CHM 403: Quantum Chemistry

Quantum theory of radiation

Course Outline

i. Concept of quantum radiation

ii. Black body radiation

iii. Photoelectric effect

iv. Simple calculations on photoelectric effect

By Dr. E.A. Ofudje
eaofudje@mtu.edu.ng

- When light strikes on any surface of a body, part of the radiant energy is absorbed, part is reflected and the remaining is transmitted.
- A black body is a material that absorbs or emits at all incident (frequencies) of radiation.
- Max Plank in 1900 proposed the black body radiant energy and according to him, light radiation was produced discontinuously by the molecules of the hot body, each of which was vibrating with specific frequency which increased with temperature.

❖Thus a hot body radiates energy **not in a continuous waves but in a small unit of** (2) **waves called quanta or quantum**.

❖ The general quantum theory of EMR states that when atoms or molecules absorbed or emits radiant energy, they do so in a separate units of waves called quanta or photons.

The energy E, of a quantum/photon is given by:

$E = hv$ (1)

Where v is the frequency of the emitted radiation and h is Planck's constant

The value of h = 6.62×10^{-27} ergsec or 6.62×10^{-34} Jsec

But, c which is the velocity of light or radiation is given by the equation

$c = \lambda$ and $v = c/\lambda$

Substitute this into equation 1

$$E = \frac{hc}{\lambda} \qquad (3)$$

Example: Calculate the frequency and energy of the photon or quantum associated with light of wavelength 6057.8A° (1A° = 10^{-8} cm).

Solution:

(i) Using v = c/λ

$$v = \frac{3x10^{10}}{6057.8x10^{-8}}$$

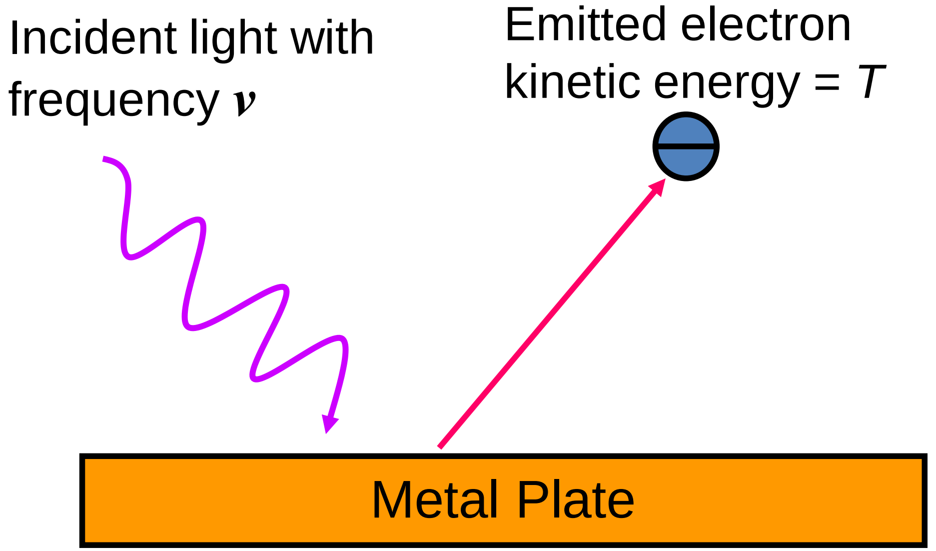
v = 4.952 x 10^{14} sec^{-1}

(ii) Energy $E = hv$ $\quad E = 6.625x10^{-27}x4.952x10^{14}$

$$E = 3.281x10^{12}erg$$

PHOTOELECTRIC EFFECT

Albert Einstein 1905 used Plank idea of quantization to explain his findings on photoelectric effect. When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface and this phenomenon is known as photoelectric effect and the ejected electrons as photo electrons.



The following observations can be made:

- An increase in the intensity of incident light does not increase the energy of the photo electrons; it merely increases their rate of emission.
- The kinetic energy of the photo electrons increases linearly with the frequency of the incident light.

•No electron will be ejected irrespective of the light intensity unless the threshold frequency is exceeded.

•The total energy of the ejected electrons is the sum of the amount of energy needed to free the electrons (the binding energy hv_o) and the kinetic energy due to its velocity i.e

$$hv = hv_o + \tfrac{1}{2}mv^2 \qquad (4)$$

Where v_o is the threshold frequency. Note that hv is also the energy of the incoming photon and hv_o is the minimum energy for an electron to escape from the metal. On rearrangement, we have:

$$\tfrac{1}{2}mv^2 = hv - hv_o \qquad (5)$$

hv_o is a constant for a particular solid and is designated as W i.e the work function

Therefore, $\frac{1}{2}mv^2 = hv - W$

If $hv < hv_o$ (when the frequency of light is less than threshold value), then there will be no electrons emitted. This implies that enough energy is needed to overcome the bonding energy holding the electrons to the metal surface.

On the other hand, if $hv_o < hv$, greater intensity means that more energies are available, hence more electrons will be released.

Example 1: What is the maximum energy that photons must possess in order to produce photo electric effect with platinum metal? Given that the threshold frequency for platinum is 1.3 x 10^{15} sec^{-1}.

Solution

The threshold frequency (v_o) is the lowest frequency that photons may possess to produce the photoelectric effect and the energy corresponding to this frequency is the minimum energy (E).

$$E = h\nu_o$$

E = 6.625 x 10^{-27} ergsec^{-1} x 1.3 x 10^{15} sec

E = 8.6 x 10^{-12} erg

Example 2: calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function = 3.62 x 10^{-12} erg) by light of wavelength 5.5 x 10^{-8}cm.

Solution

$$\tfrac{1}{2}mv^2 = h\nu - W; but \quad \nu = \frac{c}{\lambda}$$

$$\nu = \frac{3.0x10^{10}\, cm \sec^{-1}}{5.5x10^{-8}\, cm} \qquad \nu = 5.5x10^{17} \sec$$

$$K.E. = (6.6x10^{-27}\, erg)(5.5x10^{17}) - (3.62x10^{-12})$$

K.E. = 3.63 x 10^{-9} erg

Note that in photoelectric effect;

i. if UV light is used, electrons are emitted, but

ii. if visible light is used, no electrons are emitted no matter how bright the light

Light is also quantized

- light seems to carry energy in discrete packets
- we call these packets photons and in this sense, light behaves like a particle,
- but light also has many wave-like properties
- particle-wave duality: it is both at the same time!

whenever radiation interacts with matter, it displays particle like properties.(Black body radiation and photoelectric effect)

When a white light is passed through a prism, it splits into a series of coloured bands known as spectrum.

Spectrum is of two types: continuous and line spectrum

- ✓ The spectrum which consists of all the wavelengths is called continuous spectrum.
- ✓ A spectrum in which only specific wavelengths are present is known as a line spectrum. It has bright lines with dark spaces between them.

•

Electromagnetic spectrum is a continuous spectrum. It consists of a range of electromagnetic radiations arranged in the order of increasing wavelengths or decreasing frequencies.

It extends from radio waves to gamma rays.

Spectrum is also classified as emission and Absorption spectrum.

• **Emission spectrum:** The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.

Absorption spectrum is the spectrum obtained when radiation is passed through a sample of material.

The sample absorbs radiation of certain wavelengths. The wavelengths which are absorbed are missing and come as dark lines.

The study of emission or absorption spectra is referred as spectroscopy.

More exercise

1. Calculate wave number of yellow radiations having wavelength of 5800 A^0. Ans. 1.72×10^6 m^{-1} (Wavelength = 5800 A^0= 5800×10^{-10} m).
2. Find energy of each of the photons which
(i) correspond to light of frequency 3×10^{15}Hz.
(ii) have wavelength of 0.50 Å, given that Planck's constant = 6.626×10^{-34}Js. (Ans. (i) 1.988×10^{-18}J and (ii) 3.98×10^{-15}J)

3. State photo electric effect. The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. (c) If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron. (Ans (a) 6.53×10^{-7} m or 653 nm, (b) $4.593 \times 10^{14} s^{-1}$ and (c) 9.3149×10^{-20} J

$$W_0 = \frac{hc}{\lambda_0}$$

Where,

λ_0 = threshold wavelength h = Planck's constant

c = velocity of radiation

Substituting the values in the given expression of (λ_0):

$$W_0 = h\nu_0$$

Kinetic energy = h ($v - v_0$)

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$