mol of photons:}$$

$$(6.022 \times 10^{23}\ \text{photons})(3.83 \times 10^{-19}\ \text{J per photon}) = 231\ \text{kJ/mol}$$

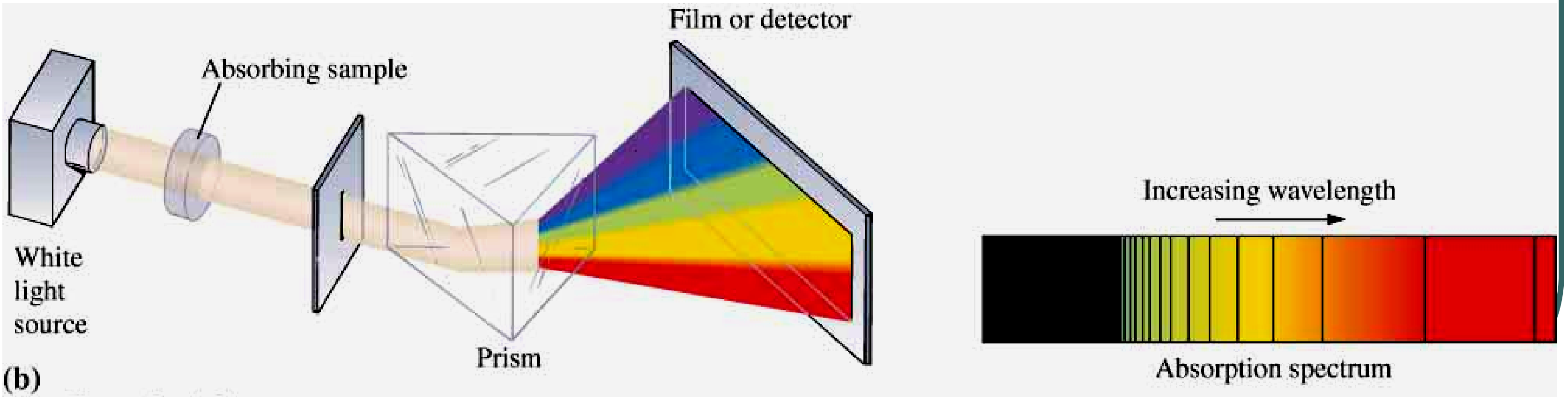
Atomic Spectra and the Bohr Atom

- An ***emission spectrum*** is formed by an electric current passing through a gas in a vacuum tube (at very low pressure) which causes the gas to emit light.
  - Sometimes called a ***bright*** line spectrum.



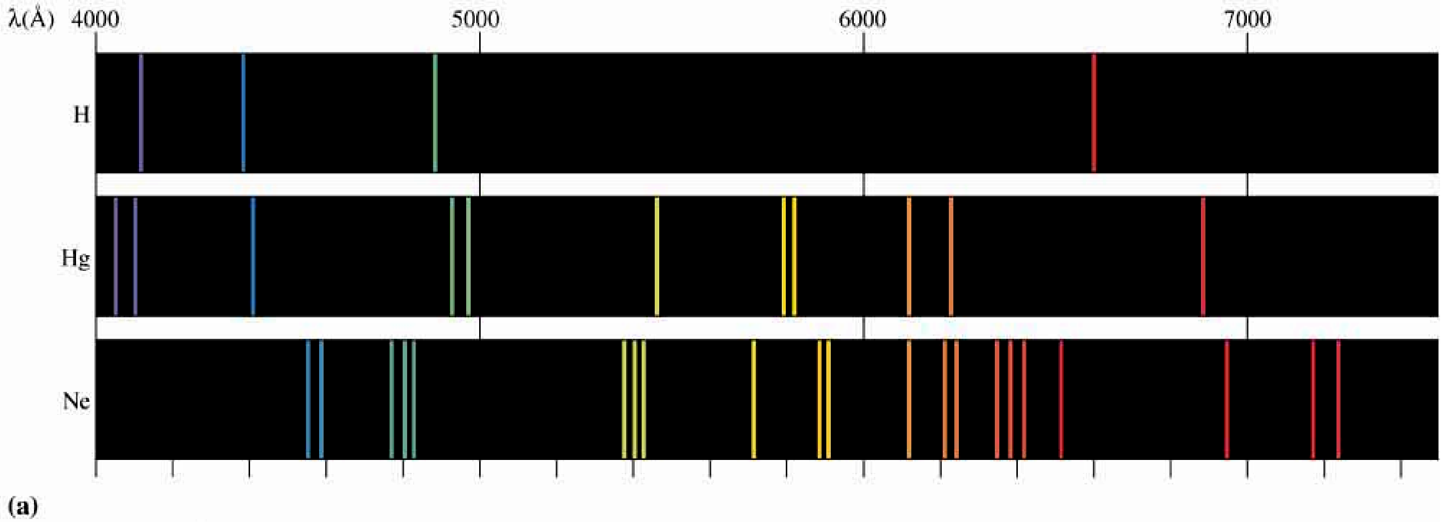
Atomic Spectra and the Bohr Atom

- An ***absorption spectrum*** is formed by shining a beam of white light through a sample of gas.
  - Absorption spectra indicate the wavelengths of light that have been ***absorbed***.



Atomic Spectra and the Bohr Atom

- Every element has a unique spectrum.
- Thus we can use spectra to identify elements.



Atomic Spectra and the Bohr Atom

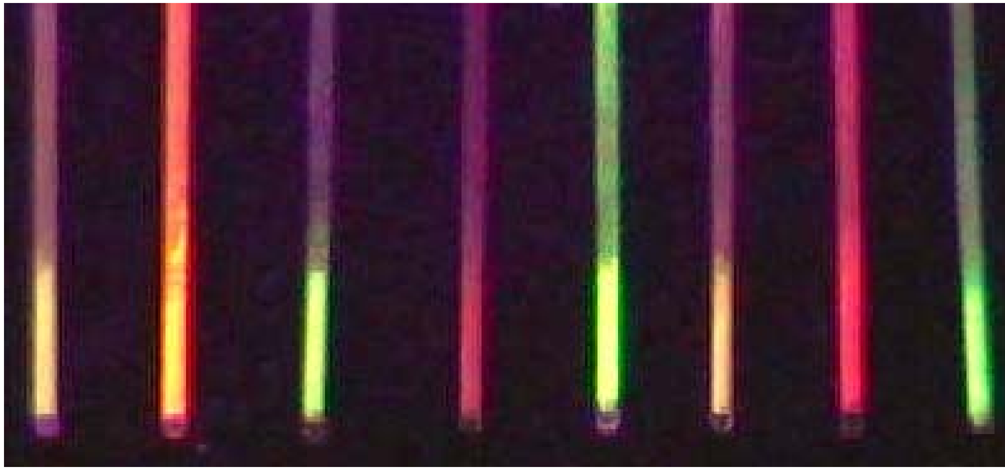
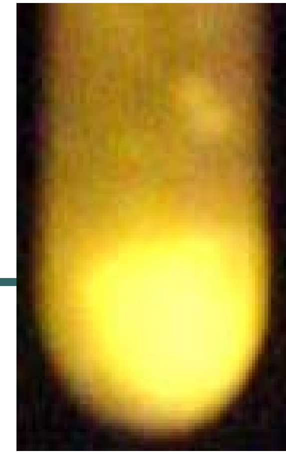
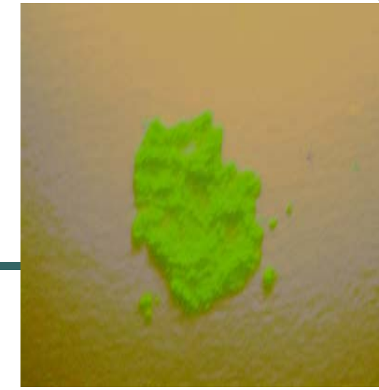
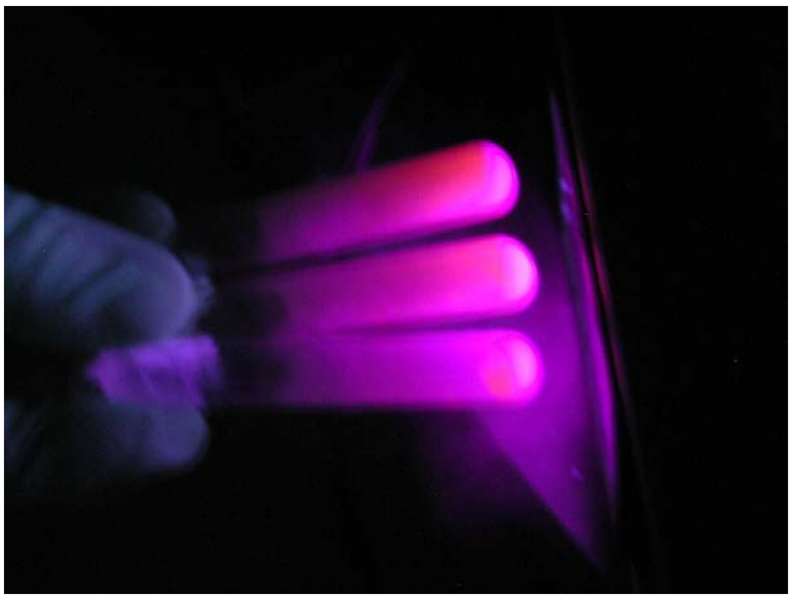
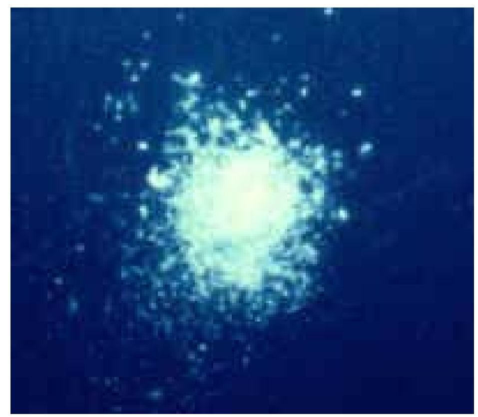
- An orange line of wavelength 5890 Å is observed in the emission spectrum of sodium. What is the energy of one photon of this orange light?

$$\lambda = 5890\ \text{Å}\left(\frac{1\times 10^{-10}\ \text{m}}{\text{Å}}\right) = 5.890\times 10^{-7}\ \text{m}$$

$$E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{\left(6.626\times 10^{-34}\ \text{J}\cdot\text{s}\right)\left(3.00\times 10^{8}\ \text{m/s}\right)}{5.890\times 10^{-7}\ \text{m}}$$

$$= 3.375\times 10^{-19}\ \text{J}$$


Gold complexes under UV or "black" light

Atomic Spectra and the Bohr Atom

- The Rydberg equation is an empirical equation that relates the wavelengths of the lines in the hydrogen spectrum.

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

R is the Rydberg constant

$$R = 1.097 \times 10^7 \text{ m}^{-1}$$

$$n_1 < n_2$$

n's refer to the numbers of the energy levels in the emission spectrum of hydrogen

Atomic Spectra and the Bohr Atom

- What is the wavelength of light emitted when the hydrogen atom's energy changes from n = 4 to n = 2?

$$n_2 = 4 \text{ and } n_1 = 2$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \text{ m}^{-1}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \text{ m}^{-1}\left(\frac{1}{4} - \frac{1}{16}\right)$$

Atomic Spectra and the Bohr Atom

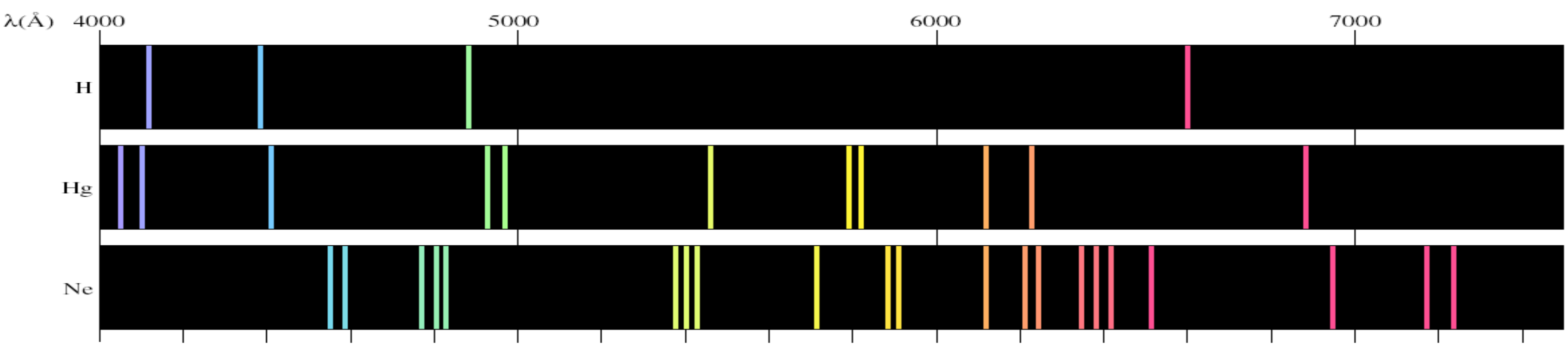
Notice that the wavelength calculated from the Rydberg equation matches the wavelength of the green colored line in the H spectrum.

$$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \mathrm{m}^{-1}\left(0.250 - 0.0625\right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \mathrm{m}^{-1}\left(0.1875\right)$$

$$\frac{1}{\lambda} = 2.057 \times 10^{6}\ \mathrm{m}^{-1}$$

$$\lambda = 4.862 \times 10^{-7}\ \mathrm{m}$$



Atomic Spectra and the Bohr Atom

- In 1913 **Neils Bohr** incorporated Planck’s quantum theory into the hydrogen spectrum explanation.
- Here are the postulates of Bohr’s theory.

1. Atom has a number of definite and discrete energy levels (orbits) in which an electron may exist without emitting or absorbing electromagnetic radiation.

    As the orbital radius increases so does the energy

    1<2<3<4<5......

Atomic Spectra and the Bohr Atom

2. An electron may move from one discrete energy level (orbit) to another, but, in so doing, monochromatic radiation is emitted or absorbed in accordance with the following equation.

$$E_2 - E_1 = \Delta E = h\nu = \frac{hc}{\lambda}$$

$$E_2 > E_1$$

Energy is absorbed when electrons jump to higher orbits.

n = 2 to n = 4 for example

Energy is emitted when electrons fall to lower orbits.

n = 4 to n = 1 for example

Atomic Spectra and the Bohr Atom

3. An electron moves in a circular orbit about the nucleus and it motion is governed by the ordinary laws of mechanics and electrostatics, with the restriction that the angular momentum of the electron is quantized (can only have certain discrete values).

Atomic Spectra and the Bohr Atom

- Light of a characteristic wavelength (and frequency) is emitted when electrons move from higher E (orbit, n = 4) to lower E (orbit, n = 1).
  - This is the origin of **emission spectra**.
- Light of a characteristic wavelength (and frequency) is absorbed when electron jumps from lower E (orbit, n = 2) to higher E (orbit, n= 4)
  - This is the origin of **absorption spectra**.

Atomic Spectra and the Bohr Atom

- Bohr's theory correctly explains the H emission spectrum.
- <u>The theory fails for all other elements</u> because it is not an adequate theory.

The Wave Nature of the Electron

- In 1925 Louis de Broglie published his Ph.D. dissertation.
  - A crucial element of his dissertation is that electrons have wave-like properties.
  - The electron wavelengths are described by the de Broglie relationship.

$$\lambda = \frac{h}{mv}$$

$$h = \text{Planck's constant}$$

$$m = \text{mass of particle}$$

$$v = \text{velocity of particle}$$

The Wave Nature of the Electron

- De Broglie's assertion was verified by Davisson & Germer within two years.
- Consequently, we now know that electrons (in fact - all particles) have both a particle and a wave like character.
    - This wave-particle duality is a fundamental property of submicroscopic particles.

The Wave Nature of the Electron

- Determine the wavelength, in m, of an electron, with mass 9.11×10^{-31} kg, having a velocity of 5.65×10^{7} m/s.
  - Remember Planck's constant is 6.626×10^{-34} Js which is also equal to 6.626×10^{-34} kg m^2/s^2.

$$\lambda = \frac{\mathrm{h}}{\mathrm{mv}}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ \mathrm{kg\,m^2 \cdot s^2}}{\left(9.11 \times 10^{-31}\ \mathrm{kg}\right)\left(5.65 \times 10^{7}\ \mathrm{m/s}\right)}$$

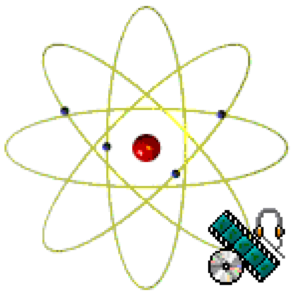
$$\lambda = 1.29 \times 10^{-11}\ \mathrm{m}$$

The Quantum Mechanical Picture of the Atom

- Werner Heisenberg in 1927 developed the concept of the Uncertainty Principle.
- It is impossible to determine simultaneously both the position and momentum of an electron (or any other small particle).
  - Detecting an electron requires the use of electromagnetic radiation which displaces the electron!
    - Electron microscopes use this phenomenon

The Quantum Mechanical Picture of the Atom

- Consequently, we must must speak of the <u>electrons' position</u> about the atom in terms of <u>probability functions</u>.
- These <u>probability functions</u> are represented as <u>orbitals</u> in quantum mechanics.



The Quantum Mechanical Picture of the Atom

Basic Postulates of Quantum Theory

1. Atoms and molecules can exist only in certain energy states. When an atom or molecule changes its energy state, it must emit or absorb just enough energy to bring it to the new energy state (the quantum condition).

The Quantum Mechanical Picture of the Atom

2. Atoms or molecules emit or absorb radiation (light) as they change their energies. The frequency of the light emitted or absorbed is related to the energy change by a simple equation.

$$E = h\nu = \frac{hc}{\lambda}$$

The Quantum Mechanical Picture of the Atom

3. The allowed energy states of atoms and molecules can be described by sets of numbers called the four quantum numbers.

- Quantum numbers are the solutions of the Schrodinger, Heisenberg & Dirac equations.

Schrödinger equation

$$-\frac{b^2}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial^2 x}+\frac{\partial^2\Psi}{\partial^2 y}+\frac{\partial^2\Psi}{\partial^2 z}\right)+\mathrm{V}\Psi=\mathrm{E}\Psi$$

Chemistry is fun!