

Spectroscopy

Definition : Spectroscopy may be defined as the interaction between the matter and electromagnetic radiations. The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is known as complete electromagnetic spectrum. The visible spectrum represents only a small portion of the electromagnetic spectrum.

Advantages :

1. Spectroscopic methods take much less time.
2. For spectroscopic analysis, only a very small amount of the substance is sufficient.

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1. The substance remains generally unaffected or unchanged during spectroscopic examination and can be re-used for other tests, if required.
2. The spectroscopic methods are comparatively much reliable in establishing the structure and identity of a compound.

Classification of Electronic Spectra :

Electronic spectra can be classified into following two types: (1)

Emission spectra

(2) Absorption spectra

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Types of Absorption Spectra :

(i) Visible and ultra-violet radiations : cover the wavelength range from 200-800 m μ . The absorption of radiation in this region causes the excitation of π -electron in a conjugated or an unconjugated system, the separation between the ground state and the excited energy level will be less and hence absorption occurs at a longer wavelength. Also carbonyl group of an aldehyde or a ketone absorbs at some characteristic wavelengths. Thus, an ultra-violet or visible spectrum is quite useful for the detection of conjugation, Carbonyl group etc.

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(ii) The Infra-red radiations which cover the wavelength range from 0.8 to 2.5 μ constitute near Infrared region and that from 15 to 25 μ is called far Infrared region. The most useful region for Infrared spectroscopy is 2.5 to 15 μ . The absorption of radiation by an organic compound in this region causes molecular vibrations. The changes in the vibrational levels are accompanied by the changes in the rotational levels. Thus, certain bands appear which characteristically absorb for the stretching vibrations and are very helpful in structure elucidation.

The absorptions at higher wavelength in the infrared region (Finger print region) are most characteristic of a compound and also help in distinguishing one compound from the other.

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(iii) NMR Spectroscopy provides a complete insight into the environment and the arrangement of atoms within a molecule. For this technique, radiations of longest wavelength range i.e., Radiowaves are useful. A sample under investigation is placed in a strong magnetic field and irradiated with Radiowaves.

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ULTRA-VIOLET AND VISIBLE SPECTROSCOPY

The Absorption Laws

- (i) Lambert's law
- (ii) Beer's law

Lambert's law : When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

Mathematically, the law is expressed as.

$$- dl / dx = kl$$

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where I = intensity of radiation after passing through a thickness x , of the medium.

dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium.

$-dI / dx$ = rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = Proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let I_0 be the intensity of radiation before entering the absorbing medium ($x = 0$).

Then I , the intensity of radiation after passing through any thickness, say x of the medium can be calculated as.

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$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k dx$$

or

$$\ln \frac{I}{I_0} = -kx \quad \text{or} \quad \frac{I}{I_0} = e^{-kx}$$

$$I = I_0 e^{-kx}$$

The intensity of the radiation absorbed, I_{abs} is given by.

$$I_{abs} = I_0 - I = I_0 (1 - e^{-kx})$$

The ; natural logarithm to the base 10. , g the

where a = extinction coeff $I = I_0 10^{-ax}$ rbing medium
($a = k / 2.303$)

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Beer's Law

This law states that; when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

Mathematically,

$$-\frac{dI}{dx} = K' Ic$$

where c = conc. of the solution in moles per litre.

k' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.

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Suppose I_0 be the intensity of the radiation before entering the absorbing solution. (when $n = a$), then the intensity of radiation, I after passing through the thickness x , of the medium can be calculated.

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k' c dx$$

$$I = I_0 e^{-k' c x}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 \cdot 10^{-a' c x} \quad \text{or} \quad \log \frac{I_0}{I} = \epsilon c l$$

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Here $k' / 2.303 = a'$ where a' = molar extinction coefficient of the absorbing solution. Beer's law can also be stated as.

When a monochromatic light is passed through a solution of an absorbing substance, its absorption remains constant when the conc (c) and the thickness of the absorption layer (x) are changed in the inverse ratio.

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$$\int_{I_0}^I \frac{dI}{I} = -k c \int_0^l dx$$

$$\ln \frac{I}{I_0} = -k c l$$

$$2.303 \log \frac{I_0}{I} = -k c l$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} c \cdot l = \epsilon \cdot c \cdot l = A$$

Where $\epsilon = k / 2.303$ is called the molar absorptivity coefficient and $\log I_0 / I = A$ is called the absorbance.

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$$A = \epsilon \cdot c \cdot l$$

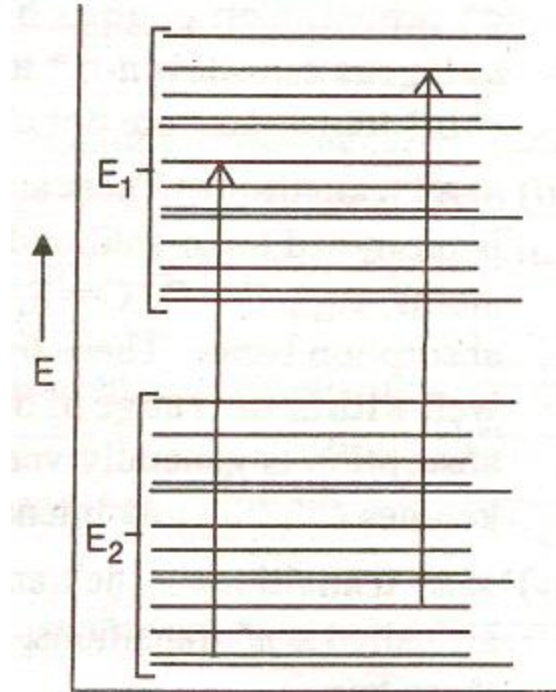
which is Beer-Lambert's law. Thus the absorbance A is directly proportional (i) to the molar concentration c as well as (ii) to the path length l .

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Principle : Absorption of ultraviolet and visible light brings changes in the electronic states of molecules associated with the excitation of an electron from a lower to a higher energy level. Each electronic level in a molecule is associated with a number of vibrational sub-levels (with smaller energy separation) and each vibrational sub-level in turn is associated with a number of rotational sub-levels (with still smaller energy separation). Thus, in its transition to a higher energy level, an electron can go from any of the sub-levels (corresponding to various vibrational and rotational states) in the ground state to any of the sub-levels in the excited state . Had the electronic excitation in the molecule occurred without any accompanying changes in vibrational and rotational sub-levels, the spectrum would have consisted of sharp lines with each line representing a change in electronic state.

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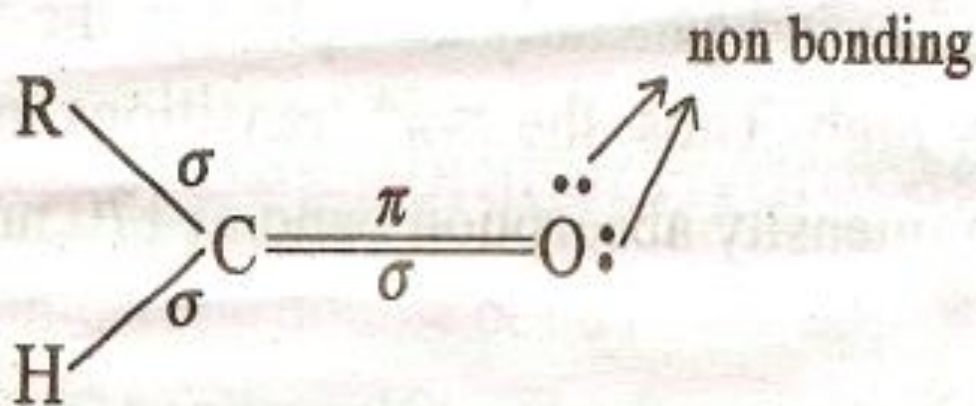
But due to the mixing of vibrational and rotational changes with electronic changes in the molecules, there will be a large number of possible transitions requiring only slightly different energies. This will require the absorption of a large number of wavelengths resulting in the formation of broad bands in the spectrum.



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Electronic Excitations : Electronic transition involves the promotion of an electron from one orbital to another orbital of higher energy. In a molecule, the electron promoted may be a σ -electron, a π -electron or an n-n electron.

Example : Aldehyde



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The higher energy orbitals where the electron can be promoted are those which are vacant in the ground state of the molecule and are commonly called **antibonding molecular orbitals**. The antibonding orbital associated with the σ -bond is called the σ^* orbital and that associated with π -bond is called the π^* orbital. Since the n electrons are not concerned in bond formation, here are no antibonding orbitals associated with them and hence during promotion they may promote either to σ^* or to π^* .

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Types of electronic transitions :

- (i) **σ - σ^* transitions** : The transition in which a σ -electron is excited to an antibonding σ^* orbital are called σ - σ^* transitions. The energy required for these transitions is very high and hence they occur at shorter wavelengths . Thus, the compounds in which all the valence shell electrons are involved in σ bond formation such as saturated hydrocarbons, do not show absorption in the ordinary ultraviolet region.
- (ii) **n - σ^* transition** : These are the excitations from a non-bonding atomic orbital to an antibonding σ^* orbital. Compounds having non-bonding electrons on oxygen, nitrogen, sulphur or halogens can show n - σ^* transitions. These transitions are of lower energy than σ - σ^* transitions.

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- (iii) **n- π^* transition** : These are the transitions in which an electron in a non-bonding atomic orbital is promoted to an antibonding π^* orbital. Compounds having multiple bonds between hetero atoms, *e.g.*, C=O, C=S, N=O, show these transitions which appear as weak absorption bands. These transitions require only small amounts of energy and take place well within the range of ordinary ultraviolet region. The intensity of absorption is very low.
- (iv) **π^* - π^* transition** : The transitions in which a π -electron is excited to an antibonding π^* orbital are called π - π^* transitions. In case of simple molecules containing isolated unsaturated carbons, these transitions require relatively higher energy and generally take place in the far UV region.

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Terms used in UV Spectroscopy :

- 1. Chromophore:** A structural group such as a double bond that can absorb ultraviolet radiations is called a chromophore.
- 2. Bathochromic shift:** When the absorption maximum of a compound shifts to a longer wavelength due to the presence of an auxochrome, the compound is said to have undergone a bathochromic shift or red shift .
- 3. Auxochrome:** An auxillary group that causes bathochromic shift in a chromophore is called an auxochrome.

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- 4. Hypsochromic shift** : When the absorption maximum of a compound shifts to a shorter wavelength on certain treatment, the compound is said to have undergone a hypsochromic shift/ Blue shift .
- 5. Hyperchromic effect** : It is an effect due to which the intensity of absorption of maximum increases.
- 6. Hypochromic effect** : It is an effect due to which the intensity of absorption maximum decreases.

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UV Spectra of Unsaturated Hydrocarbons : Carbon-carbon double bond is the simplest chromophore. Ethylene ($\text{H}_2\text{C}=\text{CH}_2$), has λ_{max} at 165 nm ($\epsilon = 100$). As the value 165 nm lies in the far UV region, such a λ_{max} can be determined only in a special vacuum spectrometer. When a C=C bond is substituted by auxochromic groups like alkyl, there is a bathochromic shift of λ_{max} . When there is an additional double bond in a non-conjugated position, the λ_{max} is almost the same but ϵ is approximately doubled. When these bonds are conjugated as in 1,3, 5-butadiene, there is significant bathochromic shift and the λ_{max} falls in the near UV or visible regions. 1, 3-Butadiene, shows λ_{max} at 217nm There is also a little increase in their ϵ value.

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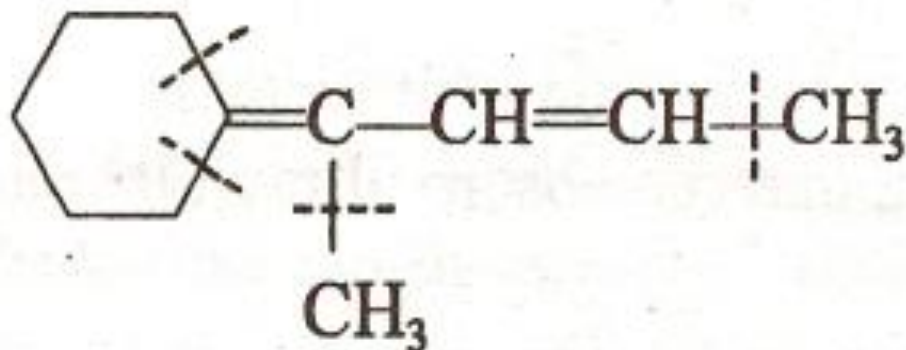
Woodward Rules for Dienes :

The rules are as follows:

1. The basic λ_{max} of conjugated dienes is 217 nm.
2. Add 5 nm for each alkyl substituent on the doubly bonded carbon.
3. Add 5 nm for each exocyclic double bond. In case the same bond is exocyclic to two rings, 2 x 5 nm may be added.

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Example :



Butadiene (Basic Value) = 217 nm

2 Alkyl substituents (2×5) = 10 nm

2 Ring residues = 10 nm

1 Exocyclic double bond = 5 nm

Calculated Value = 242 nm

Observed Value = 242 nm

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Applications of U.V. spectroscopy :

1. U.V. spectroscopy is used for characterizing aromatic compounds and conjugated olefins.
2. It is one of the best way for detecting impurities in organic compounds.
3. U.V. spectroscopy can be used to study the kinetics of chemical reactions.
4. Dissociation constants for weak acids and bases can be determined by U.V. spectroscopy.
5. Structure of chloral can be confirmed by U.V. spectroscopy.
6. **Detection of geometrical isomers:** UV spectroscopy can be used for detecting the geometrical isomers of a given compound. Trans isomers exhibit λ_{\max} at slightly longer wavelengths and have larger extinction coefficients than the cis-isomers.