SPECTROSCOPY

Spectroscopy deals with the transition of a quantum system (an atom or a molecule) between two energy levels upon the absorption of a photon of energy hv. If hv is equal to ΔE, the energy difference between the two energy levels, then hv = ΔE or v = ve/h. In atoms, he energy levels are the electronic energy levels whereas in molecules the energy levels are, broadly speaking, of three kinds Electronic, vibrational rotational. If the three kinds of motions are considered independent, then the total energy of a molecule is given by the Bom-oppenheimer approximation.

$E_{total} = E_{rot} + E_{vib} + E_{el}$

$E_{el} >> E_{vib} > E_{rot}$

Absorption and Emission Spectra:

If the molecule absorbs a photon, the resulting spectrum is called absorption spectrum. If the molecule emits a photon as it undergoes a transition from the excited energy state to the ground state, the resulting spectrum is called emission spectrum.

Atomic and Molecular spectra:

Atomic spectra are very simple since there is only electronic motion in atoms. These are called line spectra because the spectrum consists of well-defined sharp lines. Molecular spectra are complicated because the molecule on the absorption of radiation energy may undergo rotational, or vibrational motion or may simultaneously undergo electronic, vibrational and rotational motions.

Molecular spectra are called band spectra because they consist of several overlapping spectral times giving rise to a band. Spectra are best investigated in the gaseous state at very low pressures because under such conditions the intermolecular interactions are negligible. Using the Bom - oppenheimer approximation we can investigate rotational spectra (in the microwave region), vibrational spectra (in the infrared region) and electronic spectra (in the ultraviolet/visible region). These regions of electromagnetic spectrum have the following approximate ranges:

Microwave region 1-100 cm^{-1}

Infrared region 500-4000 cm^{-1}

Visible region 10,000-25,000 cm^{-1}

UV region 25,000 - 70,000 cm^{-1}

Selection rules in spectra arc very important. They tell which quantum numbers change during a transition and by what amount. Transitions which obey a selection rule are called

1

allowed transitions and those which violate the selection rules arc called forbidden transitions. Allowed transitions are more intense (stronger) than forbidden transitions.

Rotational Spectra of Diatomic Molecules:

A diatomic molecule which rotates about its centre of mass so that its bond distance does not change during rotation is called a rigid rotor. The rotational energy levels of a rigid rotor arc given by

$E_1 = BJ (J + 1)$; J=0, 1, 2, 3, ...

where B is the rotational constant &

J is the rotational quantum number

The selection rule for rotational transitions for a rigid diatomic rotor is $\Delta J = \pm 1$. Using the selection rule and the energy level expression, the rotational spectrum consists of a series of equally spaced tines with spacing equal to 2B where $B = \dfrac{h}{8\pi^2 I_c}$

The requirement for a molecule to show rotational spectrum is that it should have a permanent dipole moment, i.e. $u \neq 0$ and it should be in the gaseous state for it is only in this state that molecules can freely rotate.

Vibrational (Infrared) Spectra of Diatomic Molecules:

A diatomic molecule is said to undergo simple harmonic motion (vibrational motion) when its atoms of mass m_1 and m_2 are displaced slightly from their equlibrium positions such that the centre of mass of the molecule does not change.

The fundamental vibrational frequency of the molecule is given by

$V = \dfrac{1}{2\pi} \left(\dfrac{K}{\mu}\right)^{1/2}$ and

$\overline{V} = \dfrac{V}{c} = \dfrac{1}{2\pi c} \left(\dfrac{K}{\mu}\right)^{1/2} \text{cm}^{-1}$

The potential energy of the S.H.O is given by the Hooke's law potential, $V(x) = \dfrac{1}{2} kx^2$

If the diatomic molecule vibrates as an anharmonic oscillator, then in addition to the fundamental vibrational wave number, overtones of weak intensity are observed in the IR spectra. For a molecule to be IR-active (i.e. to show vibrational spectrum in the IR region), the requirement is that the dipole moment must change with the vibrational motion. Thus, homohuclear diatomic molecules are IR - inactive but heteronuclear diatomic molecules are IR-active.

2

Raman Effect:

The phenomenon of scattering of light by a substance when the frequencies of radiations scattered at right angles are different (generally lower or higher) from the frequency of the incident light is known as Raman scattering or Raman effect. The lines of lower frequencies are known as the Stokes lines and those of higher frequencies are called anti-stokes lines.

If $\bar{v}_1$, is the frequency of incident light and $\bar{v}_s$ that of a particular line in the scattered spectrum, then $\Delta\bar{v} = (\bar{v}_1 - \bar{v}_s)$ is called Raman frequency. This is characteristic of the substance exposed to the incident light. For a molecule to be Raman-active, its polarizability must change during rotation or vibration.

A striking feature of Raman scattering is that the Raman frequencies are identical with frequencies obtained from infrared spectra. Raman spectroscopy has several advantages over the infrared spectroscopy.

Electronic spectra:

The elctronic spectra of molecules, observed in the ultraviolet/visible regions, are quite complex since electronic transitions are accompanied by vibrational and rotational transitions. These spectra appear as broad bands in solutions. However, they can be analyzed in the gaseous state giving information about molecular structure. There are no definite selection rules here.

The Franck-Condon principle is very helpline in interpreting the intensity of the vibrational transitions accompanying an electronic transition. The Franck-Condon principle states that an electronic transition takes place so rapidly that a vibrating molecule does not change its inter-nuclear distance appreciably during the transition.

In the case of organic compounds containing chromophores, the electronic transitions of interest are

$\sigma^* \leftarrow \sigma$, $\pi^* \leftarrow \pi$ and $\pi \leftarrow \sim$.
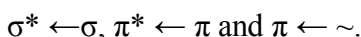
The functional groups and as -C=C- and -N=N- which absorb at wavelengths longer than 180 nm are called chromophores. The $\sigma^* \leftarrow$ transitions occur in the UV region. The transitions are allowed by symmetry and are thus allowed transitions. They are highly intense. The $\pi^* \leftarrow \pi$ transitions are forbidden transitions and are thus weak. In highly conjugated systems. Such as R-$(CH=CH)_n$ -R, the absorption band shifts to longer wave lengths as the extent of conjugation increases. A quantity of interest is λ_{max} , i.e. wavelength corresponding to the maximum of the absorption band.

1. **Bathochromic shift (or red shift):**
   A shift of λ_{max} to longer wave lengths.
2. **Hypsochromic shift (or the blue shift):**
   A shift of λ_{max} to shorter wave lengths.

3. **Hyperchromic shift:**

   Hyperchromic shift is an increase in intensity of an absorption band with reference to its molar absorption (extinction) coefficient, E_{max} .

4. **Hypochromic shift:**

   Hypochromic shift is a decrease in intensity of an absorption band with reference to E_{max} .

   Nuclear Magnetic Resonance (NMR) Spectroscopy:

   NMR Spectroscopy arises when a spinning ride nucleus, placed in an external magnetic field, called the Zeeman field is subjected to a radiofrequency (rf) radiation. Thus, NMR spectra are observed in the rf region of the electromagnetic spectrum. All atomic nuclei possess nuclear spin (I) which may be considered as the resultant of the spins of resilions and protons present in the nucleus. The nuclear spin may be integral (i.e. 1, 2, 3 etc. or half-integral $\left(\text{i.e.} \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \text{etc.} \right)$ upon the number of nucleons (collective term for protons and neutrons).

   The angular momentum associated with a nuclear spin is given by $\sqrt{I(I+1)}(h/2\pi)$

   Since a nucleus possesses an electric charge, the spinning nucleus gives rise to a magnetic field whose axis coincides with the axis of spin. Thus each nucleus with $I > 0$, has magnetic moment μ which is given by,

   $$\mu = g_N \mu_N \sqrt{I(I+1)}$$

   Energy of nuclear spin of a base proton is defined only by the component m, of the nuclear spin I.

   Since I for a base proton (H) is equal to 1/2, hence $m_1 = \pm 1/2°$.

   Accordingly,

   Energy, $E_{1/2} = -\frac{1}{2} g_N \mu_N B_2$ for $m_1 = \frac{1}{2}$

   and $E_{1/2} = \frac{1}{2} g_N \mu_N B_2$ for $m_1 = -\frac{1}{2}$

   $\therefore \Delta E = E_{-1/2} - E_{1/2} = g_N \mu_N B_z = hv$

   Thus, the NMR frequency of a

   b are proton is given by

   $n = \frac{\Delta E}{h} = \frac{g_N \mu_N B_z}{h}$

   The magnetic field at which a free or bare nucleus resonates is different from the magnetic field at which the same nucleus in a molecule resonates. The difference between the two magnetic fields is called chemical shift. If a molecule has a number of protons, the chemical shift of each proton would be different depending upon its environment. That is why the NMR spectrum of ethanol (CH_3-CH_2-OH) shows three peaks corresponding to three protons having different environment.

4

Join Us on FB :

For English – Examsdaily   **For Tamil – Examsdaily Tamil**

Join US on Whatsapp

For English - Click Here   **For Tamil – Click Here**

5