ELECTROMAGNETIC RADIATION

Electromagnetic radiations can interact with matter in various ways. Each interaction gives us insights about certain properties of the matter and use of electromagnetic radiations of different energies can give different information about the matter under study. Different regions of electromagnetic spectrum have different kinds of spectroscopic techniques associated with them (Figure 1 & 2).

Radiowaves :   ESR and NMR spectroscopy

Microwaves :   Rotational spectroscopy.

Infrared waves :   IR spectroscopy

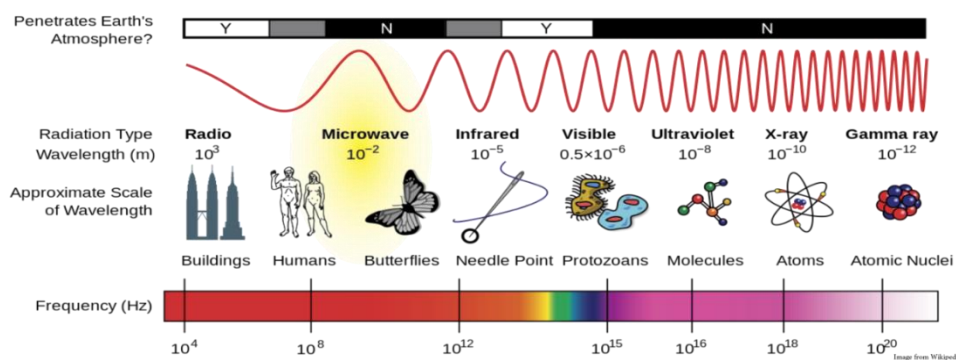UV/ VIS waves :   UV/VIS spectroscopy
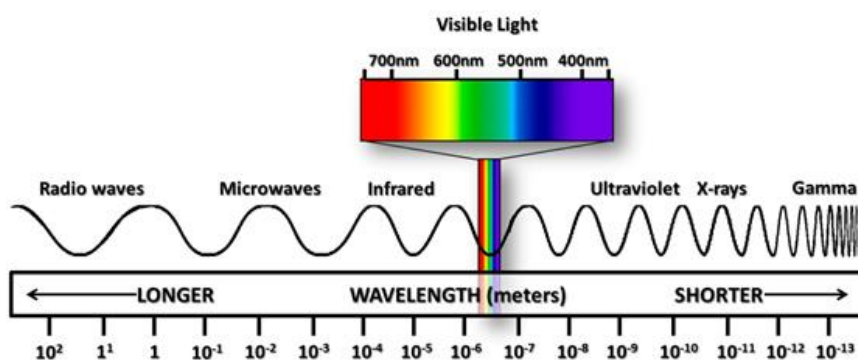

Figure 1. Electromagnetic spectrum

Figure 2. Electromagnetic spectrum

The visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of

electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength.

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave travelling through space is represented by a sinusoidal trace (Figure 3). A wave is an oscillating displacement that depends on position and time. A region of positive displacement is called a *crest*, and a region of negative displacement is called a *trough*. A location where the displacement of a wave equals zero is called a *node*. The distance from one crest to the next is called the *wavelength* λ. The distance A is known as the maximum amplitude of the wave. The *period* τ of a wave is the time for the first return of the oscillating object to an initial state. The *frequency* (ν) is the reciprocal of the period, or the number of oscillations per second. Although a wave is frequently characterized in terms of its wavelength λ, often the terms such as wavenumber ($\bar{\nu}$), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.
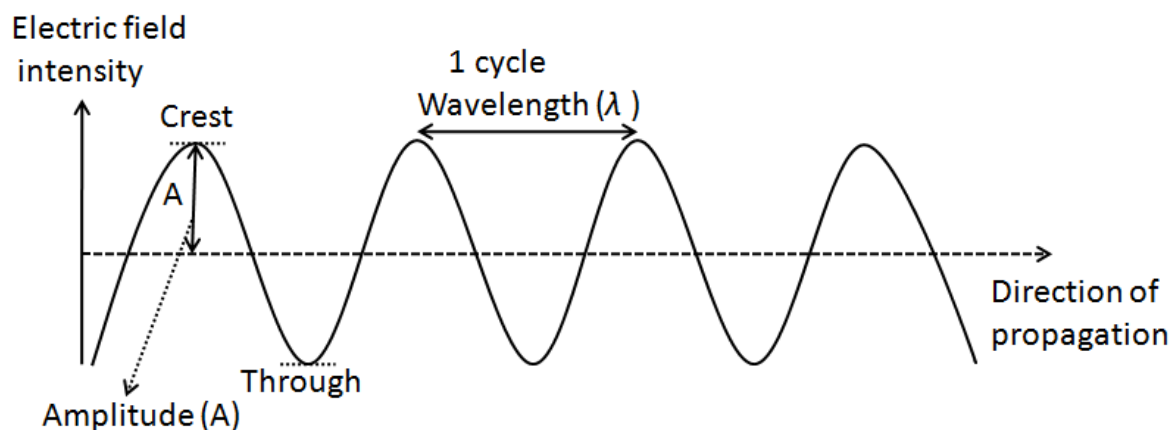

Figure 3. Wave like propagation of light (λ = wavelength, A = amplitude)

$$1 \text{ Å} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

The four quantities wavelength, wavenumber, frequency and velocity can be related to each other by following relationships

$$\text{Wavelength } (\lambda) = 1 / \bar{\nu} = c / \nu$$

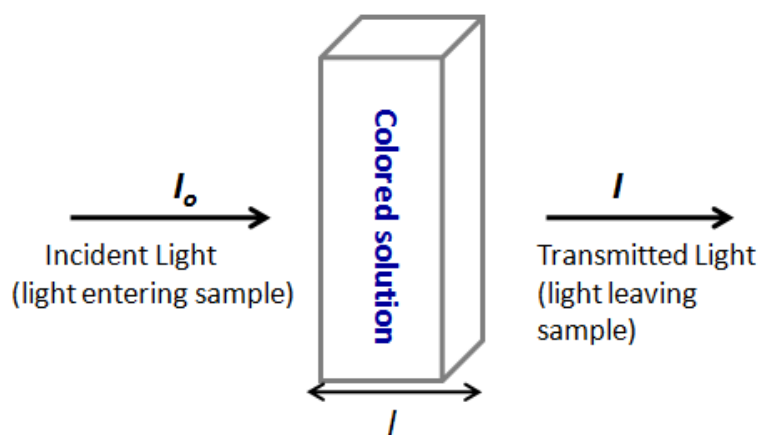$$\text{Wave-number } (\bar{\nu}) = 1 / \lambda = \nu / c$$

Frequency $(\nu) = c / \lambda = c\bar{\nu}$

Velocity $(c) = \nu \lambda = \nu / \bar{\nu}$

THE ABSORPTION LAW

BEER-LAMBERT LAW

In optics, that portion of physics that deals with the properties of light, the measurement of the number of photons delivered at a point in a given unit of time is called the Intensity, I. (Higher intensity could be thought of as "brighter" and lower intensity could be thought of as "dimmer"; hence high intensity light will be bright and low intensity light will be dim.) If we measure the intensity of the beam of light entering our sample (I_o) and compare it with the intensity of the beam of light exiting our sample (I) we can take the ratio I/I_o to get an indication of what fraction of the light entering the sample was found exiting the sample. This ratio is called the Transmittance:

Transmittance T $= \dfrac{I}{I_o}$

We can convert this ratio into a percentage by multiplying by 100 to get Percent Transmittance (% T):

% Transmittance: % T $= \dfrac{I}{I_o}$ x 100

Thus if the intensity of the light exiting our sample is 76 and the intensity of the light entering our sample is 100, then the Transmittance would be 0.76 and the % Transmittance would be 76 %, indicating that 76 % of the photons entering our sample are finding their way out of our sample.

For our purposes it is mathematically convenient to define a new concept, Absorbance (A):

$$\text{Absorbance: } A = -\log_{10}\frac{I}{I_0} = -\log_{10}T$$

Absorbance is a direct measure of how much light is absorbed by our sample. If you play with the formula in your calculator you will find that absorbance can take on values between 0 (at 100% Transmittance) and about 2.0 (at 1% Transmittance); thus large values of absorbance are associated with very little light passing entirely through the sample and small values of absorbance (i.e. those approaching 0) are associated with most of the light passing entirely through the sample.

Beer-Lambert Law

When a monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with the thickness of the absorbing solution is proportional to the intensity of the incident radiation as well as the concentration of the solution.

Mathematically, this law is stated as

$$-\frac{dI}{dl} = kIc$$

Where, c = conc. of the solution in moles lit^{-1}. k = molar absorption coefficient. I = intensity of radiation after passing through a thickness l of the solution. dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness dl of the medium. $-\frac{dI}{dl}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium. k = absorption coefficient

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{l=0}^{l=l} kc\,dl$$

$$\ln \frac{I}{I_o} = -kcl$$

$$\log \frac{I_o}{I} = \frac{k}{2.303} cl$$

$$\log \frac{I_o}{I} = \varepsilon cl$$

The constant ε is called the molar *absorption coefficient* or *extinction coefficient*, by writing

$$\frac{k}{2.303} = \varepsilon$$

The ratio of the transmitted intensity to the incident intensity, $\dfrac{I}{I_o}$ is called the **transmittance, T,** $\log T = -\varepsilon cl$

The **absorbance** (or **optical density**) of the species, $A = -\log \dfrac{I}{I_o}$

VALIDITY OF BEER LAMBERT LAW

✓ This law is valid for dilute solutions

✓ This law is valid for monochromatic light only and for each wavelength there will be corresponding value of ε.

✓ This law is valid except when very high intensities of radiation are employed (e.g lasers).
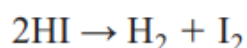
LIMITATIONS OF BEER LAMBERT LAW

This law is not obeyed

✓ When different forms of the absorbing molecules are in equilibrium as keto-enol tatutomers.

✓ When fluorescent compound are present

✓ When solute and solvent form complexes through some sort of association

Example 1. 2.5 X 10^{-4} M solution of a substance in a1 cm length cell at λ_{max} = 245 nm has absorbance 1.17, Calculate ε_{max} for this solution.
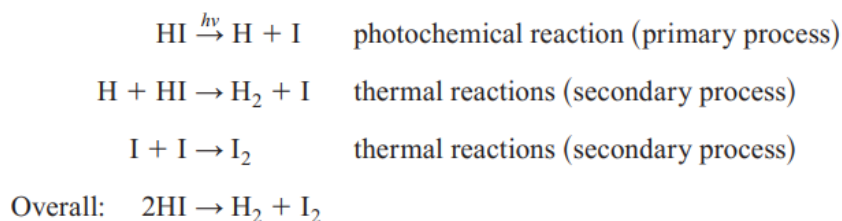
Photochemistry is the study of chemical reactions produced by light. Absorption of a photon of light may raise a molecule to an excited electronic state, where it will be more likely to react than in the ground electronic state. In **photochemical reactions,** the activation energy is supplied by absorption of light. In **thermal reactions,** in which the activation energy is supplied by intermolecular collisions.

Primary Versus Secondary Processes

Photochemical reactions are subclassified as *primary* or *secondary processes*. Primary processes include vibrational relaxation, or loss of vibrational energy, by collision with other molecules; fluorescence; phosphorescence; isomerization; and dissociation. Dissociation of excited molecules may provide reactive intermediates that can undergo secondary processes of a thermal nature. Let us illustrate the primary and secondary processes with the decomposition of hydrogen iodide in the gas phase. The overall reaction is

$$2HI \rightarrow H_2 + I_2$$

When light of the appropriate wavelength is applied, the reactions are

$$HI \xrightarrow{hv} H + I \quad \text{photochemical reaction (primary process)}$$
$$H + HI \rightarrow H_2 + I \quad \text{thermal reactions (secondary process)}$$
$$I + I \rightarrow I_2 \quad \text{thermal reactions (secondary process)}$$
$$\text{Overall:} \quad 2HI \rightarrow H_2 + I_2$$

here *hv* represents the energy of the photon absorbed.

EINSTEIN'S LAW

A photochemical reaction involves excitation of the reactant species up and over an activation energy barrier before transmission to the product state. In a photochemical reaction, the *activation energy* is supplied by incident light instead of ambient heat. The Bohr–Einstein concept of a particle of light (a photon) carrying a *quantum* of energy $E = hv$ leads one to suppose that the energy of an incident light particle is concentrated in one reactant molecule

only, rather than being distributed evenly over an entire collection of molecules. This mechanism of energy transmission means that if the quantum E is sufficiently large, all struck molecules will acquire the activation energy and the number of molecules reacting will be equal to the number of photons striking and retained by the system. This is Einstein's law.

molecules reacting = photons absorbed

Laws of Photochemistry

The effects of radiation on chemical reactions are governed by two laws. These are:

Grothus-Draper Law:

This law is referred to as the "first law of photochemistry". This law was given by Grothus in the year 1818 and was later reaffirmed by J.W. Draper in 1841. The law may be stated as: "When light falls on any substance, only a fraction of it is absorbed whereas the rest is either reflected or transmitted. It is only the absorbed light which is effective in bringing about a chemical reaction."

It is not necessary that the absorbed light will always lead to a chemical reaction. The absorbed light may simply get transformed into thermal energy or may bring about phenomena such as fluorescence, phosphorescence, etc. It is also observed in few cases that the reacting substance does not absorb the light energy directly. The energy is first absorbed by some other substance which is present along with the reacting substance and thereafter it is transferred into the reacting substance. This phenomenon is called photosensitization.

Stark-Einstein Law:

Most photochemical reactions are governed by the *Stark–Einstein law of photochemistry*, which states that absorption of one photon causes the reaction of one molecule. However, the number of molecules that react is not necessarily equal to the number of photons absorbed. Some of the excited molecules might undergo internal conversion, intersystem crossing, fluorescence, or phosphorescence processes leading to unreactive states and therefore not react chemically. A *chain reaction* might occur in which the reaction of one molecule can lead to the reaction of other molecules without absorption of additional radiation.

The *quantum yield* of a photochemical reaction, Φ, is defined by

$$\emptyset = \frac{Number\ of\ molecules\ reacted}{Number\ of\ photon\ absorbed}$$

Equation (23.6-1) can also be stated in terms of moles of reactant and moles of photons. One mole of photons is called an *einstein*, so that

$$\emptyset = \frac{Amount\ reacted\ in\ moles}{Amount\ of\ photon\ absorbed\ in\ einstein}$$

In a chain reaction, Φ can exceed unity, but in a nonchain reaction, $\Phi \leq 1$.

When a quantum yield is less than 1, as in the first entry in Table 21.1, we suppose that there are energy dissipating processes going on. In a complicated molecule, the quantum of incident energy may be split up among several degrees of freedom and dissipated eventually as heat. In some molecules, a part of the incoming quantum of energy is reemitted as light. The system might emit part of the excitation energy as light and the remainder as heat.
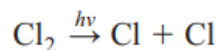
TABLE Some Experimental Quantum Yields

Reaction	Quantum Yield
$(CH_3)_2C{=}O \rightarrow CH_3C^\bullet{=}O + {}^\bullet CH_3$	0.17
$CH_3COOH \rightarrow CH_4 + CO_2$	1
$H_2 + Cl_2 \rightarrow 2HCl$	$\sim 10^5$

The quantum yield of photochemical reactions varies greatly from one system to another, and the value of Φ often reveals the mechanism involved in the process. For the hydrogen iodide reaction discussed above, the quantum yield is 2 because the absorption of one photon leads to the removal of two reactant molecules (HI). When irradiated with UV light at about 280 nm, acetone forms a methyl and an acetyl radical with high yield:

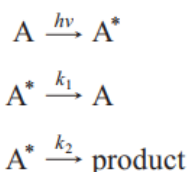$$(CH_3)_2CO \xrightarrow{h\nu} CH_3\cdot + CH_3CO\cdot$$

In the liquid phase, however, these radicals are likely to recombine because of the solvent cage effect. Therefore, the overall quantum yield for this reaction is below 0.1.

A mixture of gaseous hydrogen and chlorine is stable at room temperature. When exposed to visible or UV light ($\leq$ 400 nm), the gases react explosively to form hydrogen chloride. The mechanism is

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$

$$Cl + H_2 \rightarrow HCl + H \qquad\qquad\qquad (a)$$

$$H + Cl_2 \rightarrow HCl + Cl \qquad\qquad\qquad (b)$$

This is a chain reaction in which the propagation steps are (a) and (b). The quantum yield of this reaction is about 10^5! In general, a quantum yield greater than 2 is evidence of a chain mechanism.

Alternatively, a photochemical reaction can be analyzed in terms of rate constants. Consider the following situation,
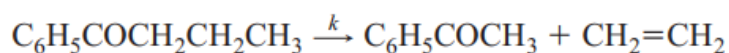
$$A \xrightarrow{h\nu} A^*$$

$$A^* \xrightarrow{k_1} A$$

$$A^* \xrightarrow{k_2} product$$

where A is the reactant, and A* is an electronically excited molecule. Assuming steady-state conditions, we write

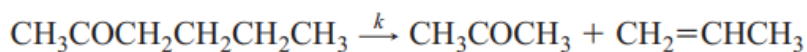$$\text{rate of formation of } A^* = \text{rate of removal of } A^*$$

$$= k_1[A^*] + k_2[A^*]$$

The quantum yield of product formation is given by

$$\Phi_P = \frac{\text{rate of product formation}}{\text{total rate of formation of } A^*}$$

$$= \frac{k_2[A^*]}{k_1[A^*] + k_2[A^*]} = \frac{k_2}{k_1 + k_2}$$

Note that photochemical efficiency as measured by Φ and photochemical reactivity as measured by rate constant are not fundamentally related. Two reactions may have very similar Φ values but differ greatly in their rate constants. Consider the following photochemical decompositions:

$$C_6H_5COCH_2CH_2CH_3 \xrightarrow{k} C_6H_5COCH_3 + CH_2{=}CH_2$$

$$\Phi = 0.40 \quad k = 3 \times 10^6 \text{ s}^{-1}$$

$$CH_3COCH_2CH_2CH_2CH_3 \xrightarrow{k} CH_3COCH_3 + CH_2{=}CHCH_3$$

$$\Phi = 0.38 \quad k = 1 \times 10^9 \text{ s}^{-1}$$

References

✓ Chang, Raymond. *Physical chemistry for the chemical and biological sciences.* University Science Books, 2000.

✓ Levine, I. N. Physical Chemistry, Tata McGraw-Hill

✓ Mortimer, R. G. Physical Chemistry, Elsevier

[The information, including the figures, are collected from the above references and will be used solely for academic purpose.]