SPECTROSCOPIC TECHNIQUES AND APPLICATION

Easy

1. Which type of charge is carried by electromagnetic waves?

No charge.

2. Which spectroscopic technique is most useful to identify the presence of known impurity in a drug substance?

NMR

3. What is the full form of MRI

Magnetic Resonance Imaging.

4. Write one name of a molecule which have infrared active vibrations.

NO

Moderate

1. What is fingerprint region range in IR spectra?

1600 – 400 cm^{-1}

2. Which is detected by IR spectra?

Functional group.

Hard

1. What will be the absorbance if % Transmittance = 80?

Absorbance A = log (1/Transmittance) = log (100/80) = 0.097

2. The wavelength of an absorption is 495 nm. In what part of the electromagnetic spectrum does this lie?

UV – Visible range.

5 marks

Easy

1. Intensity of spectral line depends on which factor? What is Lambert – Beer Law?

Intensity of spectral lines depends on

i) It depends on the wave functions of the two states between which the transition occurs i.e. on the transition probability.

ii) It depends on the population in the initial energy level from which transition into other levels occur. Greater is the population in the initial energy level more intense is the spectral lines.

iii) The intensity of spectral lines depends also on the amount of absorbing species giving rise to the spectrum.

Lambert – Beer Law:

Extent of absorption by an absorbing solute in a solution is given by Lambert – Beer Law. If I_0 is the intensity of incident monochromatic radiation of a particular frequency and I_t is the intensity of transmitted radiation then by this law, $I_t = I_0 e^{-kCl}$.

where k is a constant characteristic of the absorbing solute. C is molar concentration of the solute and l is the total length of absorption cell.

Hard

1. Distinguish between diffraction and scattering. What do you understand by an isobestic point? 3 + 2

i) Diffraction is a process observed only in waves, whereas scattering takes place in waves as well as particles.

ii) Diffraction is a coherent process i.e., it requires that the surface must be regular so far as distances are concerned in comparison to the wavelength of the diffracted wave. But scattering is an uncoherent process i.e., it will take place when the surface is rough in terms of distances as compared to wavelength of light.

An isobestic point for different absorption spectra is that point where the wavelength corresponding to those spectra is equal and the corresponding wavelength at this point is called isobestic wavelength.

Moderate

1. What kind of molecules shows IR spectra? “IR spectra is often characterized as molecular finger prints”. Justify statement. 2 + 3

Molecules must possess permanent dipole moment e.g., CO, NO, CN etc. For a diatomic molecule if they don’t have a permanent dipole moment then these molecules during vibration must show a change in the dipole moment. For example, O_2, N_2, H_2, are IR inactive because they are not satisfying either of the above conditions.

Different functional groups produce recognizable peaks at nearly definite positions in IR spectra. Most of the peaks can be assigned due to presence of specific groups in the molecule. So IR spectra can be used in establishing the identity of the compounds e.g., it can be characterized as finger print of the molecule.

15 marks

Moderate

(a)What do you mean by shielding and deshielding effects involved in NMR spectroscopy? 3

(b)Given that the spacing of the lines in the microwave spectrum of $^{27}Al\ ^{1}H$ is constant at 12.604 cm^{-1}. Calculate the moment of inertia and bond length of the molecule. (Mass of ^{27}Al = 26.981 amu). 5

(c) ^{13}C is NMR active while ^{12}C is not. Explain. 2

(d) Predict the kind of electronic transition in (a) Cl_2 and (b) carbonyl group. Also give their intensity. 5

(a) Shielding and deshielding is related to NMR spectra. A hydrogen nuclei is said to be shielded from an external magnetic field if it is in electron rich environment. Proton adjacent to electron withdrawing group are said to be deshielded.

If a nucleus is surrounded by many electrons the magnetic field of the electrons usually opposes the applied magnetic field B_0. So the magnetic field at the nucleus is less than the applied field. The nucleus of interest is said to be shielded by the electrons, this is khown as shielding effect.

(b) Spacing of the lines in microwave spectra for $^{27}Al\ ^{1}H$ = 2B

2B = 12.604 cm^{-1}. So B = 6.302 cm^{-1}

I (moment of inertia) = $h/8\pi^2BC$ = 6.6626×10^{-34} Js /8 x $(3.14)^2$ x (6.302 cm^{-1}) (3 x 10^{10} cms^{-1})

= 4.443×10^{47} Js^2 = 4.443×10^{-47} kgm^2 (since 1J = 1 kg m^2 s^{-2})

Reduced mass $\mu = m_{Al}m_H/(m_{Al} + m_H)$

= (26.98g /mol / N_A) x (1.01g /mol / N_A) / (26.98g /mol / N_A + 1.01g /mol / N_A)

=(26.98 x 1.01)$(g/mol)^2$/ N_A^2 / 1/N_A (26.98 + 1.01) g/mol

$= 1/N_A[(26.98 \times 1.01)/ 27.99]$ g/mol = $(1/6.02 \times 10^{23}/\text{mol}) \times 0.9735$ g/mol

$= 1.617 \times 10^{-24}$ g = 1.617×10^{-27} kg.

$I = \mu r^2$ where r is bond length.

$R = \sqrt{(I/\mu)} = \sqrt{(4.443 \times 10^{-47}\ \text{kgm}^2)/(1.617 \times 10^{-27}\text{kg})} = \sqrt{(2.748 \times 10^{-20}\text{m}^2)} = 1.658 \times 10^{-10}$ m.

So, Moment of inertia (I) = 4.443×10^{-47} kg m^2 ; Bond length (r) = 1.658×10^{-10} m.

(c) ^{12}C does not have a nuclear spin and cannot be used in an NMR experiment. In contrast; its isotope ^{13}C, whose natural abundance is only 1.1%, has a nuclear spin ½.

(d) The transition in Cl_2 are: (i) $\sigma \rightarrow \sigma^*$(allowed transition), which is strong in intensity, (ii) $n \rightarrow \sigma^*$ (forbidden transition) which is weak in intensity.

In C=O group, $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, both are allowed transitions and strong in intensities, whereas $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$, both are forbidden and of weak intensity.

Hard

1. (a) Calculate the force constant for the bond in HCl from the fact that the fundamental vibration frequency is $8.667 \times 10^{13}\ s^{-1}$. 4
   (b) Calculate the energy of one photon of light of wavelength 2450Å. Will it be able to dissociate a bond in diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mole. 6
   (c) Write the principal and application of NMR and MRI. 5

   (a) Fundamental vibration frequency (υ) of HCl is related to force constant (k) by equation
   $\upsilon = 1/2\pi \sqrt{k/\mu}$ where μ is reduced mass of HCl. (Frequency is in Hz $=s^{-1}$)
   Reduced mass of HCl is given by $\mu = m_H m_{Cl}/(m_H + m_{Cl})$
   Where m_H and m_{Cl} are mass of one atom of H and Cl respectively.
   Mass of one atom of H = 1 gm/ N_A = 1gm/ $6.023 \times 10^{23} = 1.66 \times 10^{-24}$ gm
   Mass of one atom of Cl = 35.5 gm/ N_A = 35.5gm/ $6.023 \times 10^{23} = 58.94 \times 10^{-24}$ gm
   So, reduced mass of HCl = $(1.66 \times 10^{-24}$ gm) $(58.94 \times 10^{-24}$ gm)/ $(1.66 + 58.94) \times 10^{-24}$ gm
   $= 97.84 \times 10^{-48}$ gm^2/ 60.6×10^{-24}gm = 1.614×10^{-24} gm.

   $\upsilon = 1/2\pi \sqrt{k/1.614 \times 10^{-24}}$ gm.
   $\upsilon^2 = 1 / 4\pi^2 \times k/ 1.614 \times 10^{-24}$ gm.
   $k = (4\pi^2\upsilon^2) \times (1.614 \times 10^{-24}$ gm.) $= 4 \times (3.14)^2 \times (8.667 \times 10^{13}\ s^{-1})^2 \times (1.614 \times 10^{-24}$ gm.)
   $= 4 \times (3.14)^2 \times (75.12 \times 10^{26}\ s^{-2}) \times (1.614 \times 10^{-24}$ gm.) $= 4781.6 \times 10^2\ g\ s^{-2} = 4.7816 \times 10^5\ g\ s^{-2}$
   $= 4.78 \times 10^5\ gs^{-2} = 4.78 \times 10^5$ dyn cm^{-1} (since 1 dyn = 1 g cm s^{-2}
   We can express force constant (k) in SI unit, that is in Nm^{-1}
   $k = (4.78 \times 10^5) \times (10^{-5N}) \times (10^2 m^{-1})$ since 10^5 dyn = 1N and 10^2 cm = 1m
   $= 478$ N m^{-1}

   (b) Energy of one photon, $\varepsilon = h\upsilon = h\ c/\lambda$ since $c = \upsilon\lambda$
   If h, c and λ all are taken in SI unit then energy ϵ will be obtained in joule (J) which is SI unit of energy.
   $h = 6.626 \times 10^{-34}$ Js , $c = 2.998 \times 10^8$ ms^{-1}
   λ = 2450Å = 2450×10^{-8} cm = $(2450 \times 10^{-8} \times 10^{-2})$ m = 2450×10^{-10}
   $\epsilon = (6.626 \times 10^{-34}$ Js) $\times (2.998 \times 10^8$ ms^{-1}) / $(2450 \times 10^{-10}$ m) = 8.108×10^{-19} J.

   Energy of one mole photon, $E = N_A \epsilon$ where N_A is Avogadro number
   $= (6.023 \times 10^{23}) \times (8.108 \times 10^{-19}$ J)

$= 48.83 \times 10^4$ J = 488.3 kJ

Bond energy of diatomic molecule = 95 kcal / mol = (95 x 4.184) kJ / mol

=397.48 kJ / mol

To break one mole of diatomic molecule 397 kJ energy is required whereas one mole of photon can supply 488 kJ energy. So the radiation of wavelength 2450Å will not be able to dissociate the diamagnetic molecule.

(c) Application of NMR: Nowadays proton NMR spectroscopy is used widely to diagnose disease. Living tissue is rich in proton nucleus ^1H and ^{31}P is also present in the cells. Both the nuclei ^1H and ^{31}P have magnetic moments and can show NMR absorption signals. NMR studies of both these nuclei have found application in medicine. ^{31}P shows wide range of chemical shiefts and its coupling patterns to nearby hydrogens can give structural information in the cell. Disorders in the soft tissue in a body can occur due to alteration in the type or concentration of phosphorous – containing chemicals in the cells and NMR studies can be useful in the diagnosis of damage of tissues.

Application of MRI: Proton NMR spectra has now developed in medical science in a different way. The technique is known as Magnetic Resonance Imaging (MRI). In this technique proton NMR spectra of the cells in living tissue is not produced, rather a density map (or image) of the proton in the tissue is produced. From image it become possible to know whether there has been a damage of the soft tissue in the part of the body studied. The most important fact about MRI photograph is that it can distinguish between normal cell and cancerous cell.

In the MRI technique part of the body such as, eyes nose, spinal cord, brain can be studied. The part of the body to be studied is placed in a magnetic field with a known varying gradient and the size of the proton NMR signals is measured as a function of distance along field.

Easy:

(a) Most of absorption bands in the UV – Visible spectra are very broad. Give reasons. 3
(b) Why does 1, 3 butadiene possess higher λ_{max} value than that of ethane? 3
(c) Why the colour of sky is blue? 2
(d) Predict the proton NMR spectra of CH_4. 3
(e) Name any four surface characterization techniques. 4

(a) UV visible spectra involve transitions between electronic energy level which are associated with vibrational and rotational energy levels. The electronic transition may occur from any of the several vibrational and rotational states of one electronic level to any of the various corresponding states of higher level. Since a large number of transitions are possible, so a large number of absorptions will take place corresponding to different wavelengths. Hence, spectra are very board.
(b) In 1, 3 butadiene $\pi_2 \rightarrow \pi_3^*$ excitation takes place, which requires lesser energy (of higher wavelength) than $\pi \rightarrow \pi^*$ excitation in ethane.
(c) The Rayleigh scattering causes the blue light from the sun to be scattered more than other wavelength light.
(d) In CH_4 contain equivalent protons which do not show spin – spin interaction. Hence, their proton NMR spectra will consist of one signal only, i.e. a singlet.
(e) The important surface characterization techniques are:
    (i) Macromolecular crystallography (MX)
    (ii) X – Ray Reflectively (XRR)
    (iii) Scattering – SAXS and WAXS
    (iv) X – Ray Photoelectron Spectroscopy (XPS) in Surface Chemical Analysis
    (v) Dynamic Secondary Ion Mass Spectrometry.