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Introduction to Spectroscopy (Spectrometry)

1.1 Spectroscopy and Electromagnetic Radiations

Organic chemists use spectroscopy as a necessary tool for structure determination. Spectroscopy may be defined as the *study of the quantized interaction of electromagnetic radiations with matter.* Electromagnetic radiations are produced by the oscillation of electric charge and magnetic field residing on the atom. There are various forms of electromagnetic radiation, e.g. light (visible), ultraviolet, infrared, X-rays, microwaves, radio waves, cosmic rays etc.

1.2 Characteristics of Electromagnetic Radiations

All types of radiations have the same velocity (2.998×10^{10} cm/s in vacuum) and require no medium for their propagation, i.e. they can travel even through vacuum. Electromagnetic radiations are characterized by frequencies, wavelengths or wavenumbers.

Frequency ν is defined as the *number of waves which can pass through a point in one second,* measured in cycles per second (cps) or hertz (Hz) (1 Hz = 1 cps).

Wavelength λ is defined as the *distance between two consecutive crests C or troughs T* (Fig. 1.1) measured in micrometer (μm) or micron (μ) (1 μm = 1 $\mu = 10^{-6}$ m), nanometer (nm) or millimicron (mμ) (1 nm = 1 m$\mu = 10^{-9}$ m) and angstrom (Å) (1 Å = 10^{-10} m).

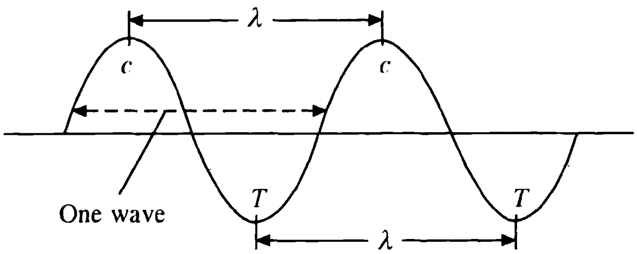

Fig. 1.1 Wavelength λ of an electromagnetic radiation

Wavenumber $\bar{\nu}$ is defined as the *number of waves which can pass through per unit length* usually 1 cm. It is the reciprocal of wavelength expressed in centimeter (cm^{-1}), i.e.

$$\bar{\nu} = \frac{1}{\lambda \text{ (in cm)}}$$

By their definitions, frequency and wavelength are inversely proportional, i.e.

$$\nu \propto \frac{1}{\lambda} \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

where c is velocity of light (2.998×10^{10} cm/s).

Electromagnetic radiation is energy. When a molecule absorbs radiation, it gains energy, and on emitting radiation, it losses energy. The emission or absorption of electromagnetic radiations is quantized and each quantum of radiation is called a quantum or photon. Energy E for a single photon

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

where h is Planck's constant (6.626×10^{-27} erg s).

The higher the frequency (or the shorter the wavelength) of the radiation, the greater is its energy.

Energy for a mole of photons. One mole of photons is one Einstein.

$$E = Nh\nu = \frac{Nhc.}{\lambda \text{ (in cm)}} = Nh\bar{\nu}c \text{ erg}$$

where N is Avogadro's number (6.023×10^{23} molecules/mole).

Or $$E = \frac{Nhc}{\lambda \text{ (in cm)}} = \frac{2.86 \times 10^{-3}}{\lambda \text{ (in cm)}} = \bar{\nu} \times 2.86 \times 10^{-3} \text{ kcal/mole}$$

(4.184×10^7 erg = 4.184 J = 1 cal; 1 eV = 23.06 kcal/mole).

1.3 Solved Problems

1. Convert the following wavelengths into the corresponding wavenumbers in cm^{-1}:

(i) 5 μ and (ii) 10^4 nm

Solution

(i) Wavenumber $\bar{\nu} = \dfrac{1}{\lambda \text{ (in cm)}}$

The given $\lambda = 5$ and $\mu = 5 \times 10^{-4}$ cm

Hence $$\bar{\nu} = \frac{1}{5 \times 10^{-4}} = \frac{1 \times 10^4}{5} = 2000 \text{ cm}^{-1}$$

(ii) Wavenumber $\bar{\nu} = \dfrac{1}{\lambda \text{ (in cm)}}$

The given $\lambda = 10^4 \text{ nm} = 10^4 \times 10^{-7} = 10^{-3}$ cm (1 nm = 10^{-7} cm)

Therefore $$\bar{\nu} = \frac{1}{10^{-3}} = 1 \times 10^3 = 1000 \text{ cm}^{-1}$$

2. Convert wavenumber 1755 cm^{-1} into the corresponding wavelength in μm.

Solution

Wavelength λ (in cm) = $\frac{1}{\bar{\nu}}$

Hence $$\lambda = \frac{1}{1755} = 0.00057 \text{ cm}$$

$$= 0.00057 \times 10^4 \ \mu\text{m} \ (1 \text{ cm} = 10^4 \ \mu\text{m}) = 5.7 \ \mu\text{m}$$

3. Calculate the frequency of the electromagnetic radiations corresponding to the wavelengths (i) 2000 Å and (ii) 4 μm.

Solution

(i) Frequency $\nu = \frac{c}{\lambda}$

The given wavelength 2000 Å = 2000 × 10^{-8} cm (1 Å = 10^{-8} cm)

$$\text{Hence } \nu = \frac{2.998 \times 10^{10} \text{ cm/sec}}{2000 \times 10^{-8} \text{ cm}} = 1.499 \times 10^{15} \text{ per sec}$$

$$= 1.499 \times 10^{15} \text{ Hz (cps) or } 1.499 \times 10^9 \text{ MHz}$$

(ii) $\nu = \frac{c}{\lambda}$

The given wavelength 4 μm = 4 × 10^{-4} cm (1 μm = 10^{-4} cm)

$$\text{Therefore } \nu = \frac{2.998 \times 10^{10} \text{ cm/sec}}{4 \times 10^{-4} \text{ cm}} = 74.95 \times 10^{12} \text{ per sec}$$

$$= 74.95 \times 10^{12} \text{ Hz (cps) or } 74.95 \times 10^6 \text{ MHz}$$

4. Calculate the wavelength in Å of an electromagnetic radiation having frequency 7 × 10^{14} Hz.

Solution

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{10} \text{ cm/sec}}{7 \times 10^{14} \text{ Hz (cps)}} = 0.4283 \times 10^{-4} \text{ cm or } 4283 \text{ Å } (1 \text{ cm} = 10^8 \text{ Å})$$

5. Calculate the energy associated with an ultraviolet radiation having wavelength 250 nm. Give the answer in kcal/mole and also in kJ/mole.

Solution

$$E = \frac{Nhc}{\lambda \text{ (in cm)}} = \frac{2.86 \times 10^{-3}}{\lambda \text{ (in cm)}} \text{ kcal/mole}$$

The given λ = 250 nm = 250 × 10^{-7} cm (1 nm = 10^{-7} cm)

Hence $$E = \frac{2.86 \times 10^{-3}}{250 \times 10^{-7}} = 114.4 \text{ kcal/mole}$$

$$= 114.4 \times 4.184 = 478.65 \text{ kJ/mole } (1 \text{ kcal} = 4.184 \text{ kJ})$$

6. Calculate the energy associated with an ultraviolet radiation having wavelength 286 mm. Give the answer in kcal/mole and also in kJ/mole.

Solution

$$E = \frac{2.86 \times 10^{-3}}{\lambda \text{ (in cm)}} \text{ kcal/mole}$$

The given λ = 286 mμ = 286 $\times$ 10^{-7} cm (1 mμ = 10^{-7} cm).

Therefore

$$E = \frac{2.86 \times 10^{-3}}{286 \times 10^{-7}} = 100 \text{ kcal/mole or } 100 \times 4.184 \text{ kJ/mole}$$
$$= 418.4 \text{ kJ/mole}$$

1.4 Electromagnetic Spectrum

Electromagnetic spectrum covers a very wide range of electromagnetic radiations from cosmic rays (having wavelengths in fractions of an angstrom) to radio waves (having wavelengths in meters or even kilometers) at the other end. The arrangement of all types of electromagnetic radiations in order of their wavelengths or frequencies is known as the *complete electromagnetic spectrum* (Fig. 1.2).

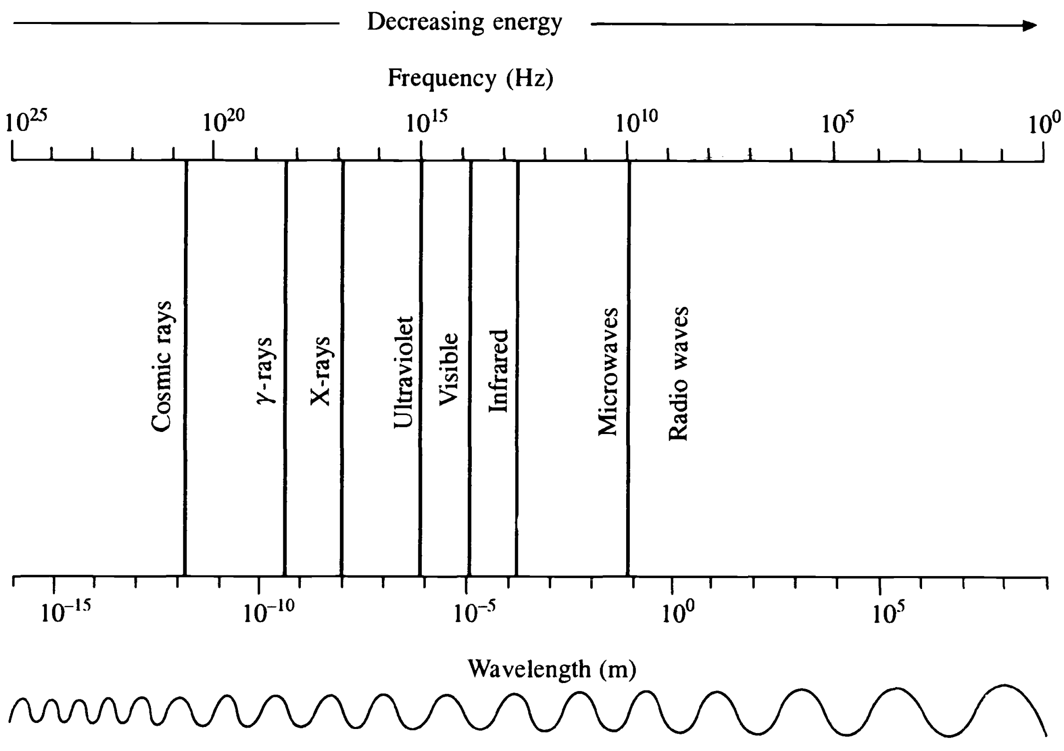

Fig. 1.2 Electromagnetic spectrum

The visible region (400-800 nm) represents only a small portion of the electromagnetic spectrum. Similarly, ulraviolet (UV), X-rays, γ-rays, cosmic rays, infrared (IR), microwaves and radio waves are the other important regions of the electromagnetic spectrum. The apprcximate wavelengths and frequencies of various regions of the electromagnetic spectrum are given in Fig. 1.2. Except the visible region, various regions overlap. The regions of greatest interest to organic chemists are 200-400 nm (ultraviolet), 400-800 nm (visible) and 2.5-15 μ (infrared).

1.5 Absorption and Emission Spectra

When electromagnetic radiations are passed through an organic compound, they may be absorbed to induce electronic, vibrational and rotational transitions in the molecules. The energy required for each of these transitions is quantized. Thus, only the radiation supplying the required quantum (photon) of energy is absorbed and the remaining portion of the incident radiation is transmitted. The wavelengths or frequencies of the absorbed radiations are measured with the help of a spectrometer. Generally, a spectrometer records an absorption spectrum as a plot of the intensity of absorbed or transmitted radiations versus their wavelengths or frequencies. Such spectra which are obtained by absorption of electromagnetic radiations are called *absorption spectra* (Fig. 1.3). UV, visible, IR and NMR spectra are examples of absorption spectra. Absorption band in an absorption spectrum can be characterized by the wavelength at which maximum absorption occurs and the intensity of absorption at this wavelength.

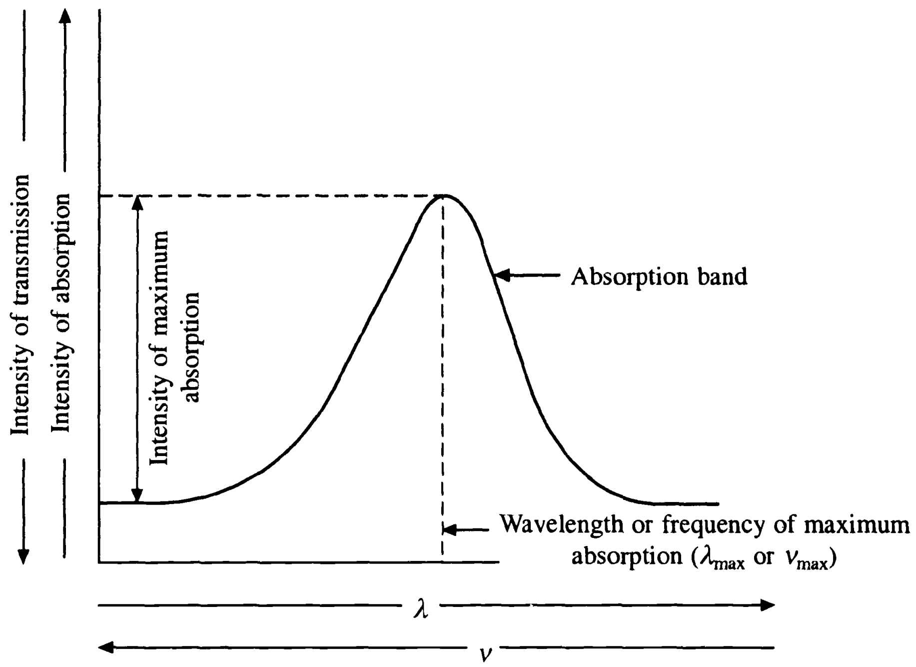

Fig. 1.3 Schematic absorption spectrum

The spectra which are obtained by emission of electromagnetic radiations from the excited substances are known as *emission spectra*, like atomic emission spectra. The excitation is caused by heating the substance to a high temperature either thermally or electrically. The excited substance emits certain radiations when it comes to the ground state and a spectrometer records these radiations as an emission spectrum.