KARNATAKA STATE OPEN UNIVERSITY

Mukthagangothri, Mysore – 570 006

M.Sc. PHYSICS

(SECOND SEMESTER)

COURSE –MP 2.4

Spectroscopy

M.Sc. PHYSICS

SECOND SEMESTER

Course: MP 2.4

SPECTROSCOPY

Course Design

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Publisher

The Registrar
Karnataka State Open University
Mukthagangothri, Mysore - 570 006

Developed by Academic Section, KSOU, Mysore

Karnataka State Open University, 2014

Further information on the Karnataka State Open University Programs may obtained from the University's office at Mukthagangothri, Mysore - 6

Printed and Published on behalf of Karnataka State Open University. Mysore – 6 by **Registrar (Administration)**

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PRELUDE

Spectroscopy is an often used for the phrase **The Knowledge of Light.** Most of what we know about the structure of atoms and molecules comes from studying their interaction with light (electromagnetic radiation). Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions. Realizing that light may be considered to have both wave-like and particle-like characteristics, it is useful to consider that a given frequency or wavelength of light is associated with a "light quanta" of energy we now call a photon. Spectroscopy is a general methodology that can be adapted in many ways to extract the information you need (energies of electronic, vibrational, rotational states, structure and symmetry of molecules, dynamic information). Spectroscopy helps us to understand how light interacts with matter and how you can use this to quantitatively understand your sample.

In this Course, you will study the different types of spectroscopy and the instrumentations. The Course consists of four blocks.

The first block deals with “**Atomic spectroscopy”.** Atomic spectroscopy is the study of the electromagnetic radiation absorbed and emitted by atoms. Atomic spectroscopy exploits different energetic transitions experienced by atoms that are associated with either the absorption or emission of photons. When these transitions involve the excitation and relaxation of the valence (outer or bonding) shell electrons of metal atoms and ions, the corresponding photons have energies within the ultraviolet and visible regions of the spectrum. Here you are going to understand about the spectroscopic notations and different kinds of effects like Zeeman, Pascen-back, Stark effects in depth.

The second block throws light on two major types of Spectroscopy- Nuclear Magnetic Resonance Spectroscopy and Microwave Spectroscopy, and their applications. NMR spectroscopy has the ability to distinguish the distinct isotopes of the elements in a compound. Remember that isotopes are different forms of the elements caused by a variation in the number of neutrons. Chemical properties are independent of the isotopic constitution of an element, but physical properties in general will vary among isotopes. Thus the mass of the isotope will alter properties such as the boiling point, or indeed the velocity of ions on a curved path (mass spectroscopy). The nuclear properties of an isotope will also differ and can be detected using the appropriate instrumentation. NMR is used for the functional group analysis, bonding connectivity, orientation and dynamics of the molecule.

The third block discusses about the IR Spectroscopy and Raman Spectroscopy. Infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples. Raman Spectroscopy is the shift in wavelength of the inelastically scattered radiation that provides the chemical and structural information. Raman shifted photons can be of either higher or lower energy, depending upon the vibrational state of the molecule under study.

The last block deals with the principles of Spectral analysis. Here, the different techniques and applications of Spectroscopy are explained extensively. A list of equipments is also given which helps the reader to understand more about Spectroscopy.

Contents

Unit-1: Atomic Spectroscopy

1.0.1 Objectives

1. To measure the wavelengths of visible light emitted by atomic hydrogen.

2. To verify the measured wavelengths against those predicted by quantum theory.

3. To identify an unknown element through its emission spectra and examine an absorption spectrum.

1.0.2 The Bohr Model

1.0.3 Postulates

1. An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.

2. The electron moves in an orbit, and its orbital angular momentum L is an integral multiple of h.

3. Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy E remains constant.

1.0.4 The Spin-Orbit Effect

In order to explain the fine structure of the hydrogen atom, need to consider electron's orbital angular momentum **L**, and its intrinsic angular momentum **S**, called spin.

Consider an electron moving through an electric field **E** experiences an effective magnetic filed **B** is given by,

$$B = -\frac{1}{c^2}\mathbf{v} \times E$$

The electric field in terms of the gradient of the potential energy V and unit vector in the radial direction

$$E = \frac{1}{e}\frac{\partial V}{\partial r}\frac{\mathbf{r}}{r}$$

The electron's potential energy V equals its charge $-e$ times the electrostatic potential.

$$B = \frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\mathbf{r} \times m_e\mathbf{v}$$

$$B = \frac{\hbar}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\mathbf{l}$$

Where the orbital angular momentum is

$$\hbar\mathbf{l} = \mathbf{r} \times m_e\mathbf{v}$$

The electron has an intrinsic magnetic moment, then

$$\mu = -g_s\mu_{\mathrm{B}}\mathbf{s}$$

Where,

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m_e}$$

is called the **Bohr magneton** and g_s is called the **spin gyromagnetic ratio** of the electron. And from Dirac theory, expected value of $g_s \approx 2$ (experimentally $g_s = 2.00232$). Spin has a magnitude of $|\mathbf{s}| = s = 1/2$.

The interaction of electron's magnetic moment with the orbital field gives the Hamiltonian,

$$H = -\mu \mathbf{B}$$

$$H = g_s \mu_{\rm B} \mathbf{s} \cdot \frac{\hbar}{m_e c^2} \left(\frac{1}{er} \frac{\partial V}{\partial r} \right) \mathbf{l}$$

However, this expression gives energy splitting about twice as large as observed. The discrepancy comes from the **Thomas precession** - a relativistic effect that arises because we are calculating the magnetic field in a frame of reference that is not stationary, but rotates as the electron moves about the nucleus.

Therefore, the spin-orbit interaction including Thomas precession factor will be,

$g_s = g_s - 1 \approx 1$,

$$H_{\text{s-o}} = (g_s - 1) \frac{\hbar^2}{2m_e^2 c^2} \left(\frac{1}{r} \frac{\partial V}{\partial r} \right) \mathbf{s} \cdot \mathbf{l}$$

An expectation value of this Hamiltonian gives, change of energy,

$$E_{\text{s-o}} = \frac{\hbar^2}{2m_e^2 \ c^2} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle \langle \mathbf{s} \cdot \mathbf{l} \rangle$$

This equation lead to separation into a product of **radial** and **angular** expectation values.

And we know for hydrogen atom,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3 \ a_0^3 \ l(l + \frac{1}{2})(l+1)}$$

The total angular momentum of the atom, is the sum of its orbital and spin angular momenta, which is a conserved quantity.

$$j = l + s$$

Thus the spin-orbit interaction produces a shift in energy,

$$E_{\text{s-o}} = \frac{\hbar^2}{2m_e^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{Z^3}{n^3a_0^3l(l+\frac{1}{2})(l+1)}\ \frac{1}{2}\left[j(j+1)-l(l+1)-\frac{3}{4}\right]$$

A single electron has $s = \frac{1}{2}$, therefore, for each l, its total angular momentum quantum number j has two possible values,

$$j = l + \frac{1}{2} \qquad \text{or} \qquad j = l - \frac{1}{2}$$

Thus the energy interval between these levels,

$$\Delta E_{\text{s-o}} = E_{j=l+\frac{1}{2}} - E_{j=l-\frac{1}{2}}$$

$$\Delta E_{\text{s-o}} = \frac{\hbar^2}{2m_e^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{Z^3}{n^3a_0^3l(l+\frac{1}{2})(l+1)}\frac{1}{2}\left[(l+\frac{1}{2})(l+\frac{3}{2})-l(l+1)-\frac{3}{4}\right]$$

$$\Delta E_{\text{s-o}} = \frac{\beta}{2}\left[l+(l+1)\right]$$

Where,

$$\beta = \frac{\hbar^2}{2m_e^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{Z^3}{(na_0)^3l(l+\frac{1}{2})(l+1)}$$

$$\Delta E_{\text{s-o}} = \beta\left(l+\frac{1}{2}\right)$$

1.0.5 Kinetic Energy Correction

The fine structure of an atom, describes the splitting of the spectral lines of atoms due to first order relativistic corrections.

For a hydrogen atom, initially thought that the gross structure energy levels only depend on the principal quantum number n. However, a more accurate model takes into account relativistic and spin effects, which break the degeneracy of the energy levels and split the spectral lines.

The fine structure can be separated into three corrective terms: the kinetic energy term, the spin-orbit term, and the Darwinian term. Therefore, complete Hamiltonian is given by

$$H = H_0 + H_{\text{kinetic}} + H_{\text{s-o}} + H_{\text{Darwinian}}$$

According to theory of relativity,

$$m_e = \frac{m_0}{\sqrt{1-(v^2/c^2)}}$$

Classically, the kinetic energy term of the Hamiltonian is,

$$T = \frac{p^2}{2m}$$

Expanding,

$$T = \frac{p^2}{2m_e} = \frac{p^2}{2m_0}\left[1-\frac{v^2}{c^2}\right]^{-1/2}$$

Then, the first order correction to the Hamiltonian is

$$H_{\text{kinetic}} = -\frac{p^4}{8m^3c^2}$$

with approximation $p^2 = (m_0 v)^2$ and retaining only the term up to $(v/c)^2$.

Using this as a perturbation, we can calculate the first order energy corrections due to relativistic effects.

$$E_n^{(1)} = \langle\psi^0|H'|\psi^0\rangle = -\frac{1}{8m^3c^2}\langle\psi^0|p^4|\psi^0\rangle$$

$$E_n^{(1)} = -\frac{1}{8m^3c^2}\langle\psi^0|p^2p^2|\psi^0\rangle$$

where ψ_0 is the unperturbed wave function. Recalling the unperturbed Hamiltonian, we see

$$H^0|\psi^0\rangle = E_n|\psi^0\rangle$$

$$\left(\frac{p^2}{2m}+V\right)|\psi^0\rangle = E_n|\psi^0\rangle$$

$$p^2|\psi^0\rangle = 2m(E_n - V)|\psi^0\rangle$$

We can use this result to further calculate the relativistic correction:

$$E_n^{(1)} = -\frac{1}{8m^3c^2}\langle\psi^0|p^2p^2|\psi^0\rangle$$

$$E_n^{(1)} = -\frac{1}{8m^3c^2}\langle\psi^0|(2m)^2(E_n - V)^2|\psi^0\rangle$$

$$E_n^{(1)} = -\frac{1}{2mc^2}(E_n^2 - 2E_n\langle V\rangle + \langle V^2\rangle)$$

For the hydrogen atom,

$$\langle V^2\rangle = \frac{e^4}{(l+1/2)n^3a_0^2}$$

where a_0 is the Bohr Radius, n is the principal quantum number and l is the azimuthal quantum number. Therefore the relativistic correction for the hydrogen atom is

$$E_n^{(1)} = -\frac{1}{2mc^2}\left(E_n^2 - 2E_n\frac{e^2}{a_0n^2} + \frac{e^4}{(l+1/2)n^3a_0^2}\right)$$

$$E_n^{(1)} = -\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+1/2} - 3\right)$$

$$H_{\text{s-o}} = \frac{\hbar^2}{2m_e^2c^2}\frac{Ze^2}{4\pi\epsilon_0\ r^3}\quad \mathbf{l}\cdot\mathbf{s}$$

$$H_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2c^2}4\pi\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\delta^3\left(\vec{r}\right)$$

The Darwin term changes the effective potential at the nucleus. It can be interpreted as a smearing out of the electrostatic interaction between the electron and nucleus due to *zitterbewegung*, or rapid quantum oscillations, of the electron.

1.0.6 The Lamb shift

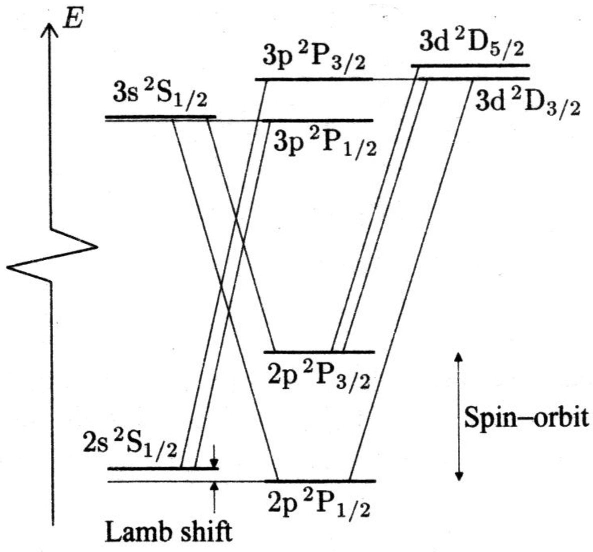

Figure 1.1: The fine structure of the $n = 2$ and $n = 3$ shells of hydrogen, and the allowed transitions between the levels.

According to relativistic quantum theory, **the $2S_{1/2}$ level should be exactly degenerate with** $2P_{1/2}$, because they both have $n = 2$ and $j = 1/2$, but in reality there is an energy interval between them.

The small difference in energy between two energy levels $2S_{1/2}$ and $2P_{1/2}$ of the hydrogen atom is explained using **quantum electrodynamics (QED)**. QED–the quantum field theory that describes electromagnetic interactions. According to Dirac theory, the $2S_{1/2}$ and $2P_{1/2}$ orbitals should have the same energies.

The theoretical positions of the energy levels of hydrogen calculated by the relativistic theory of Dirac depend on n and j only (not l), for $n = 3$ shell. The difference in energy between two energy levels,

$$E(2S_{1/2}) - E(2P_{1/2}) \simeq 1GHz$$

This small discrepancy in hydrogen was of great importance in physics. Although the predictions of the Dirac equation are very precise, and theory couldn't account for Lamb and Retherford's experimental measurement that **the $2S_{1/2}$ level is indeed higher than the $2P_{1/2}$ level**.

1.0.7 Questions

1. Discuss the theory of spin-orbit interaction in hydrogen atom and obtain the spin orbit interaction energy.
2. Explain the Lamb shift in hydrogen atom.
3. Explain the relativistic correction to the energy levels of the hydrogen atom.
4. The spin-orbit effect splits $3P \rightarrow 3S$ transition into two lines 5890 Å corresponding to $2P_{3/2} \rightarrow 2S_{1/2}$ and 5896 Å corresponding to $2P_{1/2} \rightarrow 2S_{1/2}$. Calculate by using this wavelengths, the effective magnetic induction experienced by outer electron in Sodium atom as a result of its orbital motion.

Unit-2: Zeeman Effect

2.1 Objectives

1. To observe the normal Zeeman effect.
2. To observe the triplet spectral lines for the normal transverse Zeeman effect.
3. To determine the polarization state of the doublet components.
4. To calculate the value of the Bohr magnetron.

2.1.1 Magnetic moment and angular momentum

From the classical electrodynamics, a current (i) is conducted in a closed circuit of area (A) may be treated as a small magnet of magnetic moment

$$\mu = IA$$

Since the rotation of an electron in its orbit is equivalent to the rotation of a negative point charge circumscribing the nucleus $\omega/2\pi$ time per second then the current will be,

$$I = -(\omega/2\pi)e$$

For a circular orbit of radius r, the magnetic moment will be

$$\mu = \left(-\frac{\omega e}{2\pi}\right) \pi r^2$$

$$\mu = -\frac{\omega e r^2}{2}$$

The angular momentum (p) due to rotation of an electron of mass m

$$\mu = -\frac{e}{2m} \cdot p$$

Where p is the angular momentum (p) and We know from quantum mechanics, for an atom

$$\mu = -\frac{e}{2m}\sqrt{J(J+1)}\hbar$$

$$\mu = -\mu_{\mathrm{B}} J^*$$

where $\mu_{\mathrm{B}} = eh/4\pi m$ represents a smallest unit of magnetic moment and is called **Bohr magneton**.

When an atom is placed in a magnetic field, the total angular momentum is resulted from the interaction between the atomic magnet and the external field $\mathbf{B}$, and $J^*\hbar$ is made to precess /blue

about the direction of the field. Then the frequency of the precession is given by,

$$\nu_L = \frac{\mathbf{B}e}{4\pi m}$$

ν_L is known as **Larmor frequency**. ν_L is independent of the angle between $J^*\hbar$ and B.

2.1.2 The normal Zeeman effect

The magnetic moment of an atom is given by,

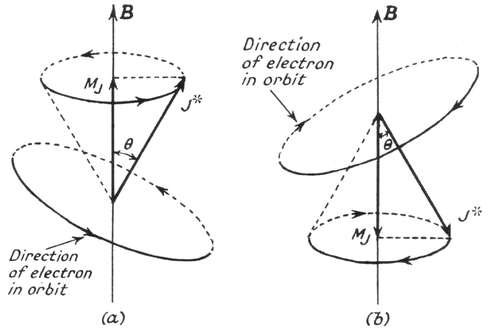

Figure 2.2: Precession of total angular momentum about an applied magnetic field. $M_J = +1$ and -1.

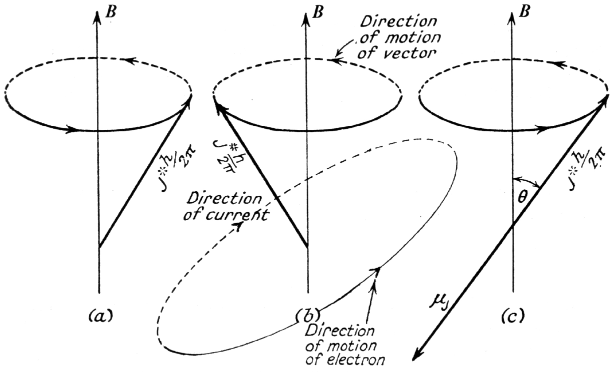

Figure 2.3: Precession of total angular momentum about an applied magnetic field, direction of flow of current, and precision of total angular momentum and the magnetic moment μ_J in a magnetic field.

$$\mu = -\mu_{\mathrm{B}} J^*$$

If a homogeneous magnetic field is applied, precessional motion takes place about the direction of the magnetic field.

If E_0 is the energy of an atom in the absence of magnetic field, then the total energy E_{M_J} in the presence of an external magnetic filed strength is given by

$$E_{M_J} = E_0 - \mu_J \mathbf{B} \cos\theta$$

Where θ is the angle between the direction of the magnetic field and μ_J. Therefore, the change in energy due to the magnetic field is

$$E_{M_J} - E_0 = -\mu_J \mathbf{B} \frac{M_J}{J^*}$$

For an atom, where $S = 0$, $\mu_J = \mu$; μ_J is the magnetic moment along the direction $J^*\hbar$

$$E_{M_J} - E_0 = +\frac{e\hbar}{2m} \cdot \mathbf{B} \cdot M_J$$

$$E_{M_J} - E_0 = h\nu_L M_J$$

For a transition between the energy states E′ and E″

$$\Delta E = (E_0^{'} + h\nu_L M_J^{'}) - (E_0^{''} + h\nu_L M_J^{''})$$

$$\nu = \nu_0 + \nu_L \Delta M_J$$

where ν_0 is the frequency of the spectral line in the absence of a magnetic field.

As we know from selection rule, $\Delta M_J = 0, \pm 1$, when the observation are made perpendicular to the applied magnetic field.

$$\Delta M_J = 1 \qquad \nu_1 = \nu_0 + \nu_L$$

$$\Delta M_J = 0 \qquad \nu_2 = \nu_0$$

$$\Delta M_J = -1 \qquad \nu_3 = \nu_0 - \nu_L$$

Thus irrespective of $M_J^{'}$ and $M_J^{''}$ values, only three spectral lines result when the selection rule is obeyed.

This splitting of spectral lines into three components in the presence of a suitable perpendicular magnetic field is known as **normal Zeeman effect**.

These spectral lines are always symmetrical about the central line (ν_0). If $\Delta M_J = 0$ is polarized with electric vector in a plane parallel to the magnetic field, referred as a π line. While $\Delta M_J = +1$ and -1 are plane polarized with the electric vector perpendicular to the magnetic filed and σ lines.

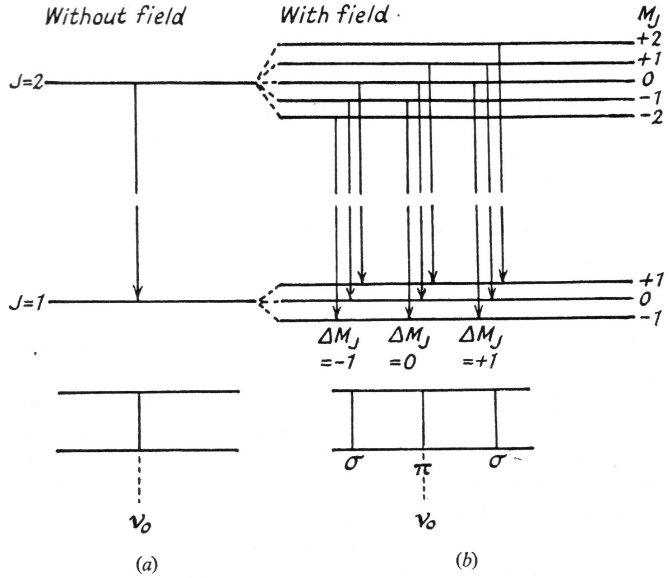

Figure 2.4: Transitions of spectral lines (a) in the absence of a magnetic field, and (b) on the application of magnetic a field (normal Zeeman effect).

2.1.3 The anomalous Zeeman effect

For all atoms (spin, $S > 0$), in the presence of a suitable magnetic filed each spectral line is split into more than three components known as **anomalous Zeeman effect**.

The additional lines are explained by the fact that the spacing of the upper energy levels, explained as

$$E_{MJ} = E_0 - M_J g_J \mu_{\mathrm{B}} \mathbf{B}$$

Where g_J is called the Landé g_J-factor, whose value can be calculated when values of L, S and J are known.

When an atom is placed in a weak magnetic field, change in energy is given by

$$E_{MJ} - E_0 = -\mu_J \mathbf{B} \frac{M_J}{J^*} \qquad (1)$$

And we know that

$$\mu = -\frac{e\hbar}{2m} \cdot J^*$$

then

$$\mu_J = -\frac{e\hbar}{2m} \cdot J^* \cdot g_J$$

substitute in equation (1)

$$E_{M_J} = E_0 + h\nu_L M_J g_J$$

Then for a transition between energy states $E_0^{'}$ and $E_0^{''}$

$$\Delta E = (E_0^{'} + h\nu_L M_J^{'} g_J^{'}) - (E_0^{''} + h\nu_L M_J^{''} g_J^{''})$$

$$\nu = \nu_0 + h\nu_L (M_J^{'} g_J^{'} - M_J^{''} g_J^{''})$$

Thus the separation of the spectral lines in Zeeman pattern depends on g_J.

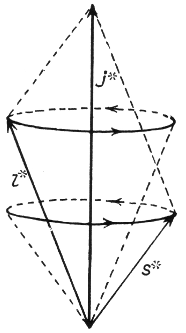

Figure 2.5: Precession of $l^*h/2\pi$ and $s^*h/2\pi$ about their resultant $J^*h/2\pi$.

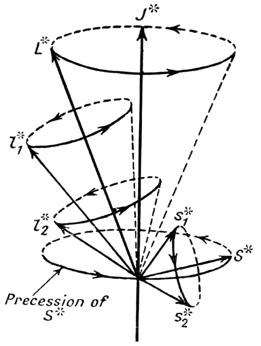

Figure 2.6: Precession of $l_1^*h/2\pi$ and $l_2^*h/2\pi$ about $L^*h/2\pi$ and its precession about $J^*h/2\pi$ and the precession $s_1^*h/2\pi$ and $s_2^*h/2\pi$ about $S^*h/2\pi$ and its precession about $J^*h/2\pi$.

2.1.4 The Landé g_j-formula

The resultant orbital angular momentum is given by

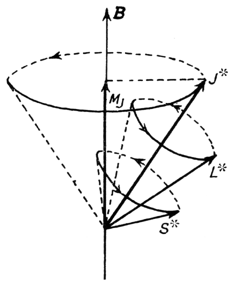

Figure 2.7: Precession of $J^*h/2\pi$ about an applied magnetic field B.

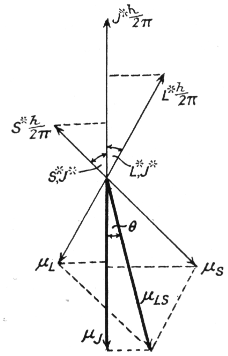

Figure 2.8: Direction of the vectors $J^*h/2\pi$, $L^*h/2\pi$, and $S^*h/2\pi$ and the magnetic moments μ_{LS}, μ_L, and μ_S. where μ_{LS} is the magnetic moment of the atom (μ) and is obtained by the vectorial combination of μ_L, and μ_S.

$$P_L = \sqrt{[L(L+1)]}\hbar$$

And its magnetic moment is given by

$$\mu_L = -\mathbf{L}^* \cdot \frac{e\hbar}{2m}$$

and

$$\mu_S = -\mathbf{2S}^* \cdot \frac{e\hbar}{2m}$$

$$\mu_L + \mu_S = -\left\{L^* \cos(L^*, J^*) + 2S^* \cos(S^*, J^*)\right\} \frac{e\hbar}{2m}$$

$$J^* g_J = L^* \cos(L^*, J^*) + 2S^* \cos(S^*, J^*)$$

Using cosine law to the S^*, L^*, and J^* vectors in figure,

$$\cos(L^*, J^*) = \frac{L^{*2} + J^{*2} - S^{*2}}{2L^* J^*}$$

$$\cos(S^*, J^*) = \frac{S^{*2} + J^{*2} - L^{*2}}{2S^* J^*}$$

Thus g_J will be,

$$g_J = \frac{L^*}{J^*}\left\{\frac{L^{*2} + J^{*2} - S^{*2}}{2L^* J^*}\right\} + \frac{2S^*}{J^*}\left\{\frac{S^{*2} + J^{*2} - L^{*2}}{2S^* J^*}\right\}$$

$$g_J = \frac{1}{2J^{*2}}\left\{L^{*2} + J^{*2} - S^{*2} + 2S^{*2} + 2J^{*2} - 2L^{*2}\right\}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Thus the g_J – factor value depends on the values J, S, and L. Different levels will have different values of g_J.

2.1.5 The Paschen-Back Effect

When the magnitude of the field strength (magnetic field) is continuously increased then the coupling between orbital and spin angular momenta completely breaks down and we obtain the Paschen-Back effect. Where $L^*\hbar$ and $S^*\hbar$ are quantized independently.

From the figure, the magnetic field **B** is so strong that, $L^*\hbar$ and $S^*\hbar$ precess independently around **B**.

The quantum conditions are that the projection of $L^*\hbar$ along the direction of $\mathbf{B} = M_L\hbar$

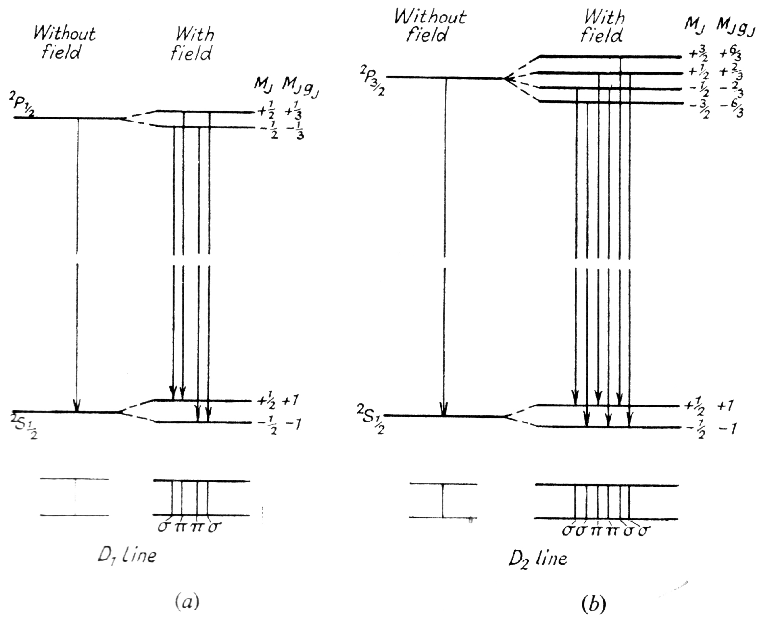

Figure 2.9: Spectral lines (a) in the absence and (b) presence of a suitable magnetic field, the anomalous Zeeman pattern of lines is produced.

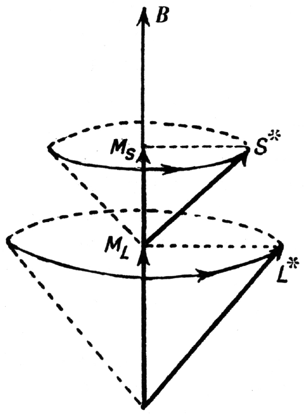

Figure 2.10: Precession of the uncoupled $L^*h/2\pi$ and $S^*h/2\pi$ vectors in a strong magnetic field.

And $S^*\hbar$ along $\mathbf{B} = M_S\hbar$.

The permissible value of M_L and M_S are

$$L, L-1, L-2, \ldots, -L$$

$$S, S-1, S-2, \ldots, -S$$

And the selection rule for M_L and M_S, when the spectrum is taken perpendicular to the applied field are

$$\Delta M_L = 0, \;\; \pm 1 \qquad\qquad \Delta M_S = 0$$

The total interaction energy with the magnetic field in the Paschen-Back effect involves the following conditions.

The energy of interaction of the spin magnetic moment μ_S

$$E_S = -\mu_S B \cos(\mu_s, B)$$

The energy of interaction of the orbital magnetic moment μ_L

$$E_S = -\mu_L B \cos(\mu_L, B)$$

Energy due to a small amount of remaining interaction between μ_S and μ_L

$$\Delta E_{LS} = hcAM_LM_S$$

where A is a coupling constant between the orbit and electron spin momenta.

Then the total energy (E) is given by

$$E = E_0 + E_L + E_S + \Delta E_{LS}$$

where $E_0 + \Delta E_{LS}$ gives all the forms of energy which the atom has in the absence of a magnetic field.

Then E will be

$$E = E_0 - \mu_S B \cos(\mu_s, B) - \mu_L B \cos(\mu_L, B) + hcAM_L M_S$$

$$E = E_0 + 2\frac{e\hbar}{2m} BM_S + \frac{e\hbar}{2m} BM_L + hcAM_L M_S$$

$$E = E_0 + \mu_{\mathrm{B}} B(2M_S + M_L) + hcAM_L M_S$$

Let this theory will now be applied to the Paschen-Back effect for the case of sodium D-lines, that is for the transitions $3^2P_{3/2} \rightarrow 3^2S_{3/2}$ and $3^2P_{1/2} \rightarrow 3^2S_{1/2}$.

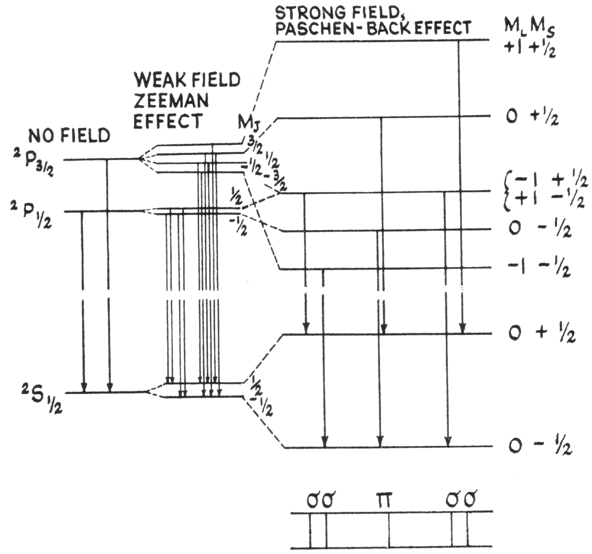

Figure 2.11: Splitting of spectral lines in the presence of a weak and a strong magnetic field.

From the figure, when the applied field is sufficiently strong, five spectral lines result from the sodium doublet, although six transitions take place. The spacing of the energy levels is such that two spectral lines coincide.

$$\begin{array}{llllll}
{}^2P & L = 1 & M_L = +1; & 0; & \text{-1;} \\
& S = \frac{1}{2} & M_S = +\frac{1}{2}; -\frac{1}{2}; & +\frac{1}{2}; -\frac{1}{2}; & +\frac{1}{2}; -\frac{1}{2}; \\
{}^2S & L = 0 & M_L = 0; & & \\
& S = \frac{1}{2} & M_S = +\frac{1}{2}; -\frac{1}{2}; & &
\end{array}$$

2.1.6 The Stark Effect

The shifting and splitting of spectral lines in an electric field is called **Stark effect**.

There are two types of Stark effect.

1. **Quadratic Stark effect** – observed in most of the atoms.
2. **Linear Stark effect** – for the excited state of the atom and in atom of very strong field.

The Stark shift of an atom is harder to observe than the Zeeman effect. Because, it is very difficult to produce very high potential gradient of the order of 10^7 volt/mtr.

Here, electric field does not interact with the magnetic moment of the atom. The electric polarization, and the electric field displaces the center of the negative charge and consequently the centers of negative and positive charge no longer coincide. The extent of separation depends on the field strength **E**. The result is an electric dipole moment can interact with the electric field.

When $E = 0$ (electric field), the negative charge electron cloud is arranged symmetrically about the nucleus and there is no electric dipole.

Total angular momentum $J^*\hbar$ precesses along the direction of the electric filed is constant.

Thus the energy shift is

$$\Delta E = \mu_F E$$

where μ_F is the induced electric dipole moment in the direction of the field.

The magnitude of μ_F is proportional to E, the splitting energy levels increases quadratically with E.

For example, in the case of potassium doublet transitions, $5^2P_{3/2}--4^2S_{1/2}$ and $5^2P_{1/2}--4^2S_{1/2}$ at the wavelengths 4044 Åand 4047 Å, respectively.

The original potassium doublet is split into three components in the electric field, in accordance with the above explanation, the plot of $\Delta\lambda$ against E^2 results in a straight line for all the three spectral lines.

The important difference between the Zeeman and Stark effects is that each pair of levels $M_J = +J$ and $M_J = -J$ arising from a given level has exactly the same energy in an electric field but different energies in a magnetic field.

An electron may rotate either clockwise or anticlockwise in its orbit. Then the component of the magnetic moment in the direction of field ranges from $-\mu_J \cos\theta$ to $\mu_J \cos\theta$ and the corresponding interaction energies range from

$$E_{MJ} - E_0 = \mu_J \mathbf{B} \cos\theta \quad \text{to} \quad E_{MJ} - E_0 = \mu_J \mathbf{B} \cos\theta$$

Since there are $(2J+1)$ values of $\cos\theta$, then there are $(2J+1)$ values of interaction energies in a magnetic field. The mechanism of interaction of the electric field with the atom is purely electrostatic.

Therefore, the dipole moment remains unaltered on reversing the direction of rotation ($+M_J$to $-M_J$), it follows that the energy will be the same for M_J components which are numerically the same but differ in sign.

Although there are $(2J+1)$ orientations of the orbit to the field, because of this degeneracy in an electric field there are only $(J+\frac{1}{1})$ different energy levels when J is half-integral, or $(J+1)$ levels if J is integral.

For example, $J=\frac{5}{2}$, instead of having six components in the magnetic field, has only three components in an electric field.

But the selection rules for M_J are identical with those for the Zeeman case.

The transitions $\Delta M_J = \pm 1$ give rise to spectral lines which are polarized with the electric vector perpendicular to the electric field.

$\Delta M_J = 0$, the line is polarized with the electric vector parallel to the applied filed.

For sodium D-lines, the transitions involved are:

$$3^2P_{1/2} - -3^2S_{1/2} \quad \text{and} \quad 3^2P_{3/2} - -3^2S_{1/2}$$

when $J=\frac{3}{2}, M_J = \pm\frac{3}{2}, \pm\frac{1}{2}$ and $J=\frac{1}{2}, M_J=\pm\frac{1}{2}$

Therefore three lines would result in the presence of electric field, when the observation is made perpendicular to the filed.

The Stark effect is more complex than explained above. In fact, the difference in energy between the field-free value and the value in the electric field is given by

$$\Delta T = AE + BE^2 + \cdots \qquad \text{for hydrogen like atoms.}$$

Dependence of ΔT on the first power of E is known as a *first-order Stark effect* and dependence of ΔT on E^2 known as *second-order Stark effect.*

2.1.7 Stark effect in a strong electric field

If the electric filed strength is increased, eventually the interaction energy between the electron and the field exceeds that between the orbit and spin motions, then the coupling between orbit and spin motion is broken down, and L^* and S^* becoming independently quantized.

Because of the induced electric dipole, the orbital angular momentum is still capable of interacting with the applied electric field. Therefore, the orbital angular momentum $L^*h/2\pi$ has the components $M_L h/2\pi$ in the direction of the applied field.

However, the electron spin,has no electric dipole associated with it and cannot interact with the electric field. Thus the spin $S^*\frac{h}{2\pi}$ may be precessing about the direction of the electric field E and having the component $M_L^{\frac{h}{2\pi}}$.

2.1.8 Quantum mechanical treatment of Stark effect

Consider an atom in an homogeneous field F in a direction parallel to Z-axis.

Then the Hamiltonian is given by,

$$H = H_0 + H'$$

where, $H_0 = T + V \rightarrow$ unperturbed Hamiltonian

H' is perturbed Hamiltonian,

$$H' = -\sum_i \mu_i F = eF \sum_i Z_i = eF_Z$$

where H' represents the sum over all electrons i of the interaction energy eF_Z with electric field.

Let ψ_0 be an eigen function of the unperturbed Hamiltonian H_0, then the expectation value of H' using ψ_0 is

$$\langle H' \rangle = \int \psi_0^* H' \psi_0 \, \mathrm{d}\tau$$

$$\langle H' \rangle = eF \int \psi_0^* Z \psi_0 \, \mathrm{d}\tau$$

In the classical system, the electric dipole moment μ in the electric field F experiences an energy shift of $-\mu F$, since the shift is zero because there is no permanent electric dipole moment in the state ψ_0.

Therefore, the transition between the two unperturbed state ψ_i and ψ_j is

$$\langle H_{ij}^{'} \rangle = \int \psi_i^* \ H' \ \psi_j \mathrm{d}\tau$$

$$\langle H_{ij}^{'} \rangle = eF \int \psi_i^* Z \psi_j \mathrm{d}\tau$$

The above integral vanishes unless ψ_i and ψ_j have opposite parity, which means elements only have transitions from odd state to even state or vice-versa.

For weak fields, the interaction energy is given by second order perturbation theory,

$$\Delta E = \sum_{i \neq j} \frac{|H_{ij}|^2}{(E_{0i} - E_{0j})}$$

$$\text{where} \quad Z_{ij} = \int \psi^* Z \psi_j \mathrm{d}\tau$$

2.1.9 Questions

1. The calcium line of wavelength 4226.73 Å exhibits normal Zeeman splitting when placed in a uniform magnetic field of 4 wb/mtr^2. Calculate the wavelength of three components of normal Zeeman pattern and the separation between them.

2. Explain the anomalous Zeeman effect and obtain the energy expression for the transition between the two energy states using Lande's g_J factor.

3. Describe complete Paschen-Back effect for sodium D-lines. And write the neat diagram showing the splitting of spectral lines in the presence of a weak and a strong magnetic field.

4. Explain the Stark effects in weak and strong field.

Unit-3: Hyperfine structure of spectral lines

3.2 Objectives

1. To observe the splitting of a spectral line into a number of components.
2. To observe the fine structure line splitting, which results due to change energy produced by electron spin-orbit coupling.

3.2.1 Hyperfine structure of spectral lines

The examination of individual multiplet components with a spectrograph composed of number of lines. This hyperfine structure is spread over a narrow wavelength range (few tenths of an Å unit).

Hyperfine spectral lines can be explained that the atomic nucleus is responsible for further splitting of spectral lines and isotope effect.

Many elements are composed of isotopes, although they are having an identical arrangement of extra nuclear electrons, differ in their masses.

For example, ${}_1H^1 \text{and} {}_1H^2$

For the hydrogen atom line (4861.33 Å), the Rydberg's constant is given by

$$\frac{1}{\lambda_H} = R_H \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

And the corresponding deuterium line

$$\frac{1}{\lambda_D} = R_D\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\lambda_D - \lambda_H = \Delta\lambda = -\lambda_H \frac{R_D - R_H}{R_D}$$

If the value of R_D and R_H are substituted in this equation for the 4861.33 Åline of hydrogen, the corresponding line of D could be

$$\Delta\lambda = -1.32\mathring{A}$$

Thus the deuterium line lies close to the hydrogen line at a wavelength 4860.01 Å.

In the case of rare earths and heavier elements the isotopic shift is not due to difference in mass, but it's purely coulombic.

Certain elements contained only one isotope but still has hyperfine structure (Ex: Bismuth had no isotopes, yet 4722 Åline contain six hyperfine components). Pauli explained that, the hyperfine structure is due to nucleus spinning, owing to the rotation of charge (positive) would be an associated magnetic moment and a corresponding angular momentum.

Therefore, the nuclear angular momentum is given by,

$$I = \sqrt{I(I+1)}\hbar$$

Where I is known as the *nuclear spin quantum number* and may take integral or half-integral values.

For hydrogen atom, $I = \frac{1}{2}$, and for deuterium is unity.

Thus the magnetic moment μ associated with nuclear spin is,

$$\mu = \frac{e}{2m_p} p_I$$

where m_p is the mass of proton, and p_I is the nuclear angular momentum, is equal to $I^* \cdot \hbar$

$$\mu = \frac{e\hbar}{2m_P} \cdot \sqrt{I(I+1)}$$

$\mu_N = \dfrac{e\hbar}{2m_p}$ is known as the nuclear magneton.

Since the mass of the proton is 1836 times the mass of an electron, the nuclear magneton 1/1836 times the Bohr magneton. But experimental observations indicate that the magnetic moment to be associated with a spinning nucleus is greater than that of

$$\mu = \frac{e\hbar}{2m_P} \cdot \sqrt{I(I+1)}$$

Therefore, the nuclear g-factor (g_N) may introduced.

$$\mu = g_N \frac{e\hbar}{2m} \cdot \frac{1}{1836} \cdot \sqrt{I(I+1)}$$

The resultant electron angular momentum $J^*\hbar$ couples with the nuclear angular momentum $I^*\hbar$ in a way exactly similar to the coupling between **L** and **S**. Thus, **I** and **J** couple to give a resultant **F**, Where $F^*\hbar$ represents the total angular momentum

of the atom for both the nucleus and the extra-nuclear electrons (See Figure).

The resultant quantum number F may take the values

$$F = J + I, J + I - 1, J + I - 2, \cdots, |J - I|$$

There are $(2J+1)$ values of F for every J value when $I > J$, and $(2I+1)$ values of F for every J value when $J > I$.

The nuclear spin angular momentum may take up different orientations relative to the resultant electron angular momentum, will give different energy

$$E_F = \frac{A}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$$

Where A is an interaction constant, and E_F is the interaction energy between the nuclear angular momentum and the electron angular momentum.

3.2.2 Questions

1. From the isotopes, ${}_1H^1\text{and}{}_1H^2$, estimate the change of wavelength.
2. Explain the nuclear spin, and obtain an expression nuclear magneton.

Unit-4: Natural width of a spectral line

4.3 Objectives

1. To observe the spectral line is made up of two components.

2. To understand the Doppler effect.

4.3.1 Width of spectral lines

The breadth of the spectral line is defined as the width in cm^{-1} between the two points whose intensities are half that of the maximum intensity.

Most of the hyperfine structure studies of spectral lines it is essential to reduce the line width as much as possible. If the detected spectral line is made up of two components, these cannot be resolved using the half-width method.

There are three causes producing the breadth of a spectral line are; its natural width, Doppler effect and External effects– such as the intermolecular fields produced by ions and dipoles.

4.3.2 Natural width of a spectral line

From quantum-mechanical approach, we know that the energy levels of an atom are not a set of discrete values, and that each of the levels belongs to a particular transition $E_2 - E_1$ has a finite energy width ΔE_1 and ΔE_2. As a result, an infinitely sharp line is not obtained but instead an intensity distribution with a half-width of the order of the sum of the two term widths.

From the Heisenberg uncertainty principle, ΔE_1 and ΔE_2 values are related to the average time Δt_1 and Δt_2, then

$$\Delta E \times \Delta t \approx h/2\pi$$

$$\Delta E \approx \frac{h}{2\pi \Delta t}$$

Thus the greater the mean life of the atom in a particular state. the smaller will be the width of the observed spectral line.

4.3.3 The Doppler effect

The frequency of the emitted radiation depends on the velocity of the source relative to that of the observer. The observed frequency increases if the motion is towards the observer and decreases if the motion is in the opposite direction.

Only for those atoms which have no velocity component in the direction of the observer, will the frequency of the emitted light be equal to the natural velocity of the spectral line.

If each of the atoms in a given gaseous system had roughly the same velocity due to overall motion of the gas (for example; in the atmosphere of a star), the width of the spectral line would be unaffected, but the spectral line would be displaced to higher or lower frequencies according to the direction of motion. However, the center of mass of the system is fixed, and the atoms are in random motion and have Maxwellian distribution of velocities, the line is broadened but not displaced. Therefore the spectral line emitted by this gas consists of a range of frequencies symmetrically disposed about the natural frequency.

From the Doppler principle, if a source of light of wavelength λ_0 is moving with a velocity v relative to the observer, the apparent wavelength (λ) measured by the observer will be

$$\lambda = \lambda_0(1 + v/c)$$

where, c is the velocity of light. Therefore, the motion away from the observer produces a shift to longer wavelengths, and such motion is taken as positive.

And range of velocities increases with temperature, and therefore the range of frequencies comprising the spectral line increase. The temperature of the atoms may be calculated in terms of the broadening of the spectral line and the mass (m) of the atoms.

4.3.4 External effects

One of the major causes in the broadening of spectral lines is due to the pressure of the gas. When two atoms collide, which lead to a shift of the spectral lines to the red region, and the effect is noticeable at high pressures. Such a pressure broadening of the lines is dependent on the density, temperature, and nature of the gas within which the absorbing or emitting atom is situated.

If atom A and B are in collision. where A is neutral atom which is emitting, is dependent on the nature of atom.B. If B is a noble gas atom, the interacting force would be van der Waals type.

4.3.5 Questions

1. Write a note on breadth of spectral lines.
2. Explain Doppler effect of spectral lines.
3. A molecule makes a transition between the ground state and an excited state having a life time of 10^{-3} sec. Calculate the uncertainty in the excited state energy level and the width of the associated spectral line.

4.3.6 References

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UNIT 5: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Structure:

5.0 Objectives

After studying this unit you will be able to understand

1. Principle of NMR spectroscopy
2. Magnetic properties of nuclei
3. NMR spectrometer

5.1 Introduction

The phenomenon of nuclear magnetic resonance (NMR) was first discovered by American Physicist, Felix Bloch of the Stanford University and Edward Purcell of the Harvard University in 1946 for which they shared the Nobel Prize in 1952. It has grown enormously in power and versatility since that time, conspicuously since late 1970 with the introduction of Fourier transform (FT) NMR spectroscopy on a routine basis. Radiation chemistry, photochemistry, structural inorganic chemistry, the study of rapid equilibrium processes and numerous other applications are based on magnetic resonance. Recently multidimensional NMR analysis has been developed. The NMR spectroscopy depends upon the fact that most isotopes of the elements possess gyromagnetic properties, meaning thereby that they behave like tiny spinning bar magnets. When a sample containing nuclei exhibiting this immutable gyromagnetic is placed in an appropriate DC magnetic field and is simultaneously irradiated by a weaker rotating radiofrequency magnetic field, the nuclei can be compelled to

a) Reveal their presence
b) Identify themselves and
c) Describe the nature of their surroundings all by means of a minute radio signal which they transmit to a receiver coil coupled closely to the sample.

5.2 Principles of NMR Spectroscopy

The nucleus of hydrogen atom (proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. The nucleus of H atom generates a magnetic field (Fig.5.1). NMR involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the H nucleus when these are placed in an external static magnetic field. The sample absorbs electromagnetic radiations in radio wave region at different frequencies since absorption depends upon the type of protons or certain nuclei contained in the sample. Consider a spinning top, it performs a slower waltz like motion in which the spinning axis of the top moves slowly around the vertical axis. This is precessional motion and the top is said to be precessing around the vertical axis of earth's gravitational field. The precession arises from the interaction of spin with earth's gravity acting vertically downwards. It is known as gyroscopic motion. Consider a small magnetic spinning in an external field. It has been seen that the tiny magnet (proton) precesses about the axis of the external magnetic field in the same manner in which a spinning gyroscope presses under the influence of gravity (Fig.5.2).

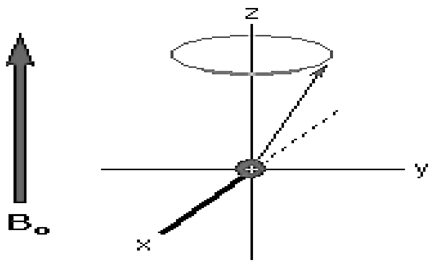

Fig.5.1 Spinning charge in nucleus

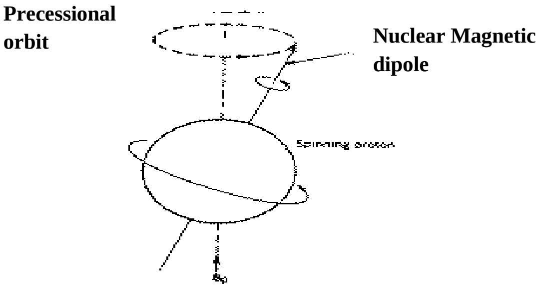

Fig.5.2. Proton precessing in magnetic field

It has been observed that

$$\omega = \gamma H_o \qquad (5.1)$$

Where, ω = angular precessional velocity, H_o = applied field in gauss.

γ = Gyromagnetic ratio = $2 \pi \mu / hI$

Here, μ = Magnetic moment of the spinning bar magnet, I = spin quantum number of the spinning magnet, h = Planck's constant. The fundamental NMR equation correlating electromagnetic frequency with magnetic field strength is

$$\nu = \gamma H_o / 2\pi \quad \text{or} \quad \gamma H_o = 2 \pi \nu \qquad (5.2)$$

where 'γ' the Gyromagnetic ratio is a fundamental nuclear constant. It is the proportionality constant between the magnetic moment 'μ' and spin number 'I', ν = frequency of electromagnetic ratio. From eqs. (5.1) and (5.2)

Angular precessional velocity $\omega = 2 \pi \nu$

The value of this frequency (ν), inserted is called precessional frequency which may be defined as the number of revolutions per second made by the magnetic moment vector of the nucleus around the external field H_o or which represents the precessional frequency of the spinning bar magnetic (nucleus) may be defined as equal to the frequency of electromagnetic radiations in mega cycles per second necessary to induce a transition from one spin state to another.

5.3 Magnetic Properties of Nuclei

One of the most important properties of nucleus is its spin 'I' or intrinsic spin angular momentum 'Iη'. This gives rise to a magnetic moment to the nucleus. The following rules are useful in determining the value of nuclear spin I.

i. If mass number A is odd and atomic number Z is even or odd, I is half integer.

Examples:$^1_1H,\ ^{13}_{6}C,\ ^{15}_{7}N,\ ^{19}_{9}F\ \ldots..$

ii. If A and Z are both even, I is zero.

Examples:$^4_2He,\ ^{12}_{6}C,\ ^{16}_{8}O,\ ^{32}_{16}S\ \ldots..$

iii. If A is even and Z odd, I is integer.

Examples: $^2_1H,\ ^{10}_{5}B,\ ^{14}_{7}N\ \ldots..$

The projection of the spin vector 'I' on any direction can have the values

$$m_I = -I, (-I+1)\ldots\ldots (I-2), (I-1), I \qquad (5.3)$$

These are 2I+1 in number and all are degenerate in the absence of an external magnetic field. In a magnetic field it splits up to 2I+1 state. The magnetic moment 'μ' associated with the spin angular momentum is given by

$$\mu = \gamma I h \qquad (5.4)$$

Here 'γ' is a scalar called the 'gyromagnetic ratio' and may take positive or negative value. An alternate expression for the magnetic moment is

$$\mu = g_N \mu_N I \qquad (5.5)$$

Where g_N, the nuclear 'g' factor is small dimensionless algebraic number, that takes different values for different nuclei, μ_N is the 'nuclear magneton' and is defined by

$$\mu_N = e\eta/2\ m_p$$

$$\mu_N = 5.051 \times 10^{-27} /T^{-1} (Nm^2) \qquad (5.6)$$

where m_p is the proton mass.

5.4 NMR Instrumentation

The basic requirements of a typical NMR spectrometer are:

i. An electromagnet giving a powerful, stable and homogeneous magnetic field. The field must be constant over the area of the sample and over the period of time of the experiment.

ii. A sweep generator, supplies a variable current to a secondary magnet, results the total applied magnetic field can be varied over a small range.

iii. A sample container, usually a glass tube (5mm OD) spun by an air driven turbine to average the magnetic field over the sample container. The process is often referred to as the spinning of the sample.

iv. An oscillator (r-f) connected to a coil, transmits the energy to the sample. As mentioned the axis of the coil has be perpendicular to the magnetic field.

v. The r-f receiver connected to a coil, called the receiver coil encircles the sample. Its axis has to be perpendicular to both the magnetic field and the axis of the transmitter coil. The transmitter and receiver coils and the sample holder are

vi. Constructed into a single unit called prone. Often the necessary small magnetic sweep field is obtained by use of sweep coils built into the NMR probe.

vii. A read out system consisting of an r-f amplifier, recorder and other accessories to increase the sensitivity, resolution and accuracy.

The schematic representations of these components are shown (Fig.5.3). The magnetic field at which the resonance occurs at a fixed frequency for a given nucleus is constant. Therefore each instrument normally works only for a particular kind of nucleus. Number nuclei can be studied by changing the oscillator, obviously, the field has to be large, and this type of high resolution investigation is not possible.

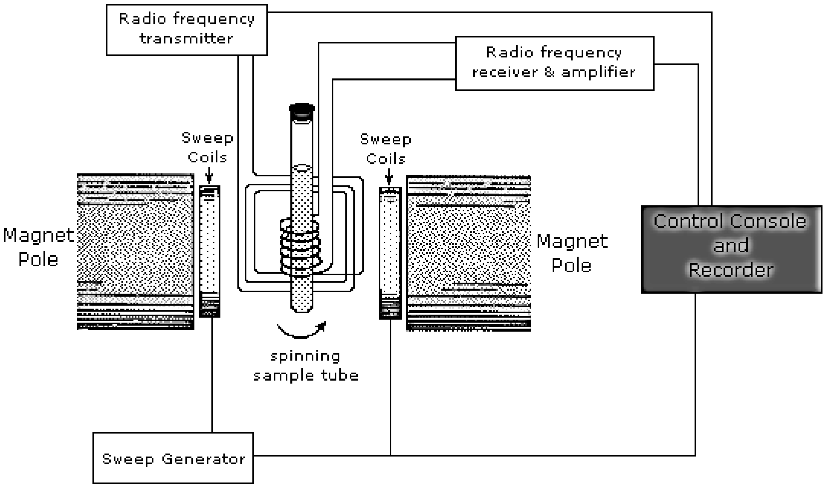

Fig.5.3. Block diagram of a NMR spectrometer.

Magnet:

Normally superconducting, electromagnets and permanent magnets (EM 360, EM-390) still around.

Frequency generator:

Creates the alternating current (at ω_o) that induces BI, Continuous wave or pulsed.

Detector:

Sends the base frequency (a constant frequency very close to ω_o) to the output frequency. It is lower frequency and much easier to deal with.

Recorder:

XY plotter, oscilloscope, computer etc.

5.5 Problems on Nuclear Magnetic Resonance

Problem 1: In a given organic compound two kinds of protons exhibit signals at 50 and 200 Hz using a 60 MHz p.m.r. spectrometer what will be their relative positions using 90 MHz spectrometer? Also convert the position of signal at 50 Hz into δ and τ units.

Solution: We know that chemical shifts are directly proportional to the spectrometer frequency. Therefore the signal at 50 Hz in a 60 MHz spectrometer

$$= \frac{50\ x\ 90}{60} = 75 \text{ Hz in a 90 MHz spectrometer.}$$

Similarly, the signal at 200 Hz in a 60 MHz spectrometer

$$= \frac{200\ x\ 90}{60} = 300 \text{ Hz in a 90 MHz spectrometer.}$$

Again, we know that : $\delta = \frac{\Delta\nu \text{ (in Hz X 106)}}{frequency\ \ used\ \ (inHz)}$

Therefore, the signal at 50 Hz in a 60 MHz spectrometer will have $\delta = \frac{50x10^6}{60x10^6}$ =0.88

Now $\tau = 10 - \delta = 10.088 = 0.912$

Problem 2: Calculate the strength of the magnetic field to give a precessional frequency of 100 MHz for ^{12}O nucleus, g_N=-0.757: μ_N=5.051x10^{-27} JT$^{-1:}$ I = 5/2.

Solution: The separation between any two adjacent levels is $g_N\mu_N B_{0.}$ue of the resonance condition gives

$$B_0 = \frac{h\nu}{g_N \mu_N}$$

$$= \frac{6.626X10^{-34}\ X100X10^6}{0.757X5.051X10^{-27}} = 17.33 \text{ T}$$

Problem 3: What is the nuclear g_N factor for ^{19}F nucleus which has a magnetic moment of 2.6273 μ_N and Nuclear spin quantum number I= $\frac{1}{2}$.

Solution: $\mu = g_N \mu_N I$

$$g_N = \frac{\mu}{I\,\mu_N} = \frac{2.6273\ \mu_N}{\frac{1}{2}\mu_N} = 5.2546.$$

5.6 Let us sum up

This unit gives in detailed information of discovery of NMR, magnetic field effect and its various applications. The principle of NMR: its explanation with mathematical form, experimental application of NMR and its components.

5.7 Key Words

NMR spectroscopy, principle of NMR, electromagnet, frequency generator.

5.8 Review Questions

1. What are Principles involved in NMR spectroscopy?
2. Explain with neat diagram of the basic requirements in NMR spectrometer.

5.9 Reference books:

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UNIT 6: CHEMICAL SHIFT

Structure:

6.0 Objectives

After studying this unit you will be able to understand

1. Chemical shift
2. Relaxation process
3. NMR in medicine

6.1 Introduction

The position of the NMR signals helps to understand the kinds of protons they are aromatic, aliphatic, primary, secondary, tertiary, benzylic, vinylic, acetylenic, and adjacent to halogen or to other groups. These various kinds of protons have different electronic environment and it is the electronic environment that determines just where in the spectrum a proton absorber.

6.2 Chemical Shift

Chemical shift is defined as nuclear shielding/applied magnetic field. Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For ^{1}H NMR, the reference is usually Tetramethylsilane (TMS), Si $(CH_3)_4$.

The shifts in the positions of NMR signals (compared with a standard reference) resulting from the shielding and deshielding by electrons are referred to as chemical shifts. The frequency at which a nucleus comes into resonance in a magnetic field may be given by the following equation

$$\nu = (\gamma/2\pi)\, H_o$$

From the above equation it is evident that the frequency can be calculated if the value of magnetic field at which resonance occurs could be derived from the NMR spectrum. But it is difficult to determine accurately the absolute value of the field corresponding to a peak and in practice the difference in peaks is observed. In order to solve this difficulty, the resonance frequencies of nuclei in a sample are quoted relative to the reference frequency. The position of the peaks in an NMR spectrum relative to the reference peak is expressed in terms of the chemical shift, δ, which is defined as

$$\delta = \frac{H_0(reference\ ) - H_0(sample\ )}{H_0(reference\ )} x10^6\, ppm \qquad (5.7)$$

The value of H_o for the reference is usually greater than Ho for the sample, so subtraction in the direction indicated gives a positive δ. In terms of frequency unit δ takes the form

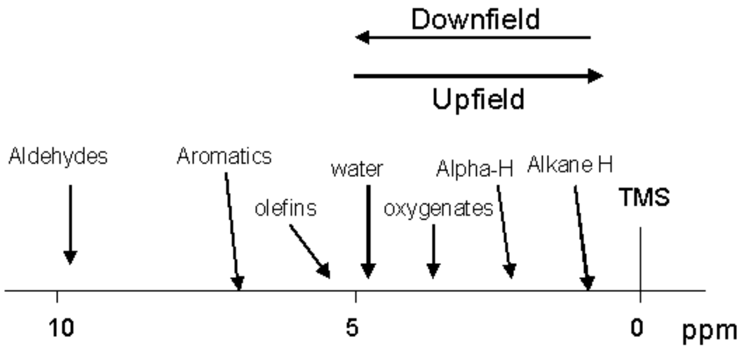
$$\delta = \frac{\upsilon(reference\ ) - \upsilon(sample\ )}{\upsilon(reference\ )} x10^4\ ppm \tag{5.8}$$

The chemical shift, δ is dimensionless and expressed in parts per million (ppm) on account of the factor 10^6 in equation (5.7) and (5.8).

An alternative system which is generally used for defining the position of the resonance relative to the reference is assigned tau (τ) scale. On this scale, the reference is assigned the arbitrary positions of 10 and the values of other resonances are given by

$\tau = 10 - \delta$ where δ has the same significance.

We have now determined that chemically different protons have different electronic environments. Differences in the electronic environments cause the protons to experience slightly different applied magnetic fields owing to the shielding/deshielding effect of the induced electronic magnetic fields. Over the years NMR spectra have been obtained on every conceivable organic molecule in nature or synthesized in a lab. In order to standardize the NMR scale it is necessary so set 'o'as a reference point to which all protons can then be compared. The standard reference that was chosen is tetramethylsilane (TMS). This compound has four CH_3 methyl groups single bonded to a silicon atom. All of the protons on the methyl groups are in the same electronic environment. Therefore only one NMR signal will be generated. Furthermore, the electronegativity of the carbon atoms is actually higher than the silicon atom to which they are bonded. This result in the sigma electrons being shifted toward the carbon atoms in the methyl groups and consequently, the protons will be heavily shielded causing the one signal to be generated at a very high magnetic field strength setting. It is that signal that all other NMR signals of a sample are referenced to. This association with the reference signal is called the chemical shift. This shift is measured in parts per million (ppm). NMR signals occurring near the TMS resonance are said to be in an upfield position while those shifted away by deshielding are said to be downfield (see figure below).



Virtually all NMR signals will be further downfield from the TMS signal because of the heavily shielded nature of the methyl protons in the TMS molecule. The proton NMR chemical shift range is 0-12 ppm. The ppm scale is another form of standardization that allows one to compare directly the ^{1}H spectra obtained on NMR instruments with different magnetic fields. After the samples have been referenced to the TMS resonance at 0 ppm the actual NMR peak position in Hz is divided by the resonance frequency of the spectrometer, which is in MHz Thus, one is dividing Hz by MHz which is a part per million (ppm). One ppm on a 58 MHz NMR instrument is actually 58 Hz from the resonance position of TMS, while on a 300 MHz NMR instrument 1ppm is 300Hz from the TMS resonance position. With this standardization/normalization in place one can always unequivocally say that all benzene protons resonate at 7.16 ppm no matter what NMR instrument is being used in the analysis. It may be remembered that greater the deshielding of protons, larger the value of δ (or smaller value of τ table 6.1).

6.2.1 Factors Influencing Chemical Shift

Following are the factors which influence the chemical shift.

a) Inductive effect

b) Van der Waal's deshielding

c) Anisotropic effects

d) Hydrogen bonding

a) Inductive Effect: A proton is said to be deshielding if it is attached to an electronegative atom or group. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more. Consider the following compounds:

i) $\overset{\textbf{b}}{CH_3}\overset{\textbf{a}}{CH_2}F$ ii) $\overset{\textbf{b}}{CH_3}\text{-}\overset{\textbf{a}}{CH_2}\text{-}Cl$

Two signals are expected for each of the two compounds. Deshielding for protons 'a' in compound (i) is more than that for similar protons in compound (ii).

As the distance from the electronegative atom increases, the deshielding effect due to it diminishes. Protons 'b' is comparatively less deshielded and hence will resonate at comparatively lower value of δ.

Table: 6.1 τ value of CH_3 protons

Compound	**τ value**
CH_3F	5.75
CH_3Cl	6.90
CH_3Br	7.36

Why deshielding? Hydrogen nuclei in a molecule are surrounded by electronic charge and shield the nucleus slightly from the influence of the applied field. Thus, to bring this proton to resonance, the applied field must be increased to overcome the shielding effect. In a magnetic field, the electrons around the proton are induced to circulate and thus, generate induced magnetic field which opposes the applied field. Greater the electron density circulating around the proton, greater is the induced magnetic field (opposing the external field) and greater will be the applied field required to overcome the shielding effect. On the other hand, electronegative atoms or groups withdraw electron density around the proton and thus causes deshielding (reverse or shielding). Due to deshielding, smaller value of applied field will be needed to bring the proton to resonance. Greater the electronegativity of the atom or group, greater will be deshielding effect on a proton.

Greater the distance of the electronegative atom or group from a particular proton, smaller is the deshielding effect on it. In TMS, four electron releasing groups (- CH_3 groups) cause powerful shielding effect and hence TMS proton (all equivalent) resonance at high field.

b) Van der Waal’s deshielding:

In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

c) Anisotropic effects (Space effect):

The deshielding effect on protons attached to C=C (Fig 6.1) is higher than that can be accounted for by the inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyne protons appear at relatively low value of δ. The values of δ (chemical shift) in each case can be justified by explaining the manner in which the π electrons circulate under the influence of the applied field. Consider an alkene. It is so oriented that the plane of the double bond is at right angles to the applied field. Induced circulation of π electrons generates induced magnetic field which is diamagnetic around carbon atom and paramagnetic in the region of the alkene protons. Thus the protons will feel greater field strength and hence resonance occurs at lower applied field.

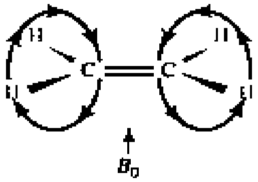


Fig.6.1 Deshielding of Ethylenic proton.

Alkynes:

In the alkynes, electronic circulation around triple bond takes place in such a way that the protons experience diamagnetic shielding effect (Fig.6.2). When the axis of the alkyne group lies parallel to the direction of the applied field, the π electrons are induced to circulate around the axis in such a way that induced field opposes the applied field. Thus, protons feel smaller field strength (shielding) and hence resonance occurs at higher applied field (low δ values).

Benzene:

In case of benzene, loops of π electrons are delocalized cylindrically over the aromatic ring (Fig.6.3). These loops of electrons are induced to circulate in the presence of the applied field producing ring current. The induced current is diamagnetic (opposing the applied field) in the center of the ring and is paramagnetic outside the ring. Thus the aromatic protons (around the periphery of the ring) experience a magnetic field greater in magnitude than the applied field. Such protons are said to be deshielded and hence, smaller applied field (higher value of δ) will be required to bring them to resonance. It may be noted that the protons held above and below the plane of the ring resonate at low δ value. In a molecule of toluene, the methyl protons resonate at 2.34 δ whereas a methyl group attached to an acyclic alkene appears at 1.95 δ. It can be explained by the greater deshielding influence of the ring current in an aromatic compound as compared to the deshielding influence caused by conjugated alkene group. From the NMR spectrum, we can thus, decide whether a particular compound has substantial aromatic character in it or not.

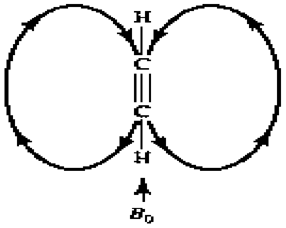


Fig.6.2. Shielding of acetylene proton

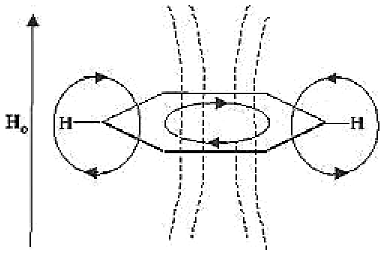


Fig.6.3. Ring current effect in Benzene

An excellent example of shielding and deshielding by ring currents is given by some of the annulenes (Fig.6.4). The protons outside the ring of annulenes are strongly deshielded and those inside the ring are strongly shielded.

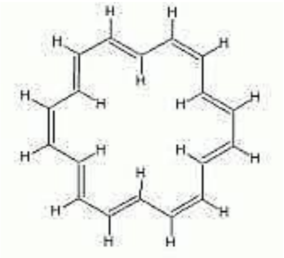


Fig.6.4 Annulene

Compared to the anisotropic effects of circulating π – electrons, the sigma electrons of C-C bond produce a small effect (Fig. 6.5). The axis of C-C bond is the axis of the deshielding cone.

The above figure accounts for the deshielding effect of successive alkyl substituents on the proton attached to a carbon atom. Thus, the protons absorb downfield in the order RCH_3, R_2CH_2 and R_3CH. Also an equatorial proton is found to absorb further downfield by 0.7 – 0.1 ppm than the axial proton on the same carbon atom in a rigid six member ring. The axial and equatorial (Fig.6.6) protons on C_1 are oriented in the same way with respect to C_1-C_2 and C_1-C_6 but the equatorial proton is within the deshielding cone of C_2-C_3 and C_5-C_6.

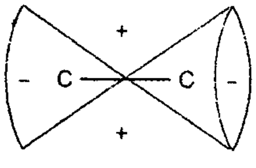


Fig.6.5. shielding (+) and deshielding (-) zones of C-

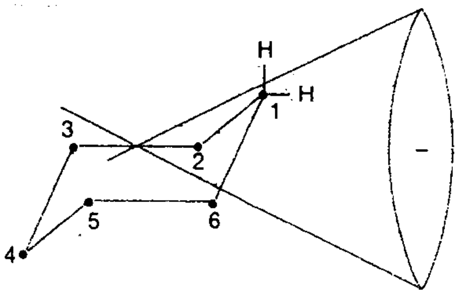


Fig.6.6. Deshielding of equatorial proton of a rigid six membered ring

d) Hydrogen Bonding:

It has been found that a hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparison to the one which does not. The hydrogen bonded protons being attached to a highly electronegative atom will have smaller electron density around it. Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield. The downfield shift depends upon the strength of hydrogen bonding. Intermolecular and intra-molecular hydrogen bonding can be easily distinguished as the latter does not show any shift in absorption due to the change in concentration. In case of phenols, absorption occurs between -2 to 6τ. But if the concentration is decreased i.e. if the volume of the solvent, say carbon tetrachloride is increased, then the absorption for OH proton occurs upfield. In case the OH group on benzene is intra-molecularly bonded with some other group in the ortho position, the absorption for OH proton may occur even at the negative tau value. For example, the OH proton in salicylic acid absorb at – 0.6τ. Enols show strong intra-molecular hydrogen bonding which is further stabilized by resonance. Due to this, a great deshielding effect is caused and absorption for such a proton occurs at the negative tau value (10.5-12δ). It is due the fact that acids exist as dimers as a result of hydrogen bonding (Fig. 6.7 & 6.8). A signal for carboxylic acid proton in ethoxy acetic acid appears at – 0.95 τ(10.95 δ).

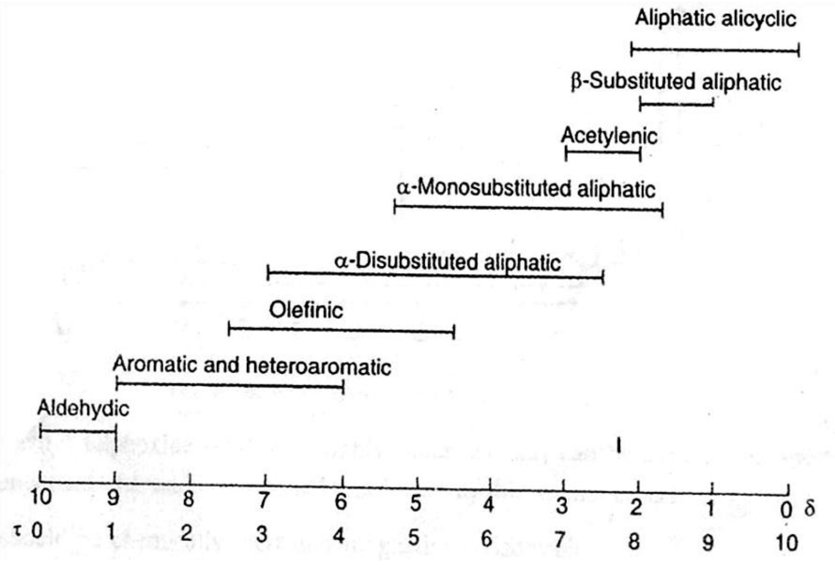


Fig.6.7. General Regions of chemical shifts

The regions of absorption for protons attached to the unsaturated linkage are shown below

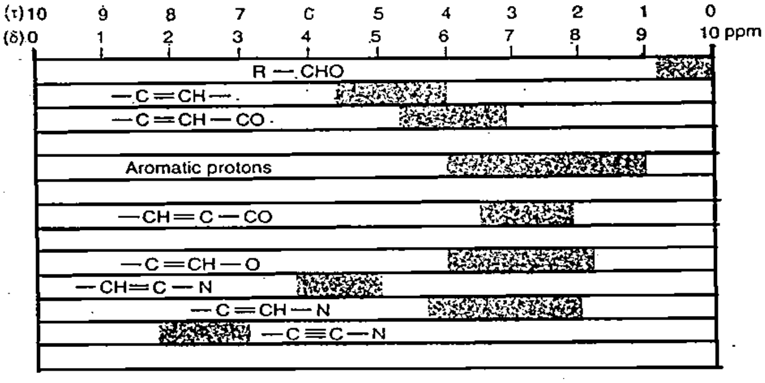


Fig.6.8. Regions of absorption for protons attached to the unsaturated linkage.

6.3 Relaxation Processes

Emission of radiation is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. We must focus on non-radiative relaxation processes.

Ideally, the NMR spectroscopic would like relaxation rates to be fast – but not too fast. If the relaxation rate is fast, then saturation is reduced. If the relaxation rate is too fast, line–broadening in the resultant NMR spectrum is observed.

There are two major relaxation processes;

a) Spin-lattice (longitudinal) relaxation

b) Spin-Spin (transverse) relaxation.

A) Spin-Lattice Relaxation

The sample in which the nuclei are held is called the lattice. Nuclei in the lattice are in vibration and rotational motion, which creates a complex magnetic field. The lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with the nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample).

The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependent on the magnetogyric ratio of the nucleus and the mobility of the lattice. AS mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with the excited nuclei. However, at extremely high motilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

The spins in the upper state transfer the excess energy to the surroundings (lattice) is called ‘spin-lattice relaxation’ and the time required for the population difference to become 1/e times the population difference at t=0 is referred to as the ‘spin lattice relaxation time or longitudinal relaxation time T_1. T_1 varies over a large range, being $10^{-2} – 10^{4}$ s for solids and $10^{-4} – 10$ s for liquids. In addition to spin lattice relaxation of spin can also occur by a direct interaction of two spin states.

B) Spin-Spin Relaxation

Spin–spin relaxation describes the interaction between neighboring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited while the excited nucleus relaxes to the lower energy state. There is not net change in the populations of the energy states, but the average lifetime of a function in the excited state will decrease. This can result in line broadening.

If initially the spins have a common phase, the phases will become random in the course of time. The dephasing time is known as spin-spin relaxation time or transverse relaxation time T_2. For solids, T_2 is of the order of 10^{-4} seconds, while for liquids $T_2 \approx T_1$. The shape of the spectral lines depends significantly on the relaxation time. When the relaxation time is very long, lower state is being repopulated at a slow rate resulting in saturation.

For the spin ½ system, let ‘N’ be the total number of spins, n (0) and n (t) be the

$$dn/dt = \omega n_2 - \omega n_1 = \omega (n_2 - n_1) = -\omega n \tag{6.1}$$

where ω is the transition probability per unit time for induced adsorption/emission.

Since $n_1+n_2 = N$ and $n_1-n_2 = n$,

$$N_1=1/2(N+n) \quad (dn/dt) = ½\,(dn/dt) \tag{6.2}$$

From eqs. (6.1) and (6.2)

$$dn/dt = -2\omega n, \quad n\,(t) = n\,(0)\,e^{-2\omega t} \tag{6.3}$$

The time required for the value n (t) to become n (0)/e is defined as the spin – lattice relaxation time T_1.

$$\text{Therefore,} \quad T_1=1/2\omega \tag{6.4}$$

That is the spin lattice relaxation time is inversely proportional to the transition probability per unit time for induced absorption.

Example: Ethanol, CH_3-CH_2OH

The spectrum of an ordinary sample of ethanol (Fig.6.9) may be described as follows:

a) Triplet, δ 1.2, 3H(CH_3)
b) Quartet, δ 3.63, 2H (CH_2)
c) Singlet, δ 4.8, 1H (OH)

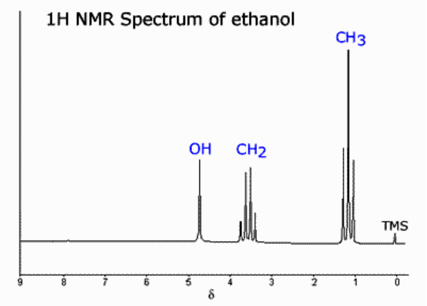


Fig.6.9. 1H NMR spectrum of ethanol

Explanation: Ethanol is having three kinds of protons and consequently exhibits three signals as given above.

The upfield triplet of δ 1.2 is because of the three equivalent methyl protons. Evidently its splitting into a triplet is because of the two neighboring on the methylene group.

The quarter at δ 3.63 is from the two methylene protons. Its multiplicity of four peaks is due coupling with the three methyl protons; there being no coupling with hydroxyl proton.

Finally the downfield single at δ 4.8 is due to hydroxyl proton which does not show any coupling with the adjacent methylene protons.

The relative areas under the peaks of methyl, methylene and hydroxyl protons are in the ratio 3:2:1. And interesting feature of the NMR spectrum of an ordinary sample of ethanol is that we do not observe any splitting of signals due to coupling between hydroxyl proton and the methylene protons although they are on adjacent atoms.

The above observation can be ascribed to the fact that the hydroxyl proton is undergoing very repaid exchange or back and forth movement, from one ethanol molecule to another.

$$CH_3CH_2\text{-}OH + CH_3\text{-}OH \leftrightarrow CH_3CH_2\text{-}OH + CH_3CH_2\text{-}OH$$

Molecule1 Molecule 2 Molecule 1 Molecule 2

Before the coupling of the hydroxyl proton with methylene protons in a particular molecule can be detected by the spectrometer, the hydroxyl proton undergoes exchange with another molecule in which the alignment of methylene protons is different than that in the first molecule and so on. In other words the hydroxyl proton does not stay in the same environment long enough for its coupling with the methylene protons to be recorded.

But if we examine the NMR spectrum of a very pure sample of ethanol, it is found that the signal from the hydroxyl proton is split into a triplet and the signal from the methylene protons is split into a multiple of five peaks. This is because in the highly purified sample the exchange the exchange process gets slow down and the coupling between hydroxyl and methylene protons can be recorded. This slowing down of the exchange process is due to the complete absence of acidic or basic impurities in ethanol which catalyze the exchange process.

6.4 NMR in Medicine

The application of nuclear magnetic resonance best known to the general public is magnetic resonance imaging for medical diagnosis and magnetic resonance microscopy in research settings, however, it is also widely used in chemical studies, notably in NMR spectroscopy such as proton NMR, carbon-13 NMR, deuterium NMR and phosphorus-31 NMR. Biochemical information can also be obtained from living tissue (e.g. human brain tumors) with the technique known as in vivo magnetic resonance spectroscopy or chemical shift NMR Microscopy.

These studies are possible because nuclei are surrounded by orbiting electrons, which are charged particles that generate small, local magnetic fields that add to or subtract from the external magnetic field, and so will partially shield the nuclei. The amount of shielding depends on the exact local environment. For example, hydrogen bonded to oxygen will be shielded differently than hydrogen bonded to a carbon atom. In addition, two hydrogen nuclei can interact via a process known as spin-spin coupling, if they are on the same molecule, which will split the lines of the spectra in a recognizable way.

As one of the two major spectroscopic techniques used in metabolomics, NMR is used to generate metabolic fingerprints from biological fluids to obtain information about disease states or toxic insults.

Magnetic resonance works by the interaction of electromagnetic radiation with the atomic nuclei in the presence of a magnetic field. Since light is nothing else than electromagnetic radiation, it seems a straightforward idea to use an approach similar to optical imaging in order to get spatially resolved NMR spectra.

This, however, does not work, at least not for the purpose of looking inside the human body. As you know, the frequency of NMR instruments is in the range of MHz (up to 1000 MHz for the largest magnets). In MRI scanners, much smaller magnetic fields around 0.5-2 Tesla are typically used. The wave length is given by

$$\lambda=2\pi c\omega=2\pi c\gamma B,$$

MRI machines make use of the fact that body tissue contains lots of water, and hence protons (^{1}H nuclei), which will be aligned in a large magnetic field. Each water molecule has two hydrogen nuclei or protons. When a person is inside the powerful magnetic field of the scanner, the average magnetic moment of many protons becomes aligned with the direction of the field. A radio frequency current is briefly turned on, producing a varying electromagnetic field. This electromagnetic field has just the right frequency, known as the resonance frequency, to be absorbed and flip the spin of the protons in the magnetic field. After the electromagnetic field is turned off, the spins of the protons return to thermodynamic equilibrium and the bulk magnetization becomes realigned with the static magnetic field. During this relaxation, a radio frequency signal (electromagnetic radiation in the RF range) is generated, which can be measured with receiver coils.

Information about the origin of the signal in 3D space can be learned by applying additional magnetic fields during the scan (Fig.6.10). These additional magnetic fields can be used to generate detectable signals only from specific locations in the body (spatial excitation) and/or to make magnetization at different spatial locations process at different frequencies, which enables k-space encoding of spatial information. The 3D images obtained in MRI can be rotated along arbitrary orientations and manipulated by the doctor to be better able to detect tiny changes of structures within the body. These fields, generated by passing electric currents through gradient coils, make the magnetic field strength vary depending on the position within the magnet. Because this makes the frequency of the released radio signal also dependent on its origin in a predictable manner, the distribution of protons in the body can be mathematically recovered from the signal, typically by the use of inverse Fourier transform.

Fig.6.10. Some examples of medical MR images

6.5 Problems on Chemical shift

Problem 1: Calculate the chemical shift in ppm (δ) for a proton that has resonance at 126 Hz downfield from TMS on spectrometer that operates at 60 MHz

Solution. The chemical shift (δ) can be calculated by applying the relation

$\Delta\upsilon$ (in cps) x 10^6

$$\delta = \frac{\Delta\upsilon(\text{incps }) X\ 10^6}{frequency\ \ of\ spectrometer\ \ in\ cps\ (Hz)}$$

Substituting the values, we get,

$$\delta = \frac{126\ \text{X}\ 10^6}{60\ X\ 10^6} = 60 \text{ x } 10^6$$

Thus, chemical shift, δ = 2.1 ppm.

Problem 2: An NMR signal for a compound is found to be 180Hz downward from TMS peak using a spectrometer operating at 60Hz. Calculate its chemical shift in ppm.

Solution:

Chemical shift in ppm= $\frac{chemical\ \ shift\ in\ Hz}{operating\ \ frequency\ \ in\ MHz} = \frac{180}{60}$ = 3 ppm.

Problem 3: The observed chemical shift of proton is 300 Hz from TMS and the operative frequency of the spectrometer is 100 MHz Calculate the chemical shift in terms of δ (ppm)

Ans: The chemical shift in terms of δ = 300/100 = 3 ppm.

Problem 4. A proton H_b is coupled to four equivalent neighboring protons H_a. What will be multiplicity and the relative intensity of the lines in the signal H_b?

Ans: H_b will appear as a quintet with relative intensities of lines in the ratio 1:4:6:4:1.

6.6 Let us sum up

This unit explains the concept of chemical shift and its detailed presentation the factor affect on chemical shift with examples. The relaxation process with evidences are given and the application of NMR in medicine. This information is helps to understand the some of the concept of NMR.

6.7 Key words.

Chemical shift, Relaxation process, shielding and deshielding, Medical applications

6.8 Review Questions

1. What do you understand by the terms shielding and deshielding?
2. Describe the major relaxation processes in NMR spectroscopy.
3. Give an account of chemical shifts in the position of NMR signals.
4. Explain briefly factors influencing in chemical shift.

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Unit 7: Microwave spectroscopy

Structure:

7.0 Objectives

After studying this unit you will be able to understand

1. Meaning of Microwave spectroscopy.
2. Difference between Infrared and Microwave spectroscopy
3. Classification of molecules.

7.1 Introduction to Microwave Spectroscopy

Microwave spectroscopy is proving in recent years a great asset in the study of various problems in physics, chemistry, electronics and even astronomy. Particularly, this has been found to be very useful in the determination of the structures of those molecules which do not give good results by using Raman and Infrared spectroscopy. The ability to measure frequencies more precisely in the microwave region allows very accurate calculations, than in the infrared-visible-ultraviolet region and accuracy of the order of 0.001 to 0.005 Å is possible.

These spectra result from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region. These spectra are shown by molecules which *possess a permanent dipole moment*, *e.g.*, HCL, CO, H_2O vapour, NO, etc. Homonuclear diatomic molecules such as H_2, Cl_2, etc., and linear polyatomic molecules such as CO_2, which do not possess a dipole moment, do not show microwave spectra.

7.2 What is Microwave Spectroscopy?

The microwave spectroscopy explores that part of the electromagnetic spectrum which is extending from 100 μm ($3x10^{13}$ Hz) to 1 centimeter ($3x10^{10}$ Hz). This region of electromagnetic spectrum is designated as the microwave region. This lies between the far infrared and conventional radio frequency region. Spectroscopic applications of microwave consist almost exclusively of *absorption* works, rather than of the *emission type.* In most of the cases, absorption of microwave energy represents changes of the absorbing molecule from one rotational level to another. Therefore, the microwave spectroscopy deals with the pure rotational motion of molecules and is also known as rotational spectroscopy. The condition for observing resonance in that region is that a molecule must possess permanent dipole moment. When a molecule having dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During the interaction, energy can be absorbed or emitted and thus the rotation of the molecule gives rise to a spectrum. If molecules are not having dipole moment, interaction is not possible and these molecules are said to be "*microwave inactive"*. Examples of such molecules are H_2, Cl_2, etc. On the other hand, the molecules like HCl, CH_3Cl, etc., are having dipole moments and their interaction will give rise to a spectrum. Such molecules are said to be "*microwave active"*.

Generally, the microwave spectra obtained in most of the molecules are absorption spectra. Theoretical consideration reveals that the probability of microwave spectra is only about *one per cent* of the optical absorption.

7.3 Differences between Infrared and Microwave Spectroscopy

The main differences between infrared and microwave spectroscopy are as follows:

1. The absorption spectrum in the microwave region is characteristic of the absorbing molecule as a whole, whereas spectrum in the infrared region is characteristic of the functional groups present in the absorbing molecule.
2. The resolution of the lines in the microwave spectrum is very much greater than that obtained by the infrared method.
3. In microwave spectroscopy, the substance must be in gaseous state. On the other hand, in the infrared spectrum the substance may be solid, liquid or gaseous state.
4. In microwave spectroscopy, the spectra observed are nearly always absorption spectra. But in the infrared spectroscopy the spectra observed may be absorption or emission spectra.

7.4 Classification of Molecules

In quantum mechanics the free rotation of a molecule is quantized, so that the rotational energy and the angular momentum can take only certain fixed values, which are related simply to the moment of inertia, I, of the molecule. For any molecule, there are three moments of inertia: I_A, I_B and I_C about three mutually orthogonal axes *A*, *B*, and *C* with the origin at the center of mass of the system. Molecules can be classified based on their three principle moment of inertia.

7.4.1 Linear molecules. Molecules belongs these groups all atoms are arranged in a straight line. For a linear molecule the moments of inertia are related by $I_A << I_B = I_C$. For most purposes, I_A can be taken to be zero. Examples of linear molecules include dioxygen, O_2, dinitrogen N_2, carbon monoxide CO, hydroxy radical, OH, carbon dioxide CO_2, hydrogen cyanide HCN, carbonyl sulfide OCS, acetylene (ethyne, HC≡CH) and dihaloethynes.

7.4.2 Spherical tops (spherical rotors). All three moments of inertia are equal to each other: $I_A = I_B = I_C$. These can have No dipole moment owing their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable. Examples of spherical tops include phosphorus tetramer (P_4), carbon tetrachloride (CCl_4) and other tetrahalides, methane (CH_4), silane, (SiH_4), sulfur hexafluoride (SF_6) and other hexahalides.

7.4.3 Symmetric tops (symmetric rotors). A symmetric top is a molecule in which two moments of inertia are the same, $I_A = I_B$ or$I_B = I_C$. By definition a symmetric top must have a 3-fold or higher order rotation axis. As a matter of convenience, spectroscopists divide molecules into two classes of symmetric tops,

Oblate symmetric tops (saucer or disc shaped) with $I_A = I_B < I_C$ and

Prolate symmetric tops (rugby football, or cigar shaped) with $I_A < I_B = I_C$.

The spectra look rather different, and are instantly recognizable. Examples of symmetric tops include

Oblate: benzene, C_6H_6, ammonia, NH_3

Prolate: chloromethane, CH_3Cl, propyne, $CH_3C{\equiv}CH$

7.4.4 Asymmetric tops (asymmetric rotors). The three moments of inertia have different values. Examples of small molecules that are asymmetric tops include water, H_2O and nitrogen dioxide, NO_2 whose symmetry axis of highest order is a 2-fold rotation axis. Most large molecules are asymmetric tops.

7.5 Problems on Microwave spectroscopy

Problem 1: Calculate (a) the reduced mass and (b) the moment of inertia of NaCl using the mean internuclear distance of 2.36 Å. The atomic masses are Cl=35×10^{-3} kg mol^{-1} and Na = 23×10^{-3} kg mol^{-1}.

Solution: The reduced mass is given as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}$$

or $$\mu = 2.304 \times 10^{-26}\ \text{kg}$$

Where $m_1=35\times10^{-3}$ kg/mol^{-1}and $m_2 = 23 \times 10^{-3}$ kg/mol^{-1}

The moment of inertia is given as $I = \mu\, r^2 = 12.83 \times 10^{-46}$ kg/mol^{-1}

Problem 2: The intermolecular distance of carbon monoxide molecule is 1.13 Å. Calculate the energy and angular velocity of this molecule in the first excited rotational level. The atomic masses are: $^{12}C=1.99\times10^{-26}$ kg; $^{16}O=2.66\times10^{-25}$ kg.

Solution: r =1.13 Å =1.13×10^{-8}cm=1.13×10^{-10}m

The reduced mass μ of CO is given as follows:

$$\mu=\frac{m_1 m_2}{m_1+m_2}=\frac{1.99X10^{-26}X2.66X10^{-26}}{(1.99+2.66)X10^{-26}}=1.14\text{x}10^{-26}\text{kg}$$

Hence the moment of inertia is as follows:

$$I=\square r^2=(1.14\text{x}10^{-26}\text{kg})\ (1.13\text{x}10^{-10}\text{m})^2=1.46\text{x}10^{-46}\text{kg m}^2$$

The rotational energy level of a rigid diatomic molecule are given by= $E_J=\frac{h^2}{8\pi^2 I}J\ (J+1)$

For the first excited rotational level, J=1.

Therefore, $E_J=\frac{h^2X\ 1(1+1)}{8\pi^2 I}=\frac{h^2}{4\pi^2 I}$ joule $=\frac{6.626X10^{-34}}{4\pi^2(1..46X10^{-46})}=7.61\text{x}10^{-23}$ joule

1eV=$1.602\text{x}10^{-19}$J

$$E_1=\frac{7.61X10^{-23}}{1.602X10^{-19}}=4.76\text{x}10^{-4}\text{eV}$$

We know that, $E_1=\frac{1}{2}I\omega^2$, where ω is the angular velocity, hence

$$\omega=\sqrt{\frac{2E_J}{I}}=\sqrt{\frac{2X(7.61X10^{-23})}{1.46X10^{-46}}}=3{,}23\text{x}10^{11}\text{radians s}^{-1}$$

Problem 3: The pure rotational spectrum of the gaseous molecule CN consists of a series of equally spaced line separated by 3.7978cm^{-1}. Calculate the internuclear distance of the molecule. The molar masses are: ^{12}C=12.011 and ^{14}N=14.007g mol^{-1}.

Solution: The spacing between the lines =2B =3.7978 cm^{-1}

$$B=3.7978/2=1.8989\ \text{cm}^{-1}$$

$$B=\frac{h}{8I_c\pi^2}\ \text{cm}^{-1}$$

$$I=\frac{h}{8\pi^2 B_c}=\frac{6.626X10^{-34}}{(8\pi^2)(1.8989)(3X10^{10})}=1.4742\text{x}10^{-46}\text{kg m}^2$$

The reduced mass is given as follows:

$\mu=\frac{m_1 m_2}{(m_1+m_2)N_A}$ where N_A refers to the Avogadro’s number and m_1, m_2 are the atomic masses of C and N respectively

$$\mu=\frac{12.011X14.007}{26.018X6.022X10^{23}}=1.0737\text{x}10^{-23}\text{g}=1.0737\text{x}10^{-26}\text{kg}$$

Since, $I=\mu r^2$

$$r=\sqrt{\frac{I}{\square}}=\sqrt{\frac{1.4742X10^{-46}}{1.0737X10^{-26}}}=1.1717\text{x}10^{-10}\text{m}=117\ \text{pm.}$$

7.6 Let us sum up

This unit gives the basic concept of microwave spectroscopy with examples and the meaning of microwave spectroscopy, explanation of difference between IR and microwave spectroscopy with these concepts the classification of molecules are given in detailed. These above concepts help to understand the importance and its applications.

7.7 Key words

Microwave spectroscopy, Infrared spectroscopy, classification of molecules

7.8 Review Questions

1. (a) What is microwave spectroscopy?

   (b) What is the difference between infrared and microwave spectroscopy?
2. Write a note on classification of molecules.

7.9 Reference books:

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Unit 8: Rotational spectroscopy

Structure:

8.0. Objectives

After studying this unit you will be able to understand

1. Meaning of rotational spectroscopy
2. Diatomic molecule
3. Rigid rotator and rigid non-rotator

8.1 Introduction.

We know that rotational energy, along with all other forms of molecular energy is quantized this means that a molecule cannot have any arbitrary amount of rotational energy i.e. any arbitrary value of angular momentum but its energy is limited to certain definite values depending on the shape and size of the molecules concerned. The permitted values the so called rotational energy levels may in principle be calculated for any molecule by solving the Schrodinger equation for the system represented by that molecule

8.2 Theory of Microwave Spectroscopy

We know that rotational energy, along with all other forms of molecular energy, is quantized. It means that rotational energy has certain permitted energy values, generally known as rotational energy levels which may be calculated for any molecule by solving the Schrodinger equation for the system represented by the molecule. For simple molecules the mathematics involved is simple whereas for complex molecule the mathematics involved is tedious and gross approximations have to be used. We will now discuss each class of molecule one by one.

8.2.1. Diatomic molecule as a rigid rotator:

A rotating diatomic molecule whose nuclei are supposed to be separated by a definite mean distance may be treated as rigid rotator with free axis of rotation. In order to provide a suitable model for the interpretation of pure rotational spectra, consider a diatomic molecule in which masses m_1 and m_2 of atoms A and B are joined by a rigid bar whose length r and is given by

$$r = r_1 + r_2 \tag{8.1}$$

Where r_1 and r_2 the distances of atoms A and B from the center of gravity G of the molecule AB about which the molecule rotates end-over-end as shown in figure 8.1. In this case, the moment of inertia about G is defined by

$$I = m_1r_1^2 + m_2r_2^2 \tag{8.2}$$

As the system is balanced about its center of gravity G, one may write

$$m_1r_1= m_2r_2 \tag{8.3}$$

On substituting equation (8.3) in (8.2), we obtain the following expression:

$$I = m_2r_2\,r_1 + m_1r_1r_2$$

$$= r_1r_2(m_1 + m_2) \tag{8.4}$$

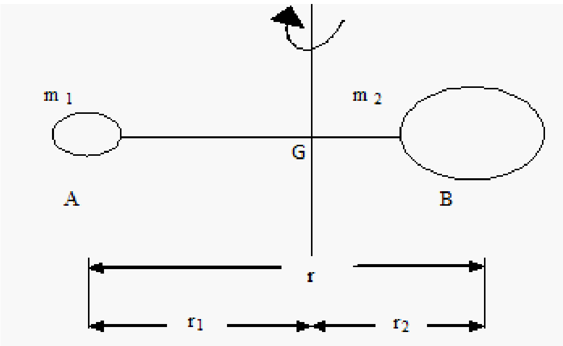

Fig.8.1. A Rotating Diatomic Molecule

But, from equation (8.1) and (8.3), we have

$$m_1r_1 = m_2r_2 = m_2(r - r_1) \tag{8.5}$$

On solving equations (8.4) and (8.5), we get

$$r_1 = \frac{m_2}{m_1+m_2}r \text{ And } r_2 = \frac{m_1}{m_1+m_2}r \tag{8.6}$$

On putting these values of r_1 and r_2 in equation (8.2), we get

$$I = \frac{m_1m_2^2}{(m_1+m_2)^2}r^2 + \frac{m_1^2m_2}{(m_1+m_2)^2}r^2$$

$$= \frac{m_1m_2^2 + m_1^2m_2}{(m_1+m_2)^2}r^2$$

$$= \frac{m_1m_2(m_1+m_2)}{(m_1+m_2)^2}r^2$$

$$I = \frac{m_1m_2}{m_1+m_2}r^2 = \mu r^2 \tag{8.7}$$

Where ‘µ’ is the reduced mass of the diatomic molecule and its value is

$$\square = \frac{m_1m_2}{m_1+m_2} \tag{8.8}$$

Equation (8.7) defines moment of inertia in terms of atomic masses and bond length.

A rotating molecule having a permanent dipole or magnetic moment generates an electric field which can interact with the electric component of the microwave region. If it is assumed that a diatomic molecule behaves like a rigid rotator, the rotational energy levels may in principle be calculated by solving the Schrodinger's equation for the system represented by that molecule.

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules where J = 0, 1, 2,} \tag{8.9}$$

Where h = Planck's constant, I = Moment of Inertia, J = Rotational quantum number, it takes integral values from zero upwards and $\frac{J(J+!)h^2}{4\pi^2}$ = the square of the rotational angular momentum.

In rotational region, spectra are generally expressed in terms of wave numbers, so it becomes useful to consider energies in these units. Thus, one may write

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 Ihc} J(J+1) \text{ cm}^{-1}$$

$$\varepsilon_J = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \tag{8.10}$$

Where c is the velocity of light expressed in cm per second. It is common to write B for $h/8\pi^2 Ic$ so that equation (8.9) reads as

$$\varepsilon_J = J(J+1)B \text{ cm}^{-1} \tag{8.11}$$

Where 'B' is called the rotational constant and may be expressed in cm per second or cm^{-1}, i.e.,

$$B = \frac{h}{8\pi^2 Ic} \text{ cm}^{-1} \tag{8.12}$$

From equation (8.11), we can show the allowed energy levels diagrammatically as in Fig.2 when J=0, equation (8.11) becomes as

$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} = B\,0(0+1) = 0 \tag{8.13}$$

From equation (8.13) it is evident that the molecule is not rotating at all. When J=1, equation (8.11) becomes as

$$\varepsilon_J = B\,1(1+1) = 2B \text{ cm}^{-1} \tag{8.14}$$

From equation (8.14), it follows that a rotating molecule has its lowest angular momentum. Similarly, one can calculate the value of ε_J for J = 2, 3, 4….The allowed rotational energy levels of a rigid diatomic molecule are shown in Fig.14.

Frequency of Rotational Spectral Lines: Consider there is a transition from rotational level of rotational quantum number '$J^{'}$' to that of higher quantum number J. The energy difference between these two levels will be given by

$$\Delta E_J = E_J - E_J^{'}$$

$$= \frac{h^2}{8\pi^2 Ih} J(J+1) - \frac{h^2}{8\pi^2 Ih} J^{'}(J^{'}+1) \qquad (8.15)$$

This energy, ΔE_J is evolved when the molecule returns to the original level of quantum number $J^{'}$ from the excited rotational level of quantum number J. According to quantum theory, the energy evolved is then given out in the form of spectral lines. The frequency of these spectral lines, expressed in wave number, is given by

$$\bar{\nu} = \frac{\Delta E_J}{hc} = \frac{h^2}{8\pi^2 Ihc}[J(J+1) - J^{'}(J^{'}+1)]$$

$$= \frac{h}{8\pi^2 Ic}[J(J+1) - J^{'}(J^{'}+1)]$$

$$= B\,[J\,(J+1) - J^{'}\,(J^{'}+1)] \quad \{\text{using equation (8.12)}\} \qquad (8.16)$$

When J =1, $J^{'}$=0, equation (8.16) becomes

$$\bar{\nu}_{J_{0\to1}} = B\left[1(1+1) - 0(0+1)\right]$$

$$= 2B\ \text{cm}^{-1} \qquad (8.17)$$

From equation (8.17) it follows that an absorption line will appear at 2B cm^{-1}. If the molecule is raised from $J^{'}$=1 to J=2 level by the absorption of more energy in the microwave region, equation (8.17) becomes as

$$\bar{\nu}_{J_{0\to1}} = B\,[2(2+1) - 1(1+1)]$$

$$= B\,(6 - 2) = 4B\ \text{cm}^{-1} \qquad (8.18)$$

It means that an absorption line will appear at 4B cm^{-1}. In general, when the molecule is raised from J to J+1, equation (8.16) becomes as

$$\nu_{J\rightarrow J+1} = B\,[(J+1)(J+2)-J(J+1)]$$

$$= B\,(J^2 + 3J + 2 - J^2 - J)$$

$$= 2B\,(J+1)\ cm^{-1} \qquad (8.19)$$

From equation (8.19), it is clear that a stepwise rising of the rotational energy gives rise to an absorption spectrum which consists of lines at 2B, 4B, 6B…cm^{-1}whereas a similar lowering would give rise to a similar identical emission spectrum. This is shown in Fig.8.2.

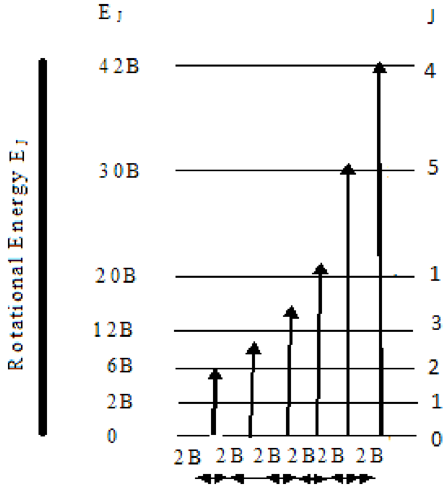

Fig. 8.2. Rotational spectrum of a Rigid Diatomic Molecule

Selection rule for rotational spectra: In order for a molecule to give rise to rotational spectrum, it becomes essential that the molecule must have a dipole moment but all transitions are not permitted. There is a selection rule which is given as

$$\Delta J = \pm 1 \qquad (8.20)$$

From the above rule, it is evident that only those transitions are permitted in which there is an increase or decrease by unity in the rotational quantum number. It means that J=0→J=2 → J = 4… transitions are not possible. In other words, these transitions are spectroscopically forbidden.

Validity of the Theory: The theory of microwave spectroscopy can be confirmed by considering the following examples:

(i) **Carbon Monoxide Molecule:** Let us now apply equation (8.19) to the observed microwave spectrum of the molecule to calculate its moment of inertia and hence the bond length. The first line corresponding to J=0 appears in the rotational spectrum of carbon monoxide at 3.84325 cm^{-1}

i.e., $\bar{\nu}_J$ = 3.84325 cm^{-1} (8.21)

From equation (8.19) we have $\bar{\nu}_J$ = 2B (J+1)

But J = 0 $\bar{\nu}_J$ = 2B (0+1) = 2B (8.22)

From equation (8.21) and (8.22), we have

$$2B = 3.84325\ \text{cm}^{-1} \text{ or } B = 1.92118\ \text{cm}^{-1} \quad (8.23)$$

Also, from equation (8.12), we have

$$B = \frac{h}{8\pi^2 Ic} \text{ or } I = \frac{h}{8\pi^2 Bc}$$

$$B = \frac{6.624X10^{-27}}{8\pi^2 X1.92118X2.99976X10^{10}}$$

$$= 1.45673 \text{ x } 10^{-39}\ \text{g cm}^{-2} \quad (8.24)$$

In order to calculate bond length, one has to find out the value of reduced mass of carbon monoxide molecule which is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}\ X\ \frac{1}{N}$$

Here m_1 = 12.0000 g (carbon) and m_2 = 15.9949 g (oxygen)

$$\mu = \frac{12X15.9949}{12+15.9949} X \frac{1}{6.024x10^{23}}\, g \quad (8.25)$$

From equation (8.7) we have, I = μr^2

on substituting equation (8.24) and (8.25) in (8.7), we get

$$1.45673X10^{-39} gcm^2 = \frac{12X15.9949}{12+15.9949} X \frac{1}{6.024x10^{23}} r^2$$

or $r^2 = 1.28 \times 10^{-16}\ cm^2$

or $r = 1.131$ Å

Gilliam and coworkers have also found the rotational absorption of $^{12}C^{16}O$ at 3.84235 cm^{-1} (C=12 and O=16) while that of $^{13}C^{16}O$ was found to be at 3.67337 cm^{-1}. The values of B and B' from these figures come out to be

$$B = 1.92118\ cm^{-1} \text{ and } B' = 1.83669\ cm^{-1}$$

$$\text{But,} \quad B = \frac{h}{8\pi^2 Ic} \text{ and } B' = \frac{h}{8\pi^2 I' c}$$

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} X \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu' r^2}{\mu r^2} = \frac{\mu'}{\mu}$$

$$\text{or} \quad \frac{\mu'}{\mu} = \frac{1.92118}{1.83669} = 1.046$$

If we take the mass of oxygen to be 15.9994 g and that of carbon to be 12.0000 g, we get

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994 X m'}{15.9994 + m'} X \frac{12 + 15.9994}{12 X 15.9994}$$

$$\text{or} \quad m' = 13.0007$$

Thus, the atomic weight of carbon-13 comes out to be 13.0007. This value agrees with those values which are obtained by other methods. From the above discussion, it follows that microwave spectroscopy can be successfully used to estimate the abundance of isotopes by comparison of absorption intensities.

(ii) **HCl Molecule:** From the microwave spectrum of HCl, it is observed that the frequency difference between successive absorption lines is found to be 20.7 cm^{-1} and is identified with 2B, i.e.,

$$2B = 20.7 \text{ or } B = 10.35\ cm^{-1}$$

$$\text{But,} \quad I_{HCl} = h/8\pi^2 Bc = 6.62 \times 10^{-27}/8 = (3.14)^2 \times (10.35)3 \times 10^{10}$$

$$= 2.70 \times 10^{-40}\ g\ cm^2$$

Reduced mass of HCl molecule is given by

$$\mu(Reduced\ mass)for\ HCl = \frac{m_1 m_2}{m_1 + m_2} X \frac{1}{N}$$

$$= 1.008\text{x}35.46/(1.008+35.46)\text{x}1/6.024\text{x}10^{23}$$

But the bond length of HCl, i.e., r_{HCl} is given by

$$r_{HCl} = 1.29\text{x}10^{-8} = 1.29\text{Å}$$

The separation between energy levels J=0 and J=1 will be given by

$$\Delta E_J = 2\ \frac{h^2}{8\pi^2 I} = 2Bhc$$

$$= 20.7 \text{ x } 6.624 \text{ x } 10^{-27} \text{x } 2.99976 \text{ x } 10^{10}$$

$$= 0.405 \text{ x } 10^{-24} \text{ erg}$$

(iii) **HI Molecule:** The microwave spectrum of HI molecule consists of a series of equidistant lines with a spacing of 12.8 cm^{-1}, i.e.,

$$2B = 12.8 \text{ cm}^{-1} \text{ or } B = 6.4 \text{ cm}^{-1}$$

$$I_{HI} = \frac{h}{8\pi^2 BC} = \frac{6.624X10^{-27}}{8X(3.14^2)6.4X2.999X10^{10}}$$

$$= 4.372 \text{ x } 10^{-40} \text{ g cm}^2$$

But $\mu = 1 \text{ x } 127/(1+127) \text{ x } 1/6.024 \text{ x } 10^{23} = 1.65 \text{ x } 10^{-25}$ g

But, bond length, $r_{HI}^2 = \frac{I_{HI}}{\mu}$ = $4.372 \text{ x } 10^{-40}/1.65 \text{ x } 10^{-24}$

or **r_{HI}** = 1.63 Å

From the above examples it is evident that the examination of microwave spectrum is an accurate method for calculating intermolecular distance, at least for simple diatomic molecules.

8.3 The Diatomic Molecule as a Non-rigid rotator:

So far we have considered the bond in a diatomic molecule to be a rigid bond. But, this is only an approximation. However, all bonds are elastic to some extent. The elasticity results in some changes which are as follows: (i) an elastic bond may have vibrational energy (ii) another consequence of elasticity is that the quantities r and B vary during a vibration.

When the spectrum of a non-rigid rotator is considered, we must take into account the above two facts. For a non-rigid rotator, Schrodinger's wave equation yields the following rotational terms:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \quad Joule$$

or $$E_J = E_J/hc = BJ(J+1) - DJ^2 (J+1)^2 \quad cm^{-1}$$

Where B is the rotational constant and its value is, as defined previously, as follows:

$$B = \frac{h}{8\pi^2 Ic} \tag{8.26}$$

And D is the centrifugal distortion constant and its value is given by

$$D = h^3/32\pi^4 I^2 r^2 kc \ cm^{-1} \tag{8.27}$$

In equation (8.27) k is a force constant and its value is given by

$$k = 4\pi^2 \overline{\omega^2} c^2 \mu \tag{8.28}$$

Where $\bar{\omega}$ is the vibrational frequency expressed in cm^{-1}. From the defining equations of B and D it may be shown directly that

$$D = 16B^3 \pi^2 c^2 \mu / k = 4B^2 / \overline{\omega^2} \tag{8.29}$$

It is generally found that vibrational frequencies are of the order of 10^3 cm^{-1} and value of B found to be 10 cm^{-1}. It means that the value of D, according to equation (8.29), is of the order 10^{-3} cm^{-1} which is very small compared to B.

Selection Rule: The selection rule for the spectrum of a rotator ($\Delta J = \pm 1$) discussed earlier is valid whether it is rigid or not. The analytical expression for the transition is as follows:

$$\bar{\nu}_J = B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \ cm^{-1}$$

$$= 2B(J+1) - 4D(J+1)^3 \tag{8.30}$$

Where $\bar{\nu}_J$ denotes the upward transition from J to J+1are the downward from J+1 to J. From equation (8.30) and (8.19), it follows that the spectrum of a non-rigid rotator is almost similar to the rigid molecule expect that each spectral line will undergo displacement towards the low frequency value and the displacement increase with $(J+1)^3$.

From the value of D, two useful measurements can be made. These are: (a) Firstly the value of vibrational frequency $\bar{\omega}$ can be found that from equation (8.29) provided the value of B is known. However, this method is not accurate. (b) Secondly knowledge of D allows us to determine the J value of line in an observed spectrum.

Example: HF (Hydrogen fluoride) molecule:

In the harmonic approximation the centrifugal constant *D* can be derived as

$$\tilde{D} = \frac{h^3}{32\pi^4 I^2 r^2 kc}$$

where *k* is the vibrational force constant. The relationship between B and D

$$\tilde{D} = \frac{4\tilde{B}^3}{\tilde{\omega}^2}$$

$\tilde{\omega}$= 16.33x10^{10} $(\text{cm}^{-1})^2$ where $\tilde{\omega}$ is the harmonic vibration frequency,

The force constant and its value is given by $k = 4\pi^2\overline{\omega^2}c^2\mu$ = 960 Nm^{-1}

This indicates, as that H-F is a relatively strong bond.

8.4 Microwave Oven.

In technological era, the microwave oven has become a very useful cooking device in the kitchen. Its mode of operation has been found to depend upon the absorption by the food of the microwave radiation in which it is placed. The water molecules in the food absorb the microwave radiation and are hereby raised to the higher rotational states. The biological molecules in the food, on the other hand, are far too big to be able to rotate. The heating in the microwave oven is mainly internal heating. In internal heating, the water molecules in the food get excited and the excess rotational energy get re-emitted as heat with the help of which the food gets cooked.

However, the microwave radiation also affects the human body. Hence, the door seal of microwave oven must be in good condition so that no radiation leaks out.

8.5 Problems on Rotational spectroscopy

Problem 1: The rotational spectrum for HCl shows a series of lines separated by 20.6 cm^{-1}. Find moment of inertia and internuclear distance.

Solutions: Since 2B = 20.6 cm^{-1}

$$B = 10.3\ \text{cm}^{-1} = 10 \times 10^{-2}\ \text{m}$$

Also $B = \frac{h^2}{8\pi^2 Ic}$ and $I = \frac{h}{8\pi^2 BC} = \frac{6.624X10^{-34}\ kg\ m^2/s}{8X(3.14^2)10\ X10^2 m^{-1}X3X10^8 m/s}$ = 2.655 x 10^{-47} kgm^2

Now $I = \mu r^2$ or $r = \sqrt{\frac{I}{\mu}}$

Since ⍰ $= \frac{m_1+m_2}{m_1 m_2}$ = 1.628 x10^{-27} kg

Therefore, $r = \sqrt{\frac{I}{\mu}}$ = 1.276 x 10^{-10} m

Problem 2. The moment of inertia of the CO molecule is 1.46x10^{-46}kg-m^2. Calculate the energy in eV, and the angular velocity in the lowest rotational energy level of the CO molecule.

Solution: We know that expression for rotational energy = $E_r=\frac{h^2}{8I\pi^2}$ J (J+1)

For lowest rotational energy level, J=1 so that $E_r=\frac{h^2}{8I\pi^2}$

Putting I= 1.46x10^{-46}kg-m^2 h=6.62x10^{-34} joule-second

$$E_r=\frac{(6.62X10^{-34})^2}{8X(3.14)^2X1.46X10^{-46}} = 2.37\text{x}10^{-4}\text{eV}$$

Angular velocity will be given by= $E_r=\frac{1}{2}I\omega^2$

$$\text{Therefore } \omega=\sqrt{\frac{2E}{I}} = \sqrt{\frac{2X2.37X10^{-4}X1.6X10^{-18}}{1.46X10^{-46}}} = 7.21\text{x}10^{11} \text{ rad/sec.}$$

8.6 Let us sum up

The rotational spectroscopy deals in detailed explanation and theory of microwave spectroscopy, diatomic molecule as rigid rotator , non rigid rotator , frequency of rotational spectral lines, its selection rule for rotational spectra with examples, detailed explanation of microwave oven helps to understand about rotational spectroscopy and its uses and applications.

8.7 Key words

Rotational spectroscopy, Diatomic molecule, rigid rotator and non- rigid rotator.

8.8 Review Questions

1. Enumerate the rotational spectra of diatomic molecule.
2. Give the brief note on microwave oven.
3. Explain the rotational spectra of rigid rotator and non- rigid rotator of diatomic molecules

8.9 Reference books:

1. Colin N. Banwell and Elain M. McCash, Fundamentals of Molecular Spectroscopy 4th edition Tata McGraw-Hil Education private limited, New Delhi, 2011.
2. Jeanne L. Mchale, Molecular Spectroscopy, Pearson education, 2009.
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UNIT 9: Infrared spectroscopy

Structure:

9.0 Objectives

After studying this unit you will be able to understand

1. Born-Oppenheimer approximation
2. Diatomic vibrating rotator
3. Vibration-rotation spectrum

9.1 Introduction

Infrared spectroscopy is one of the most powerful analytical techniques which offer the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. One of the most important advantages of infrared spectroscopy over the other usual methods of structural analysis (X-ray diffraction, electrons spin resonance, etc.) is that it provides useful information about the structure of molecule quickly, without tiresome evaluation methods. This method can solve many problems in organic chemistry and coordination chemistry, while in some other problems infrared date advantageously complement the results obtained by other methods.

Infrared spectroscopy has established itself as a valuable tool for the determination of organic, and to a lesser extent, inorganic, structure. The utilization of infrared data in conjunction with other physical measurements, such as those obtained from nuclear magnetic resonance and mass spectroscopy, has elucidated many facts about the structure and properties of organic compounds, facts which were heretofore accepted solely on a theoretical basis.

Infrared spectroscopy may be applied at all levels of expertise from a simple matching of spectra on one end to theoretical calculations at the other. The instruments are common, relatively inexpensive, and easy to operate. This, combined with the non-destructive nature of the analysis, means that records on intermediate preparative or separation products may be easily obtained. The sample may then be recovered and further utilized. While qualitative applications are most common, the absorption of infrared radiation does follow Beer’s Law and therefore lends itself to quantitative determinations.

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of a chemical substance vibrate at many rates of vibration, giving rise to close-packed absorption bands, called an IR absorption spectrum which may extend over a wide wavelength range. Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus, an IR spectrum of a chemical substance is fingerprint for its identification.

Band positions in an infrared spectrum may be expressed conveniently by the wave number whose unit is cm^{-1}. The relation between wave number, ν, wavelength λ and frequency υ is as follows

$$v = c/\lambda$$

or

$$v/c = 1/\lambda \ (\mathrm{cm}^{-1})$$

where ‘c’ is the velocity of light. From the above relations, it follows that wave number is the reciprocal of wavelength.

Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the sample. On the other hand, absorbance is defined as the logarithm, to the base, 10, of the reciprocal of the transmittance.

9.2 The Born-Oppenheimer approximation

Molecular spectra observing in the ultraviolet and visible region arise due to the transition from one electronic state to another. If the excitation energy is sufficiently large, the electrons in the molecule may undergo transition from the lower energy to higher energy state. During such transition also known as electronic excitation, these occur a large change in the vibrational energy of the molecule. These vibrational energy changes give rise to vibrational transition which results in group of various bands. The vibrational energy changes in the vibrational transitions will accompanied by large change in the rotational energy of the molecule. These rotational energy changes give rise to rotational transition forming a series of lines in each band. Due to this reason, each band in the electronic spectra is made up of a number of fine line because of the simultaneously changes in rotational and vibrational energies. Electronic spectra of molecules are usually found in visible and ultraviolet region.

This is also known as pure rotational spectra and is given by which have permanent dipole moment. The rotational spectra require a change of dipole moment during the motion where as electronic spectra are given by all molecules. It implies that molecule such as H_2 or N_2 which does not show vibrational or rotational spectra.

As first approach to the electronic spectra of diatomic molecule we may use the Born-Oppenheimer approximation. This may be written as

$$E_{total} = E_e + E_r + E_v \tag{9.1}$$

$$E_{total}' = E_e' + E_r' + E_v' \tag{9.2}$$

Where E_e, E_r and E_v be the electronic, rotational and vibrational energies of a molecule before transition and $E_e', \; E_r' \; and \; E_v'$ be the corresponding value after the transitions.

Thus ΔE_{total} change in the energy involved during electronic transition is given by

$$E_{total} = (E_e' - E_e) + (E_r' - E_r) + (E_v' - E_v)$$

$$= \Delta E_e + \Delta E_r + \Delta E_v \qquad (9.3)$$

The frequency of the emitted radiation emitted would by the following equation,

$$\bar{\nu} = \frac{\Delta E_{total}}{hc} = \frac{\Delta E_e + \Delta E_r + \Delta E_v}{hc} cm^{-1} \qquad (9.\ 4)$$

As ΔE_r and ΔE_v may have a number of values which depends upon the rotational and vibrational quantum number. Therefore electronic band spectra are generally very complex.

Equation (9.4) may be written as

$$\bar{\nu} = \frac{\Delta E_{total}}{hc} = \frac{\Delta E_e}{hc} + \frac{\Delta E_r}{hc} + \frac{\Delta E_v}{hc} \ cm^{-1} \qquad (9.\ 5)$$

These approximation orders of magnitudes of these changes are the

$$\frac{\Delta E_e}{hc} \approx \frac{\Delta E_v}{hc} X10^3 \approx \frac{\Delta E_r}{hc} X10^6 cm^{-1} \qquad (9.6)$$

From eq. (9.6) it follows that vibrational change will produce a course structure and rotational energies changes fine structure in the spectra of electron transition.

Each electronic level has its characteristic potential energy diagram. The forms of such curves may be completely unrelated. As in some spectra the (0, 0) transition is the strongest, in the intensity increases to a maximum at some value of V (vibrational quantum no.) While in other only a few vibrational lines are noted with large values of V. All these type of spectra can be easily explained in terms of Frank-Condon principle.

9.3 The diatomic vibrating rotator

A typical diatomic molecule has rotational energy separations of 1–10 cm^{-1}, while in the preceding section we found that the vibrational energy separations of HCl were nearly 3000 cm^{-1}. Since the energies of the two motions are so different we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This, which we shall call the Born-Oppenheimer approximation, is tantamount to assuming that the combined rotational-vibrational energy is simply the sum of the separate energies:

$$E_{total} = E_{rot.} + E_{vib} \quad \text{(joules)}$$

$$\varepsilon_{total} = \varepsilon_{rot.} + \varepsilon_{vib.} \quad (\text{cm}^{-1}) \tag{9.7}$$

We shall see later in what circumstances this approximation does not apply.

Taking these separate expressions for $\varepsilon_{rot.}$ and ε_{vib} we have

$$\varepsilon_{Jv} = \varepsilon_J + \varepsilon_v$$

$$\varepsilon_{Jv} = BJ\,(J+1) - DJ^2\,(J+1)^2 + HJ^3\,(J+1)^3 + \ldots\ldots$$

$$+ \left(v + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \frac{1}{2}\right)^2 \bar{\omega}_e \quad \text{cm}^{-1} \tag{9.8}$$

Initially, we shall ignore the small centrifugal distortion constants D, H, etc., and hence write:

$$\varepsilon_{total} = \varepsilon_{Jv} = BJ\,(J+1) + \left(v + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \frac{1}{2}\right)^2 \bar{\omega}_e \tag{9.9}$$

Note, however, that it is not logical to ignore D since this implies that we are treating the molecule as rigid, yet vibrating. The retention of D would have only a very minor effect on the spectrum.

The rotational levels are sketched in Fig.9.1. For the two lowest vibrational levels, $v = 0$ and $v = 1$. There is, however, no attempt at scale in this diagram since the separation between neighboring J values is, in fact, only some 1/1000 of that between the v values. Note that since the rotational constant B in Eq. (9.9) is taken to be the same for all J and v (a consequence of the Born-Oppenheimer assumption), the separation between two levels of given J is the same in the $v = 0$ and $v = 1$ states.

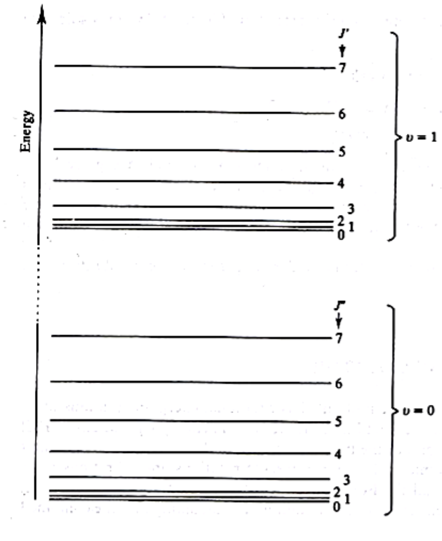

Fig.9.1 Allowed rotational-vibrational energy level pattern

The selection rule for vibrational-rotational transition are same as those for separate transition, namely $\Delta\upsilon = \pm1$ and $\Delta J = +1$. Considering a transition from lower state defined by υ'' and J'' to a higher state defined υ' and J'. Thus energy change of molecule will be

1. $\Delta J = +1$, that is $J'=J''+1$ or $J' - J''= +1$ hence

$$\Delta\varepsilon_{J\upsilon}= \varpi_0+2B\,(J''+1)\ \text{cm}^{-1} \quad J''= 0,1,2\ldots \tag{9.10}$$

2. $\Delta J = -1$, that is $J''=J'+1$ or $J' - J''= -1$ hence

$$\Delta\varepsilon_{J\upsilon}= \varpi_0 -2B\,(J''+1)\ \text{cm}^{-1} \quad J'= 0,1,2\ldots \tag{9.11}$$

These two expressions may conveniently be combined into

$$\Delta\varepsilon_{J\upsilon}= \bar{\upsilon}_{spect}= \varpi_0 +2Bm\ \text{cm}^{-1} \quad m=\pm1, \pm2\ \ldots \tag{9.12}$$

Where m, replacing $J''+1$ in Eq.(9.10) and $J'+1$ in Eq.(9.11) has positive values for $\Delta J = +1$ and is negative if $\Delta J = -1$. Note particularly that m cannot be zero since this would imply values of J' or J'' to be -1. The frequency ϖ_0 is usually called the band origin or band center.

Equation (9.12), then, represents the combined vibration-rotation spectrum. Evidently it will consist of equally spaced lines (spacing = 2B) on each side of the band origin ϖ_0, but, since $m \neq 0$, the line at ϖ_0 itself will not appear. Lines to the low-frequency side of ϖ_0, corresponding to negative m (that is $\Delta J = -1$) are referred to as the P branch, while those to the high frequency side (m positive, $\Delta J = +1$) are called the R branch. This apparently arbitrary notation may become clearer if we state here that later, in other contexts, we shall be concerned with ΔJ values of 0 and ±2, in addition to ±1 considered here; the labeling of line series is then quite consistent:

Lines arising from ΔJ =	-2	-1	0	+1	+2	
Called:	O	P	Q	R	S	branch

The P and R notation, with the lower J (J″) value as a suffix, is illustrated on the diagrammatic spectrum of Fig.9.2 this is the conventional notation for such spectra.

It is readily shown that the inclusion of the centrifugal distortion constant D leads to the following expression for the spectrum:

$$\Delta\varepsilon = \bar{\nu}_{spect.} = \varpi_0 + 2Bm - 4Dm^3\ \text{cm}^{-1} \qquad (m = \pm1, \pm2, \pm3\ldots\ldots) \tag{9.13}$$

However, we have seen that B is some 10 cm^{-1} or less, while D is only some 0.01 per cent of B. Since a good infra-red spectrometer has a resolving power of about 0.5 cm^{-1} it is obvious that D is negligible to a very high degree of accuracy.

The anharmonicity factor, on the other hand, is not negligible. It affects not only the position of the band origin (since $\bar{\omega}_0 = \bar{\omega}_e (1 - 2x_e)$), but, by extending the selection rules to include $\Delta v = \pm 2, \pm 3$, etc., also called bond origin. This is illustrated in Fig. 2.

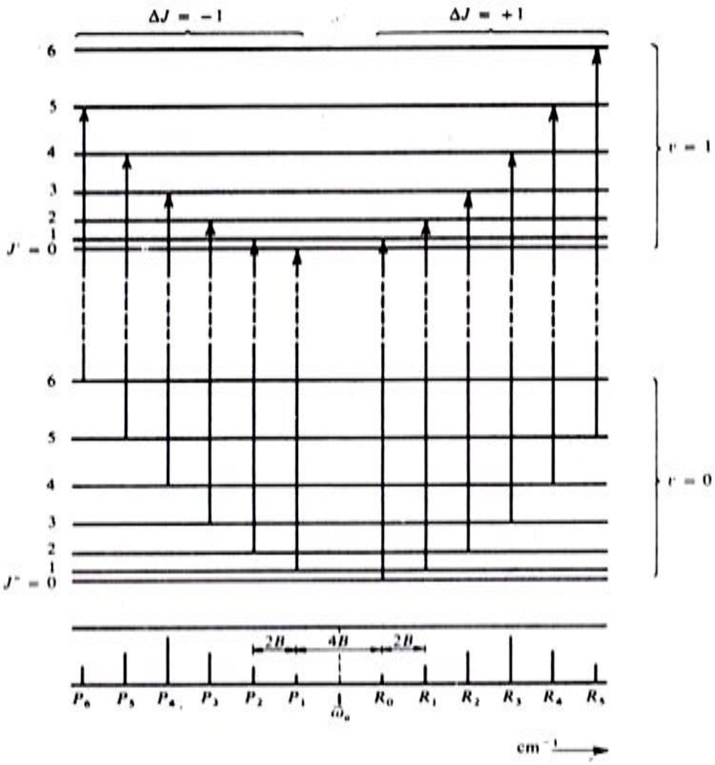

Fig. 9.2 Transition between rotational-vibrational levels of diatomic molecules.

9.4 The vibration-rotation spectrum of carbon monoxide

In fig.9.3 we show the fundamental vibration-rotation band of carbon monoxide under high resolution, with some lines in P and R branches numbered according to their J" values. Table 9.1 gives the observed wave numbers of the first five lines in each branch. Consider shortly the slight decrease in separation between the rotational lines as the wave number increase; this decrease is apparent from the table and from a close inspection of the 'wings' of the spectrum.

From the table (9.1) we see that the band center is at about 2143 cm^{-1} while the average line separation near the center is 3.83 cm^{-1}. This immediately gives:

$$2B = 3.83\ \text{cm}^{-1} \qquad B = 1.915\ \text{cm}^{-1}$$

This is in satisfactory agreement with the value B = 1.9218 cm^{-1} derived by microwave studies and we could, therefore, have obtained quite good values for the rotational constant and hence the moment of inertia and bond length from infra-red data alone.

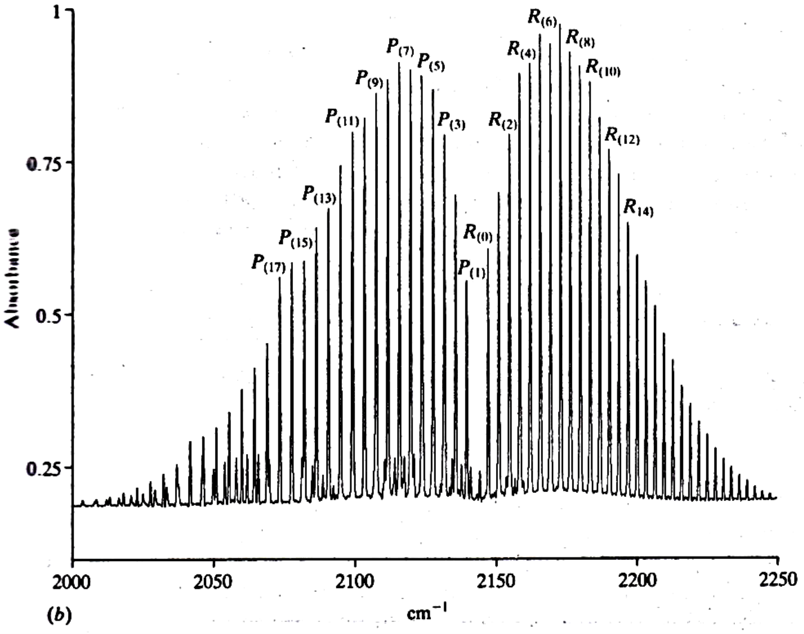

Fig.9.3. Infrared spectra of CO gas at high resolution.

Tale 9.1 Data of Infrared spectrum of CO

Line	$\bar{\nu}$	$\Delta\bar{\nu}$	Line	$\bar{\nu}$	$\Delta\bar{\nu}$
$P_{(1)}$	2139.43	3.88	$R_{(1)}$	2147.08	3.78
$P_{(2)}$	2135.55	3.92	$R_{(2)}$	2150.86	3.73
$P_{(3)}$	2131.63	3.95	$R_{(3)}$	2154.59	3.72
$P_{(4)}$	21227.68	3.98	$R_{(4)}$	2158.31	3.66
$P_{(5)}$	2123.70		$R_{(5)}$	2161.97	

Thus Fig.9.3 shows the spectrum of carbon monoxide under much poorer resolution, when the rotational fine structure is blurred out to an envelope. Now we know that the maximum population of levels and hence the maximum intensity of transition, occurs at a J value of $\sqrt{\frac{kT}{2Bhc}}-\frac{1}{2}$. Remembering that m = J +1 we substitute in Eq. (9.13) m = $\pm\sqrt{\frac{kT}{2Bhc}}+\frac{1}{2}$ and obtain:

$$\bar{\nu}_{\text{max. intensity}} = \bar{\omega}_0 \pm 2B\left\{\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}\right\}$$

Where the '+' and '–'signs refer to the R ad P branches, respectively. The separation between the two maxima, $\Delta\bar{\nu}$ is then;

$$\Delta\bar{\nu} = 4B\left\{\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}\right\} = \sqrt{\frac{8kTB}{hc}} + 2B$$

or, since B is small compared with $\Delta\bar{\nu}$, we can write

$$\Delta\bar{\nu} \approx \sqrt{\frac{8kTB}{hc}} B \approx \frac{hc(\Delta\bar{\nu})^2}{8kT} \quad \text{cm}^{-1}$$

where c is expressed in cm s^{-1}. In the case of carbon monoxide the separation is about 55 cm^{-1} while the temperature at which the spectrum was obtained was about 300 K. We are led, then, to a B value of about 1.8 cm^{-1}.

From Table 9.1 we see that the band origin, at the midpoint of $P_{(1)}$ and $R_{(0)}$, is at 2143.26 cm^{-1}. This, then, is the fundamental vibration frequency of carbon monoxide, if anharmonicity is ignored. Since the first overtone is found to have its origin at 4260.04 cm^{-1}.

$$\text{We have: } \bar{\omega}_e(1- 2x_e) = \bar{\omega}_0 = 2143.26$$

$$2\bar{\omega}_e(1- 3x_e) = 4260.04$$

From which $\omega_e = 2169.74\ cm^{-1}$, $x_e = 0.0061$

9.5 Problems on Infrared spectroscopy.

Problem 1: Calculate the wave number of stretching vibration of a carbon-carbon double bond. Give force constant $k= 10x10^5$ dynes/cm^{-1}.

Solution: Atomic force constant of carbon = 12 amu

Reduced mass

$$\mu(Reduced\ mass) = \frac{m_1m_2}{m_1+m_2} = \frac{12X12}{12+12} = 6\ amu$$

$$= \frac{6}{6.02X10^{23}}\ gm = 9.97X10^{-24}\ gm$$

Wave number

$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$= \frac{1}{18.825X10^{10}} X\sqrt{10.03X10^{28}} = 0.1680X10^{4}cm^{-1}$$

= 1680 cm^{-1}

Problem 2: Calculate the energy in joules per quantum calories per mole, and electron volts of photons of wavelength 3000 Å.

Solution: We know that E= h$\frac{c}{\lambda}$

Also know h=6.62 x10^{-34} joule- second, c= 3 x 10^{8} and λ=3000 Å =3000 x 10^{-10}

Substituting the values of λ, c and h we get

$$E=\frac{6.62X10^{-34} \quad X\ 3X10^{8}}{3000X10^{-10}}$$

$$E=6.62 \times 10^{-19}$$

Energy per mole = Nhν Where N = Avogadro's number = 6.02 x 10^{23} mol^{-1}

$$\text{Energy per mole} = 6.02x10^{23}x6.62x10^{-19}$$

$$=3.98x10^{5}\ \text{joule}\ mol^{-1}$$

$$\text{Energy per mole}=\frac{3.98x10^{5} joule\ \ mol^{-1}}{4.184\ joule\ \ cal^{-1}} = 95{,}300 cal\ mol^{-1}$$

$$\text{Energy per mole} = \frac{95{,}300\ cal\ \ mol^{-1}}{23{,}060\ cal\ \ mol^{-1}eV^{-1}} = 4.13\ eV$$

9.6 Let us sum up

This IR spectroscopy unit gives the information about analytical method which offers the possibility of chemical identification of organic, inorganic and its structures. The Born-Oppenheimer approximation: diatomic vibration rotator with mathematical treatment and its transition diagram. The vibrational- rotational spectra of carbon monoxide with frequencies this information helps to understand the IR spectroscopy.

9.7 Key words

Spectrum, Vibration-rotation spectrum, Rotator, Born- Oppenheimer approximation, IR spectrum.

9.8 Review Questions

1. Write a note Born-Oppenheimer approximation.
2. Which selection rule is used in IR spectroscopy?
3. Explain the theory of diatomic vibrating rotator.

9.9 Reference books:

1. Colin N. Banwell and Elain M. McCash, Fundamentals of Molecular Spectroscopy 4th edition Tata McGraw-Hil Education private limited, New Delhi, 2011.
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UNIT 10: VIBRATION OF POLYATOMIC MOLECULES

Structure:

10.0 Objectives

After studying this unit you will be able understand

1. Meaning of skeletal vibration
2. Group frequencies
3. Fourier transforms infrared spectroscopy FTIR

10.1 Introduction

Vibrations in a polyatomic molecule involve movement of all the atoms in a molecule. In contrast, to only two atoms vibrating at a time Modes of vibration that are independent of each other (i.e., don't affect each other) are called normal mode vibrations. For a molecule with N atoms, 3N total modes of motion exist, 3 translational modes, 3 rotational modes and 2 modes for linear molecule 3N-6 vibrational modes, 3N-5 modes for linear molecule. The guite logical extension to the simple theory is adequate to give an understanding of the spectrum. The vibration symmetry, FTIR spectrum and working of FIR spectrometer which are the most important analytical techniques of the vibrations polyatomic molecules.

10.2 The vibrations of polyatomic molecules

To understand the pure rotational spectra of polyatomic molecules, we need the number of fundamental vibration and their symmetry, the possibility of overtone and combination bands and the influence of rotation on the spectra.

10.2.1 Fundamental Vibration and their symmetry

Consider a molecule containing N atoms: we can refer to the position of each atom by specifying three coordinates (e.g. the x, y, and z Cartesian coordinates). Thus the total number of coordinate values is 3N and we say the molecule has 3N degrees of freedom since each coordinate value may be specified quite independently of the others. However, once all 3N coordinates have been fixed, the bond distances and bond angles of the molecule are also fixed and no further arbitrary specification can be made.

Now the molecule is free to move in three dimensional space, as a whole, without change of shape. We can refer to such movement by noting the position of its center of gravity at any instant–to do this requires a statement of three coordinate values. This translational movement uses three of the 3N degrees of freedom leaving 3N–3. In general, also, the rotation of non-linear molecule can be resolved into components about three degrees of freedom and the molecule is left with 3N–6 degrees of freedom. The only other motion allowed to it is internal vibration, so we know immediately that a non-linear N-atomic molecule can have 3N–6 different internal vibrations:

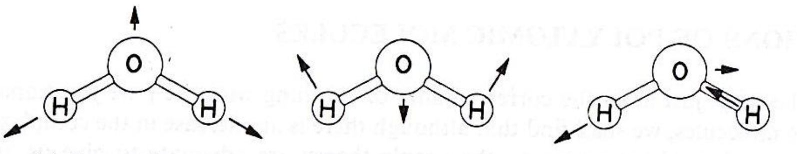
$$\text{Non-linear:} \quad 3N-6 \text{ fundamental vibrations} \tag{10.1}$$

If on the other hand, the molecule is linear, that there is no rotation about the bond axis, hence only two degrees of freedom are required, leaving 3N–5

$$\text{Linear:} \quad 3N-5 \text{ fundamental vibrations} \tag{10.2}$$

In such cases, since an N atomic molecule has N–1 bonds (for acyclic molecules) between its atoms, N–1 of the vibrations are bond stretching motions, the other 2N–5 (non-linear) or 2N–4 (linear) is bending motions.

Let us look briefly at examples of these rules. First, we see that for a diatomic molecule (perforce linear) such as we have already considered in this chapter, N = 2, 3N–5 = 1 and thus there can be only one fundamental vibration. Note however, that the 3N–5 rule says nothing about the presence, absence, or intensity of overtone vibrations–these are governed solely by anharmonicity.



(*a*) Symmetric stretch
3651.7 cm^{-1}
ν_1, parallel ($\parallel$)

(*b*) Symmetric bend
1595.0 cm^{-1}
ν_2, parallel ($\parallel$)

(*c*) Antisymmetric stretch
3755.8 cm^{-1}
ν_3, perpendicular ($\perp$)

Fig. 10.1. The symmetry of the water molecule and its three fundamental vibrations

Consider water, H_2O. This (Fig.10.1) is non-linear and triatomic. Also in the figure are the 3N–6 = 3 allowed vibrational modes, the arrows attached to each atom showing the direction of its motion during half of the vibration. Each motion is described as stretching or bending depending on the nature of the change in molecular shape.

These three vibrational motions are also referred to as the normal modes of vibration (or normal vibration) of the molecule, in general a normal vibration is defined as a molecular motion in which all the atoms oscillate with the same frequency and pass through their equilibrium positions simultaneously.

Further, each motion of Fig.10.1 is labeled either symmetric or anti-symmetric. If we rotate the vibrating molecule by 180^0 the vibration is quite unchanged in character–we call this a symmetric vibration. The bending vibration, v_2, is also symmetric. Rotation of the stretching motion of Fig.10.1 (c) about the C_2 axis, however, produces a vibration which is in anti-phase with the original and so this motion is described as the anti-symmetric stretching mode.

In order to be Infra-red active, as we have seen, there must be a dipole change during the vibration and this change may takes place either along the line of the symmetry axis (parallel to it) or at right angles to the line (perpendicular).

Figure 10.2 shows the nature of the dipole changes for the three vibrations of water, and justifies the labels parallel or perpendicular attached to them in fig.3.9. We shall see later that the distinction is important when considering the influence of rotation on the spectrum.

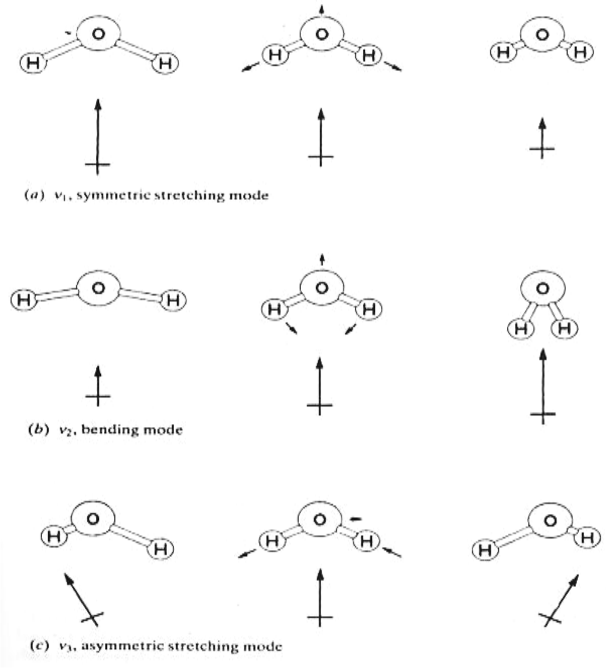


Fig.10.2 The change in the electric dipole moment produced by each vibration of the water molecule and also shows the change in the electric dipole moment produced by each vibration of the water molecule. This is seen to occur either along parallel or across the symmetric axis.

10.3 Analysis by Infra-red Techniques

Because of the 3N – 6 and 3N – 5 rules it is evident that a complex molecule is likely to have an infra-red spectrum exhibiting a large number of normal vibrations. Each normal mode involves some displacement of all, or nearly all, the atoms in the molecule, but while in some of the modes all atoms may undergo approximately the same displacement, in others the displacements of a small group of atoms may be much more vigorous than those of the remainder. Thus we may divide the normal modes into two classes: the *skeletal vibrations*, which involve may of the atoms to much the same extent, and the *characteristic group vibrations*, which involve a small portion of the molecule, the remainder being more or less stationary.

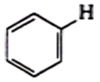
10.4 Skeletal Vibrations

For organic molecules usually fall in the range of 1400 – 1700 cm^{-1} and arise from linear or branched chain structures in the molecule. Thus such groups as Etc., each give rise to several skeletal modes of vibration and hence several absorption bands in the infra-red. It is seldom possible to assign particular bands to specific vibrational modes, but the whole complex of bands observed is highly typical of the molecular structure under examination. Further, changing a substituent (on the chain or in the ring) usually results in a marked change in the pattern of the absorption bands. Thus these bands are often referred to as the 'finger print' hands, because a molecule or structural moiety may often be recognized merely from the appearance of this part of the spectrum.

10.5 Group frequencies

Detailed information about the infrared absorptions observed for various bonded atoms and groups is usually presented in tabular form. The following table provides a collection of such data for the most common functional groups (Table 10.1).

Table. 10.1 Characteristic stretching frequencies of some molecular groups.

Group	Approximate frequency (cm^{-1})	Group	Approximate frequency (cm^{-1})
$-OH$	3600	$>C=O$	1750–1600
$-NH_2$	3400	$>C=C<$	1650
$\equiv CH$	3300	$>C=N<$	1600
	3060	$\geqslant C-C \leqslant$	1200–1000
		$\geqslant C-N<$	
		$\geqslant C-O<$	
$=CH_2$	3030		
$-CH_3$	2970 (asym. stretch)	$>C=S$	1100
	2870 (sym. stretch)	$\geqslant C-F$	1050
	1460 (asym. deform.)		
	1375 (sym. deform.)	$\geqslant C-Cl$	725
$-CH_2-$	2930 (asym. stretch)	$\geqslant C-Br$	650
	2860 (sym. stretch)		
	1470 (deformation)	$\geqslant C-I$	550
$-SH$	2580		
$-C\equiv N$	2250		
$-C\equiv C-$	2220		

The spectra of simple alkanes are characterized by absorptions due to C–H stretching and bending (the C–C stretching and bending bands are either too weak or of too low a frequency to be detected in IR spectroscopy). In simple alkanes, which have very few bands, each band in the spectrum can be assigned.

- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470-1450 cm^{-1}

- C–H rock, methyl from 1370-1350 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, from 725-720 cm^{-1}

Alkenes are compounds that have a carbon-carbon double bond, –C=C–. The stretching vibration of the C=C bond usually gives rise to a moderate band. Stretching vibrations of the –C=C–H bond are of higher frequency (higher wavenumber) than those of the –C–C–H bond in alkanes. The strongest bands in the spectra of alkenes are those attributed to the carbon-hydrogen bending vibrations of the =C–H group.

- C=C stretch from 1680-1640 cm^{-1}
- =C–H stretch from 3100-3000 cm^{-1}
- =C–H bend from 1000-650 cm^{-1}

Alkynes are (–C≡C–), the –C≡C– stretch appears as a weak band. This can be an important diagnostic tool because very few organic compounds show an absorption in this region.

- –C≡C– stretch from 2260-2100 cm^{-1}
- –C≡C–H: C–H stretch from 3330-3270 cm^{-1}
- –C≡C–H: C–H bend from 700-610 cm^{-1}

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorine, or iodine. In general, C–X vibration frequencies appear in the region 850-515 cm^{-1}, sometimes out of the range of typical IR instrumentation. C–Cl stretches appear from 850–550 cm^{-1}, while C–Br stretches appear at slightly lower wavenumbers. In terminal alkyl halides, the C–H wag of the $–CH_2X$ group is seen from 1300-1150 cm^{-1}. Complicating the spectra is a profusion of absorptions throughout the region 1250-770 cm^{-1}, especially in the smaller alkyl halides. Note that all of these bands are in the fingerprint region.

Alcohols have characteristic IR absorptions associated with both the O-H and the C-O stretching vibrations. When run as a thin liquid film, or "neat", the O–H stretch of alcohols appears in the region 3500-3200 cm^{-1} and is a very intense, broad band.

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears at 1715 cm^{-1}. Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in alpha, beta-unsaturated aldehydes and benzaldehyde, shifts this band to lower wavenumbers.

As in ketones, if the carbons adjacent to the aldehyde group are unsaturated, this vibration is shifted to lower wavenumbers.

Another useful diagnostic band for aldehydes is the O=C–H stretch. This band generally appears as one or two bands of moderate intensity in the region 2830-2695 cm^{-1}. The presence of a moderate band near 2720 cm^{-1} is more likely to be helpful in determining whether or not a compound is an aldehyde.

Carboxylic acids show a strong, wide band for the O–H stretch. This is in the same region as the C–H stretching bands of both alkyl and aromatic groups. Thus a carboxylic acid shows a somewhat "messy" absorption pattern in the region 3300-2500 cm^{-1}, with the broad O–H band superimposed on the sharp C–H stretching bands. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

The N–H stretches of amines are in the region 3300-3000 cm^{-1}. These bands are weaker and sharper than those of the alcohol O–H stretches which appear in the same region. In primary amines (RNH_2), there are two bands in this region, the asymmetrical N–H stretch and the symmetrical N–H stretch.

Secondary amines (R_2NH) show only a single weak band in the 3300-3000 cm^{-1} region, since they have only one N–H bond. Tertiary amines (R_3N) do not show any band in this region since they do not have an N–H bond.

The N–O stretching vibrations in nitroalkanes occur near 1550 cm^{-1} (asymmetrical) and 1365 cm^{-1} (symmetrical), the band at 1550 cm^{-1} being the stronger of the two. If the nitro group is attached to an aromatic ring, the N–O stretching bands shift to down to slightly lower wave numbers.

In general, then experience coupled with comparison spectra of known compounds enables one to deduce a considerable amount of structural information from an infra-red spectrum. It should perhaps be noted that the complete interpretation of the spectrum of a complex molecule can be a very difficult or impossible task. One is usually content to assign the strongest bands and to be able to explain some of the weaker ones as overtones or combinations.

10.6 Fourier Transforms Infrared Spectroscopy

The description of the working of Fourier transform infrared spectrometer is given here. Fourier transformation technique is now of great importance in nuclear magnetic resonance, microwave, infrared and Raman spectroscopy. The absorption spectrum in a Fourier transform infrared spectrometer is obtained through interference technique. Interferometry is therefore known as Fourier transform spectroscopy. We should note here that all diffraction methods also depend on interference effects. The structural information from the observed diffraction patterns are obtained through a Fourier transformation. Fourier transformation is accomplished using a digital computer.

10.6.1 Description of FT Spectrometer

The Fourier transform infrared spectrometer consists of main two parts: (i) an optical system which uses an interferometer and (ii) a dedicated computer which stores data performs computations on data and plots the spectra. A schematic diagram of the essential components of a FT spectrometer based on Michelson Interferometer is shown in Fig.10.3. It consists of two perpendicular mirrors; one of which is a stationary mirror and the other a movable mirror which can be displaced perpendicularly to the fixed mirror at a constant velocity. Between these two mirrors is beam splitter set at 45^0 from the initial position of the movable mirror. A parallel beam of radiation from an IR source passed on to the mirrors through the beam splitter. The beam splitter reflects about half of the beam to the fixed mirror which reflects it back to the beam splitter. The returning beams are again split and mixed about half going back to source and half passing through the sample compartment. The composition of the beam splitter depends on the spectral region of interest. For example, in the mid-infrared region (4000 – 400 cm^{-1}), a beam splitter of germanium coated on KBr plate (substrate) is often used. Germanium reflects the radiation while KBr transmits most of the desirable radiation. IN the far infrared region, germanium coated on CsI (800 – 200 cm^{-1}) or germanium coated on Mylar (polyethylene terephthalate) (650 – 10 cm^{-1}) are used as beam splitters. A thin film of the beam splitter material is coated on an optically flat substrate.

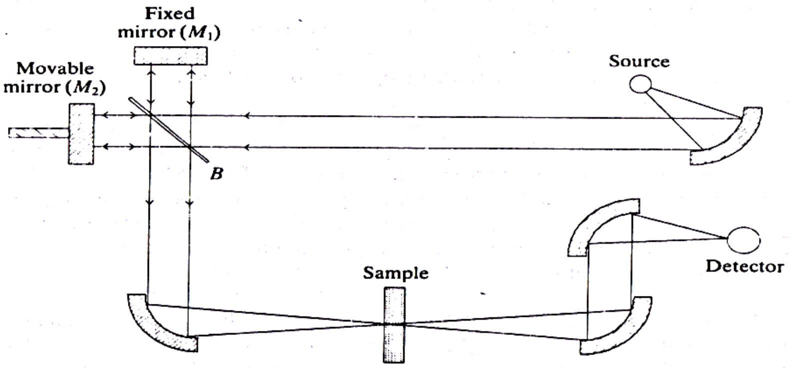


Figure 10.3. Simplified diagram of a FT Infrared Spectrometer

The return beams from both the mirrors along the same path length as their incident path are recombined into a single beam at the beam splitter. The path length of one of the return beams is changed in order to create an overall phase difference to cause an interference pattern. The recombined radiation is then directed through the sample and focused on to the detector. The detector measures the amount of energy at discrete intervals mirror movement.

The movable mirror can be moved in a range of say ± 5 cm, the mirror velocities from 0.05 to 5 cm s^{-1} are used. Interferometry instruments need detectors with response times short enough to detect and transmit rapid energy changes to the recorder. The detector used in conjunction with rapid scanning interferometers in the mid-infrared region at room temperature is triglycine sulfate with KBr windows as pyroelectric bolometer. It has a high response time. Other most common detectors used such as thermocouples, bolometer and Golay detectors have short response time.

The design of the Michelson Interferometer is such as to make measurement in any infrared region possible by simply changing the beam splitter and the detector. The simplicity of the FT Infrared optical system is an added advantage. The infrared source in an FT Spectrometer may be a water cooled globar (6000 – 50 cm^{-1}) or a high pressure mercury lamp (700 – 10 cm^{-1}). The entire interferometer is evacuated since water vapour strongly absorbs in the far infrared region.

10.6.2 Working of a FT Spectrometer

A typical interferograms from a Michelson interferometer is given in Fig. 10.4. The interferogram contains information on intensity of each frequency in the spectrum. The sample absorption will show up as gaps in the frequency distribution. The interferograms are converted into the normal infrared spectra by Fourier transformation.

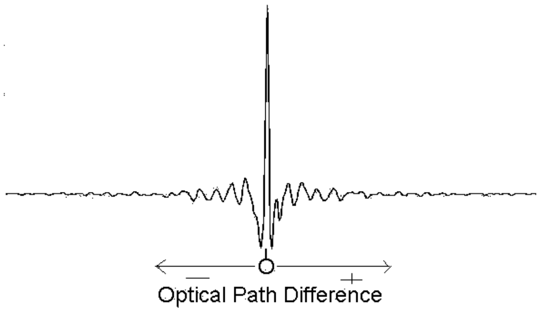


Figure.10.4. Interferogram from a Michelson Interferometer

The measurement of the spectrum may be carried out as follows. The movable mirror is moved smoothly over a period of time say one second through a distance of 1.0 cm. The movement of the movable mirror should be known very precisely. This manipulation is carried out on a digital computer after digitizing the value of the interferogram at regular intervals of mirror movement. This information is read directly into the memory of a computer or stored on a magnetic tape. The detector signal that is the interferogram may be recorded every thousandth of a second during the mirror movement and every information is stored in the computer. It is usual to refer the recordings of the interferograms as ‘scans’. Fourier transformation is performed on the stored data. The number of storage points chosen determines the resolution of the final spectrum. By increasing the storage capacity of the computer and the distance traversed by the mirror, the resolution may be increased. A spectrum recorded over the region 2200 to 200 cm^{-1},that is an interval of 2000 cm^{-1} would have a maximum resolution of about 2.0 cm^{-1} apart. Thus for low resolution spectrum over the mid infrared region as few as 1000 data points need be collected per scan. For high resolution spectra, this number should be increased by one or more orders of magnitude.

The spectrum obtained from the transformed interferogram is a single beam spectrum of the sample. To obtain the transmittance spectrum of the sample, the interferogram with no sample in the beam is obtained and Fourier transformed to obtain the intensity spectrum of the reference. The sample is then inserted and another interferogram is obtained. Fourier transformation of it yields a second intensity spectrum. The transmittance spectrum is then obtained by the ratio of the single beam sample spectrum against the single beam reference spectrum.

10.7 Problem on vibrations of polyatomic molecules

Problem 1: A molecule has strong fundamental bands at the following frequencies, C-H bend at 730 cm^{-1}; C-C stretching at 1400 cm^{-1}, C-H stretching at 2950 cm^{-1}. Write down the frequencies of the possible combination and first over tone bands.

Solution: i) the first over tone band will occur at double frequency of the fundamental band so it will be at 1460, 2800 and 5900 cm^{-1}. ii) The possible combination bands are, (a) 730+ 1400= 2130 cm^{-1} (b) 700+2950 = 3680 cm^{-1} (c) 1400+ 2950 = 4350 cm^{-1}

10.8 Let us sum up

This unit gives the fundamental of vibrations of polyatomic molecules and their symmetry structure along with modes of vibrations and their assigned frequencies of molecules. The detailed experimental studies of FT Infrared spectroscopy and in working with example these information helps to understand the polyatomic molecules.

10.9 Key words

Skeletal vibration, Group frequencies, FTIR, FTIR spectrometer

10.10 Review Questions

1. Explain the theory of diatomic vibrating rotator.
2. Describe the vibrations of polyatomic molecules.
3. Explain the working principle of FT-IR spectrometer with block diagram.

10.11 Reference books

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Unit 11: Raman Spectroscopy

Structure:

11.0 Objectives:

On successful completion and understand of this unit the students should have:

- Principle of Raman spectroscopy
- Characteristics properties of Raman lines
- Difference between Raman and IR spectra
- Application of Raman spectroscopy.

11.1 Introduction:

In 1923, Smekal predicted that in the case of light scattered by transparent medium, the scattered radiation contains frequencies other than those present in the original incident radiation. In the year 1928, physicist Sir C. V. Raman shown that when a beam of monochromatic light is allowed to pass through some organic compounds such as benzene, toluene etc., the scattered light contained some additional frequencies below and above that of incident frequencies. This phenomenon is known as Raman Effect and is an experimental conformation of the Smekal prediction.

The wavelength observed as lines because of modification in Raman Effect are called Raman lines. The lines having wave-length greater than that of the incident wavelength are called Stokes' lines and those having shorter wave length are called anti-Stokes lines.

If 'ν_i' represents the frequency of the incident radiation and 'ν_e' represents that of the light scattered by a given molecular species, then the Raman Shift, '$\Delta\nu$' is defined as $\Delta\nu = \nu_i - \nu_{e.}$ The observed Raman shift does not depend up on the frequency of the incident light but it is regarded as a characteristic of the substance causing Raman Effect. For the Stokes' lines, $\Delta\nu$ is positive and for the anti-Stokes $\Delta\nu$ is negative (figure.11.1)

11.2 Principle Raman Spectroscopy.

Scientist Rayleigh observed that, if a substance is irradiated with monochromatic light, the scattered light is observed in a direction at right angles to the incident light. When a spectroscope was used to observe the scattered light, it was found that the frequency of the scattered light was same as the frequency of the incident radiations. This phenomenon was observed by Rayleigh and is called as Rayleigh scattering.

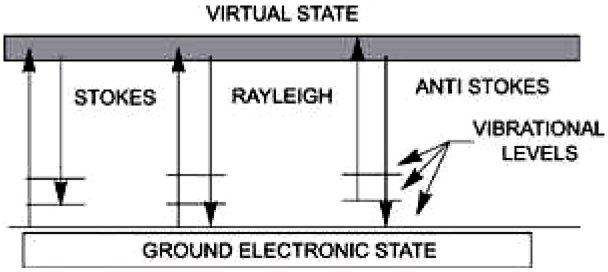


Fig.11.1. Simplified energy diagram

From 1930 to 1960, Raman spectroscopy was not much used for analytical work as was the case with IR spectroscopy. However, with the discovery of the `LASER' (light amplification by stimulated emission of radiation) by Townes, Basov and Prokhorov in the late 1950's, Raman spectroscopy has become a very important analytical tool. The laser has replaced Hg as the source of radiation. The laser radiation is coherent and monochromatic i.e., it is a radiation with very high intensity in a narrow beam with a well-defined frequency. Thus, it can be easily focused and collimated. The line width of the laser beam is also far smaller than that of the mercury-excited line. Advanced scientific research laboratories are now equipped with laser Raman spectrometers. Using a laser Raman spectrometer, the spectrum of a sample or solution can be recorded very fast.

11.2.1 Characteristic properties of Raman Lines

The lines observed in Raman Effect gives a number of characteristics which are summarized as follows.

(i) The intensity of Stokes' lines is always greater than the corresponding anti-Stokes' lines. The anti-Stokes' lines are very difficult to study in the conventional Raman spectroscopy because they correspond to the return of a molecule from the unstable excited vibrational state to the ground state and initially there are very few molecules in the excited vibrational state.

(ii) The Raman shift ($\Delta\nu$), generally lies within the far and near infrared regions of the spectrum. i.e., the Raman frequencies are generally identical with the infrared vibrational frequencies. The small difference can be attributed to experimental errors. It should be noted that it is not necessary that all Raman lines will have their corresponding infrared bands and similarly all infrared bands may not have the corresponding Raman lines.

(iii) The Raman lines are symmetrically displaced about the parent lines. When the temperature of the solvent or sample rises, their individual separations from the parent lines decrease.

(iv) The frequency difference between the modified and parent line represents the frequency of the absorption band of the material.

11.2.2 Differences between Raman Spectra and Infrared Spectra

The above characteristics are the Raman shift lines in far and near infrared regions of the spectrum. Yet Raman spectrum is quite different from Infrared spectrum as pointed out below:

Raman Spectra	**Infrared Spectra**
1. Raman Spectra arises due to the scattering of light by the vibrating molecules	1. IR observed result of absorption of light by vibrating molecules
2. Polarizability of the molecule will decide whether the Raman spectra will be observed or not	2. The presence of a permanent dipole moment in a molecule may be regard as a criterion of infrared spectra.
3. Raman spectra can be recorded only in one exposure.	3. IR requires at least two separate runs with different optical prisms to cover the whole region of infrared
4. Water can also be used as a solvent.	4. Water cannot be used as a solvent because it is opaque to infrared radiation.
5. Raman Spectroscopy method is very accurate, but is not very sensitive.	5. IR method is accurate and very sensitive.
6. Optical systems are made of glass or quartz.	6. Optical systems are made up of special crystals such as CaF_2, NaBr, etc.
7. Sometimes photochemical reactions take place in the regions of Raman lines and thus create difficulties.	7. Photochemical reactions do not take place.
8. Substance under investigation must be pure	8. This condition is not rigid.

and colorless.	
9. In Raman spectrum, vibrational frequencies of large molecules can be measured.	9. In IR, the vibrational frequencies of very large molecules cannot be measured.

11.2.3 Quantum theory of Raman Effect:

The Raman Effect phenomenon cannot be explained on the basis of classical electromagnetic theory. This problem makes necessary to apply the quantum principles for its proper explanation. Raman Effect may be regarded as the outcome of the collisions between the light photons and molecule of the substance.

Let a molecule of mass ‘m’ in the energy state ‘E_p’ (the sum of electronic, vibration and rotational energy) is moving with a velocity ‘u’ and is colliding with a light photon ‘hν’. Suppose if this molecule undergoes a change in its energy state as in its velocity. Let the energy state be ‘E_q’ and the velocity be u' after suffering collision and if we apply the principal of conservation of energy we can write.

$$E_p + \frac{1}{2}mu^2 + h\nu = E_q + \frac{1}{2}mu'^2 + h\nu' \qquad (11.1)$$

It can be easily proved that the change in velocity of the molecule is practically negligible. Thus, equation (11.1) can be written as

$$E_p + h\nu = E_q + h\nu' \quad \text{or} \quad \nu' = \nu + \frac{E_p - E_q}{h}$$

$$\nu' = \nu + \Delta\nu \qquad (11.2)$$

From eq. (11.2), three cases may arise:

(i) If $E_p = E_q$ then the frequency difference (Raman Shift) Δν (i.e. $\frac{E_p - E_q}{h}$) is zero. Hence $\nu' = \nu$ refers to the unmodified line where the molecule simply deflects the photon without receiving any energy from it. The collision thus being elastic & is analogous to Rayleigh scattering.

(ii) If $E_p > E_q$ then $\nu' > \nu$ which refers to anti-Strokes’ line. It means that the molecule was previously in the excited state and it handed over some of its intrinsic energy to the incident photon. The scattered photon thus has greater energy.

(iii) If $E_p<E_q$ then $\nu' < \nu$ which correspondence to the Stokes' line. The molecule has absorbed some energy from the incident photon and consequently the scattered photon will possess lower energy.

As the change in the intrinsic energy of the molecule is governed by quantum rules one can write.

$$E_p - E_q = \pm nh\nu_c \tag{11.3}$$

where n=1,2,3,….. This is called characteristic frequency of the molecule. In the simplest case when n=1, reduced to the form.

$$\nu' = \nu \pm \nu_c \tag{11.4}$$

It follows from equation (11.4) that the frequency different (ν-ν') between the incident the scattered photon in the Raman Effect corresponds to the characteristic frequency 'ν_c' of the molecule. The Raman lines are equally spaced from the unmodified parent line on the either side, at a distance equal to the characteristic frequency lines of the scattered photons.

11.2.4 Explanation of the intensity of Raman lines:

The molecules in a medium are supposed to be distributed among the different quantum state of energies E_1, E_2….etc., Assuming their statistical distribution to be according to Boltzmann's law, then the number of molecules N_p having particular energy state E_p is given by

$$N_p = CN_{g_p} e^{-E_p/kT} \tag{11.5}$$

where 'C' is a constant, 'N'is the total number of molecules, 'g_p' the statistical weight of the state, 'k' is the Boltzmann's constant and 'T' the absolute temperature.

Now at the room temperature, the energy E_p of a molecule will be small and therefore the $e^{-Ep/kT}$ will be high. Therefore the number of molecules possessing this low energy E_p will be numerous. As a consequence of this, the Stokes' transitions will occur more frequently than the anti-Stokes'. This will make the Stokes' line more intense than the anti-Stokes' lines.

As the temperature is raised, the kinetic energy of the molecules increases and more molecules are raised to the higher energy states. As a result the anti-Stokes' lines will gradually grow in higher intensities and becomes more prominent.

11.2.5 Pure rotational Raman Spectra:

The selection rule for rotational Raman spectra is ΔJ=0, ±2 in contrast to the corresponding selection rule in infrared spectroscopy ΔJ = ±1

$$\Delta J = 0, \pm 2$$

When ΔJ = 0, the scattering Raman radiation will be of the same frequency as that of incident light (Rayleigh scattering). The transitions ΔJ= +2 gives Stokes lines (longer wave length) whereas ΔJ = -2 gives two anti-Stokes' lines (shorter wave length). By utilizing the relation for the energy of a rigid rotators as follows

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \tag{11.6}$$

When ΔJ= +2, the values of rotational Raman shift (Stokes' line) will be given by

$$\Delta\bar{\nu} = \frac{h^2}{8\pi^2 I}\{(J+2)(J+3) - J(J+1)\}$$

$$= 2\mathrm{B}\ (2\mathrm{J}+3) \text{ where } \mathrm{B} = \frac{h^2}{8\pi^2 I} \tag{11.7}$$

When ΔJ = -2 the value of rotational Raman shift (anti-Stokes' line) will be given by

$$\Delta\bar{\nu} = -\,2\mathrm{B}\ (2\mathrm{J}+3) \tag{11.8}$$

On combing equation (11.7) and (11.8), the Raman shift can be put in the form.

$$\bar{\nu} = \pm\ 2\mathrm{B}\ (2\mathrm{J}+3) \qquad \text{where J = 0,1,2} \tag{11.9}$$

The wave number of the corresponding spectral line will be thus, given by

$$\bar{\nu} = \bar{\nu}_{ex} + \Delta\bar{\nu} \tag{11.10}$$

where $\bar{\nu}_{ex}$ is the wave number of exciting radiation.

The transition and the Raman spectrum arising from there are drawn schematically. It can be seen that the frequency of separations of successive lines is 2B cm^{-1} whereas it is 4B cm^{-1} in the far infrared spectra. While on substituting J=0, in equation (11.10) we observe that the separation of the first line from the exciting line will be 6B cm$^{-1.}$ The homonuclear diatomic molecules (e.g., O_2 and H_2) do not exhibit infra-red or microwave spectra but they do exhibit rotational Raman spectra. Therefore, their structures can be ascertained. Suppose the molecules possess a center of symmetry (e.g. H_2, O_2 and CO_2), then the effect of nuclear spin will be observed in both Raman and infra-red spectra. Thus in H_2, $O_{2,}$ and CO_2 etc every alternate rotational level will be missing from the spectrum, in the case of O_2 energy levels with even J values are missing (J= 0,2,4…..).

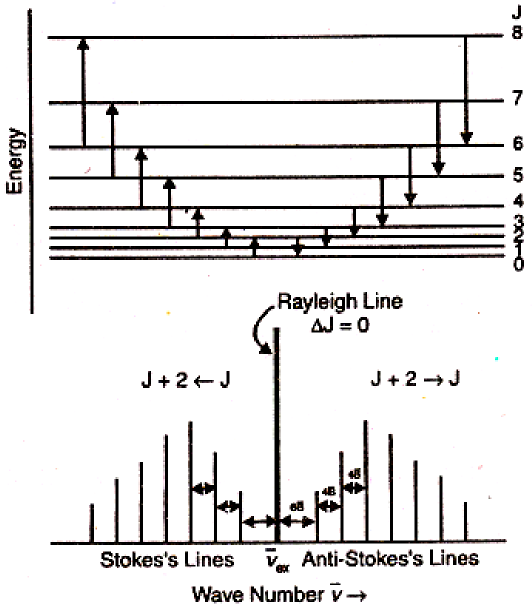


Fig. 11.2: Rotational Raman Spectrum of a Diatomic molecule.

11.2.6 Vibrational Raman Spectra

The structure of vibrational Raman spectra can be easily discussed. For every vibrational mode we can write an expression of the form.

$$\epsilon = \overline{\omega_e}\left(v+\frac{1}{2}\right) - \overline{\omega_e}\chi_e\left(v+\frac{1}{2}\right)^2\text{cm}^{-1} \qquad (v = 0,1,2\ldots.) \tag{11.11}$$

where $\overline{\omega_e}$ is the equilibrium vibrational frequency expressed in wave numbers and 'χ_e' is the anharmonicity constant. Such an expression is perfectly general whatever the shape of the molecule or the nature of the vibration. Quite genera,l too, is the selection rule

$$\Delta v = 0, \pm 1, \pm 2\ldots. \tag{11.12}$$

which is the same for Raman as for infra-red spectroscopy, the probability of $\Delta v = \pm 2, \pm 3\ldots.$ decreasing rapidly.

Particularizing, now, to Raman active modes, we can apply the selection rule (11.12) to the energy level expression (11.11) and obtain the transition energies

$$\left.\begin{array}{ll} v=0 \rightarrow v=1: \Delta\varepsilon_{\text{fundamental}} & = \overline{\omega_e}(1-2\chi_e)\ \text{cm}^{-1} \\ v=0 \rightarrow v=2: \Delta\varepsilon_{\text{overtone}} & = 2\overline{\omega_e}(1-3\chi_e)\ \text{cm}^{-1} \\ v=1 \rightarrow v=2: \Delta\varepsilon_{\text{fundamental}} & = \overline{\omega_e}(1-4\chi_e)\ \text{cm}^{-1}\text{etc} \end{array}\right\} \tag{11.13}$$

Since the Raman scattered light is the case of low intensity, we can ignore completely all the weaker effects such as overtones and 'hot' bands and restrict our discussion merely to the fundamentals. This is not to say that active overtone and hot bands cannot be observed but they add little to the discussion here.

We would expect Raman lines to appear at a distance from the exciting line corresponding to each active fundamental vibration. In other words, we can write-

$$\bar{v}_{\text{fundamental}} = \bar{v}_{ex} \pm \Delta\varepsilon_{fundmental} \quad cm^{-1} \tag{11.14}$$

where the negative sign represents the Stokes' lines (i.e. for which the molecule has gained energy at the expense of the radiation) and the plus sign refers to the anti-Stokes' lines. The latter are often too weak to be observed, very few of the molecules exist in the v=1 state at normal temperatures.

The vibrational Raman spectrum of a molecule is basically simple. It will show a series of reasonably intense lines to the low-frequency side of the exciting line with a much weaker, mirror-image series on the high-frequency side. The separation of each line from the centre of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule.

As an example we illustrate the Raman spectrum of chloroform $CHCI_3$ a symmetric top molecule (Fig: 11.3 (a)). The exciting line in this case is the 488 nm Argon ion laser line (at a power of 100 mW) and a wavenumber scale is drawn from this line as zero. Raman lines appear at 366, 668, 761, 1216, and 3019 cm^{-1} on the low-frequency (Stokes') side of the exciting line while the line at 262 cm^{-1} on the frequency (anti-Stokes') side is included for a comparison of its intensity.

For comparison also we show at Fig:11.3(b) the infra-red spectrum of the same molecule. The range of the instrument used precluded measurement below 600 cm^{-1}, but we see clearly that strong (and hence fundamental) lines appear in the spectrum at wave numbers corresponding very precisely with those of lines in the Raman spectrum but with very different relative intensities.

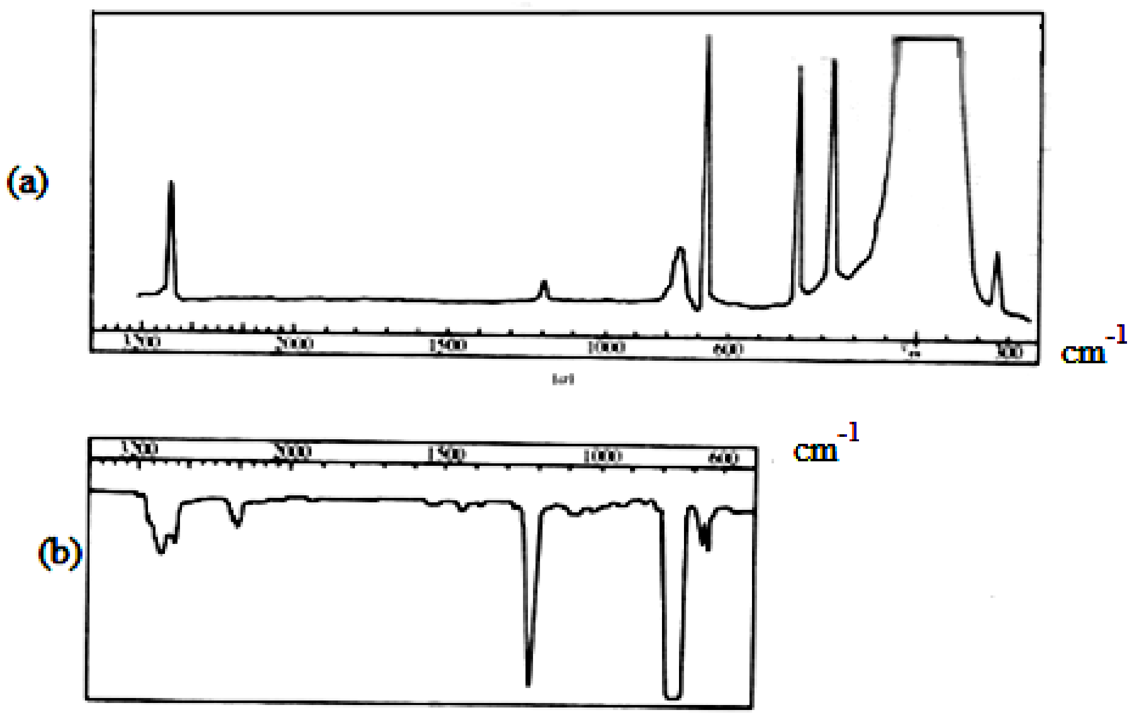


Figure: 11.3 Comparison between (a) the Raman and (b) the infra –red spectra of chloroform $CHCI_3$, showing the coincidence of bands.

For this molecule, containing five atoms, nine fundamental vibrations (that is 3N-6) are to be expected. The molecule has considerable symmetry; however, three of these vibrations are doubly degenerate (see Herzberg's infra-red and Raman spectra for details) leaving six different fundamental absorptions. We see that these are all active in both the infra-red and Raman. The immediate conclusion, not all surprisingly, is that the molecule has no centre of symmetry.

The Raman frequency shifts also conform to fundamental and its overtones in the infra-red spectrum of diatomic molecules. The spacing between the consecutive line decreases as $\Delta\nu$ decrease. It is due to anharmonic nature of the diatomic vibrator. In case the diatomic vibrator behaves as a harmonic oscillator, the vibrational lines are observed with frequencies ω_e, $2\omega_e$, $3\omega_e$ and the spacing between the lines is $\overline{\omega_e}$. Also the intensity of these line decreases sharply in the order $\mathbf{I_{\Delta v(\pm 1)} \gg I_{\Delta v(\pm 2)} \gg I_{\Delta v(\pm 3)}}$.

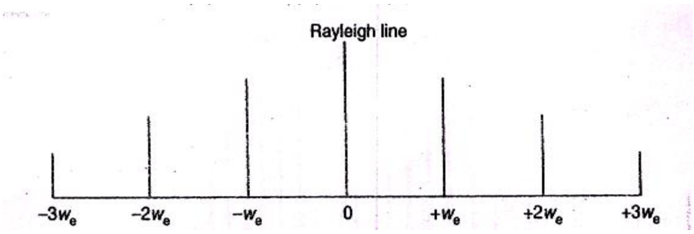


Fig:11.4 Schematic Raman spectrum of diatomic harmonic vibrator.

From the position of Stokes' or anti-Stokes' lines and the Rayleigh line, vibrational frequency and the force constant of a diatomic molecule can be predicted.

When HCI^{35} is irradiated with 4358 Å (Hg line) the Stokes' line is observed at 20057 cm^{-1}. The vibrational frequency of HCI is

$$\bar{v}_{vib} = v_0 - v_s = \frac{1}{4358x10^{-8}} - 20057cm^{-1}$$

$$= 22946 - 20057 = 2889cm^{-1}$$

Also we know $$\bar{v}_{vib}(cm^{-1}) = 1303.16\sqrt{\frac{k(millidynes\ /A^{\circ})}{\mu(amu\ )}}$$

$$\mu(Reduced\ mass) for\ HCl = \frac{m_1 m_2}{m_1 + m_2} = \frac{1X35}{1+35} = \frac{35}{36}\ amu$$

Thus $$2889 = 1303.16\sqrt{\frac{k}{35/36}}$$

or

$$k(Force\ constant) = \sqrt{\frac{0.2889X2889X35}{1303.16X1303.16X36}} = 4.77\ millidynes/Å$$

11.2.7 Application of Raman Spectroscopy

The Raman spectra are obtained from (milligrams or micrograms) the sample. Spectra of crystals or powders, single crystals, polymers and colored substances may be recorded. Some of the samples are unsuitable. i.e. sample contaminated with strongly fluorescent impurities and samples which absorb the exciting radiation. Furthermore the Raman spectra of aqueous solutions and of air-sensitive and corrosive substance can be obtained more easily than infrared spectra. The substances to be analyzed by Raman spectroscopy should be free from impurities likely to be observed in the range of the Raman spectrum. Gas chromatography or vacuum distillation can be used for purification of liquids. Crystalline substances can be examined in solutions as a melt in powered type or as single crystals. Solvents are purified by distillation in grease-free apparatus or by filtration through alumina.

The Raman spectroscopy is very important because of its large number of applications. In fact, it is a useful method for solving the intricate research problems concerning the constituents of compounds. The applications of Raman spectroscopy are very much ever increasing. Some of its applications in the physical, inorganic and organic chemistry are discussed below:

(a) Applications in Inorganic Chemistry

(i) **Structure of CO_2** : If it is assumed to be a symmetrical linear molecule **O-C-O**, one should expect two fundamental frequencies (ν_2 and ν_3) in infrared and one (ν_1) in the Raman. This has been experimentally confirmed and the following observations are made.

$\nu_1 = 1340\ cm^{-1} \nu_2 = 667\ cm^{-1}$, $\nu_3 = 2349\ cm^{-1}$.

(ii) **Structure of N_2O**: If it is assumed that N_2O is symmetrical like CO_2, ie **N-O-N**, one should expect a similar type of behavior as in CO_2. If it is unsymmetrical i.e **N-N-O**, ν_1 should become active in the infrared as well as in Raman. This additional behavior has been observed in both IR and Raman spectra. This proves that the structure of N_2O is **N-N-O**.

(iii) **Structure of mercurous salts:** When Raman spectrum of an aqueous solution of mercurous nitrate is recorded, it shows a line which is absent in the spectra of other metal nitrates. This line may be attributed to the vibration of Hg-Hg covalent bond in the diatomic molecule Hg_2^{2+}.

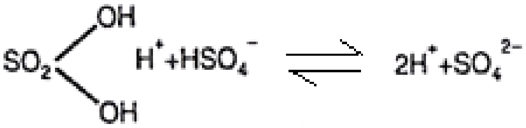
(iv) **Structure of Chloro complexes of Mercury:** When a Raman spectrum of a solution of mercuric chloride and ammonium chloride mixed in a 1:2 molar ratio is recorded, it shows a strong line at 269 cm^{-1}. This line compares with the strong line at 273 cm^{-1} for solid ammonium tetrachloromercuriate (II), indicating the formation of $HgCI_4^{2-}$in solutions.

(v) **Nature of Bonding:** When we record the infrared spectra of tetrahedral complexes ML_4 (e,g, $ZnCI_4^{2-}$and $HgCI_4^{2-}$) and octahedral complexes ML_6(e.g. $SiF_6^{2-,}$ and SF_6^{2-}) no bands will be observed because only the bond lengths change during the vibration.

However, intense lines are observed in Raman spectra. From the M-L, bond stretching force constant it becomes possible to obtain useful information about the strength of the metal-ligand bond. The oxy-anions such as PO_4^{3-}, SO_4^{2-} and ClO_4^- have much larger force constants. This is considered to be taken as evidence that there is dπ–pπ bonding between the central atom and oxygen atom in addition to the σ-bonding.

(vi) **Hydrogen Cyanide:** In the Raman spectrum exhibits two lines at 2062 cm^{-1} and 2062 cm^{-1}. These may be due to two isomers in dynamic equilibrium.

(vii) **Sulphuric Acid:** The Raman frequency of 25% H_2SO_4 corresponds to the frequency given by the $KHSO_4$ but on dilution the Raman frequency corresponds to that of K_2SO_{4-}. Thus this shows the existence of HSO_4^{-1} ion.



(viii) **Carbon Disulphide:** For CS_2 all the vibrations that are Raman active are infrared-inactive and vice versa, whereas for N_2O, the vibrations are simultaneously Raman and infrared active. From the spectral data we conclude that CS_2 has a center of symmetry whereas N_2O has no center of symmetry. Thus, the CS_2 structure is of the type S-C-S while the N_2O structure must be N-N-O rather than N-O-N.

(ix) **Carbon Monoxide:** It gives a Raman line at 2155cm^{-1} which is closely similar to –C≡N of 2200 cm^{-1}. This shows that like cyanides, carbon monoxide is having –C≡O. This is in harmony with the suggestion that CO in C=O and the isocyanide group in N≡C. Recent studies have revealed that CO has resonance structure.

(x)**Water:** The triatomic molecules having a linear bent structure should exhibit three Raman lines. In the Raman spectrum of water two frequencies have been recorded at 1665 and 3600 cm^{-1}.In addition certain other bands have also been observed which may be described polymerized molecules such as $(H_2O)_2$ and $(H_2O)_3$.

(b)Application in Physical Chemistry

Number of problems on physical chemistry concerning electrolytic dissociation, hydrolysis and transition from crystalline to amorphous state has been studied and the following results have been obtained.

(i) The amorphous state of a substance gives rise to broad and diffused bands while crystalline state gives fine sharp lines.

(ii) In the case of the phenomenon of electrolytic dissociation, the intensity of Raman lines enables us to determine the number and nature of ions produced. Therefore, we can decide whether the dissociation is complete or partial.

(iii)The degree of hydrolysis of a salt can be determined by measuring the relative intensities of a set of lines, characteristic of the base, the acid or the salt.

(iv) **Study of single crystals:** The Raman technique has proved to be particularly valuable in the study of single crystals whereas the IR technique has greater limitations on sample size and geometry. In addition, polarization data obtained from Raman spectra allow unambiguous classification of fundamentals and lattice modes into the various symmetry classes. Although Raman technique will never challenge X-ray diffraction as a tool for quantitative structural analysis, it is the preferred method when qualitative information is sufficient, because it is faster and less expensive.

(c) Application in organic Chemistry.

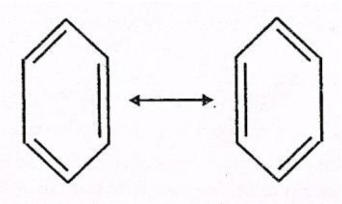
The Raman spectrum is a molecular spectrum and it helps in revealing the molecular structure of organic compounds. It has been observed that each group will have its own characteristic frequency. Raman studies provide the information about the following facts: (i) the presence of absence of specific linkages in a molecule. (ii) The structure of simple compounds. (iii) Study of isomers. (iv) The presence of impurities in dyes. (v) Classification of the compounds.

It has been shown that Raman line generally lie in the region 500-3500 cm^{-1} The Raman frequencies of some functional groups are given in Table 11.1

Table-11.1: Group and frequencies of various groups

Group	Wave number cm^{-1}	group	Wave number cm^{-1}
C-H aromatic	3050	S – H	2570
C-H aliphatic	2920 -2970	O – H	3400
		C – CI	650 – 710
		C – Br	600-570
C=O (Anhydride)	1570	C –I	500-530
C=O (Ketones)	1610	C≡N	2150
C=O (Aldhydes)	1720	C-C	1000

(i) **Benzene:** In the Raman spectrum of benzene shows two strong Raman lines at 995 cm^{-1} and 1050 cm^{-1} which are due to C-C and C-C linkages respectively. This provides support in favor of Kekule formula as shows below.



(ii) **Determining the location of groups on a benzene ring:** Raman spectrum has been used to decide the positions of substitution in benzene derivatives. For example, all meta-substituted benzenes exhibit an intense, strongly polarized line at 995 cm^{-1} which is not present in ortho and para compounds. On the other hand ortho and para compounds may be distinguished by the richer spectrum of the ortho and by a line in the neighbourhood of 625 cm^{-1} in the para, which are generally absent from the ortho derivatives.

(iv) **Information about Olefinic functional group:** The double bond (C=C) stretching vibrations for olefins gives a weak and undetected infrared absorption in various cases. Raman lines also occur at about 1600cm^{-1} which is very intensive. Its position is quite sensitive to the nature of substituent and their geometry. Thus, the Raman spectroscopy provides much more useful information about the olefinic functional group than infrared spectra.

(d) Applications in Polymer Chemistry

Raman technique has become increasingly important for the characterization of polymers. It reveals physical properties such as how the molecules are arranged with respect to each other in the polymer and the polymers crystallinty, tacticity, and amorphous character, which in turn affect structure and properties such as strength and durability. Normal IR absorption spectroscopy is difficult to use without dissolving the sample. After a sample is dissolved, its original character is destroyed and necessary information is lost. If the sample is not dissolved, it is so dense that very little radiation passes through it unabsorbed. Hence Raman technique on the original polymer is most valuable.

In their Raman spectroscopy, polymers often give properties of liquids and of crystals simultaneously. This is due to the existence of amorphous and crystalline regions in the polymers. Stretched polymers generally resemble molecular crystals. The spectra can be represented in terms of unit cells which may contain a few elements of different polymer chains. Like single crystals stretched polymers may be examined with polarized radiation. Raman spectrum also allows a number of experimental conclusions to be reached about the structural units of macromolecules, i.e., C= C bonds (1660 cm^{-1}) benzene nuclei (1000, 1600, and 3060 cm^{-1}) the symmetric Si-O -Si vibration (490cm^{-1}) in silicones and the C-S and S-S vibrations (650 and 510 cm^{-1}) in polysulphides. All these frequencies are gives very intense Raman bands, but are absent or weak in infrared spectra.

(e) Quantitative Analysis

The experimental observation of the absolute intensities of Raman spectra is even more difficult than the determination of the absolute intensity of infrared absorption bonds. For this reason the intensity of a Raman line is usually measured in terms of an arbitrarily chosen reference line, usually the line of CCl_4 at 459 cm^{-1}which is scanned before and after the spectral trace of the sample. Scattering intensities of peak height of one of the spectrum are then converted to scattering coefficients by dividing recorder height of the sample peak by the average of the heights of the dual traces of the CCl_4 peak. Both standard and sample values must be recorded in cells of the same dimension.

For quantitative determination, the intensity of Raman lines is directly proportional to the number of scattered molecules and to the scattering coefficient. For mixtures sample in which the components are all of the same molecular type, there is a direct proportionality between the scattering coefficient and volume fraction of the compound present. For mixtures sample of dissimilar type, Raman shifts will vary among the various chemical compounds and a broad band is recorded at the position characteristic of these bond types. The area under the record peak can be considered as a measurement of scattering intensity.

Raman technique can be successfully used for rapid, easy and accurate analysis of mixtures that are troublesome with any other method. Raman spectroscopy has two main advantages over infrared spectrophotometry in quantitative analysis. 1). The height of Raman peaks varies linearly with concentration where as with infrared spectrophotometry there is a logarithmic relationship between concentration and the transmitted light. 2). Raman spectroscopy gives simple spectra as compared with the infrared spectroscopy. In addition Raman instrumentation is not subject to attack by moisture and small amounts of water in a sample do not interfere. Despite these advantages, Raman technique has not been widely exploited for quantitative analysis. Nicholson has studied an eight component mixture containing benzene, isopropyl benzene 1,2-1,3- and 1,4 di-isoproylbenzens. 1,3,5- and1,2,4- tri-isopropyl-benzenses and 1,2,4,5- tetra-isopropyl benzene. The average error for each component was about 1 percent.

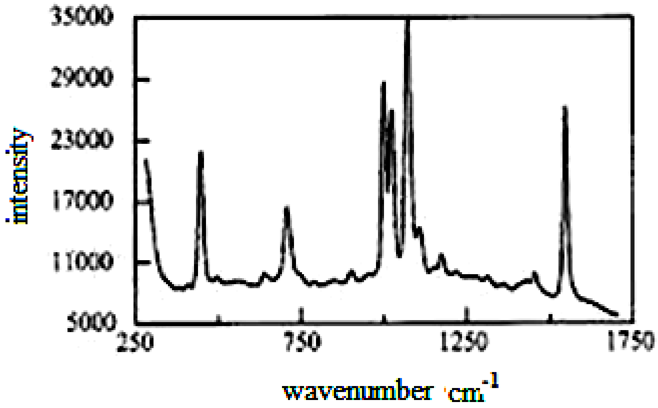


Fig11.5 shows Raman spectrum of $CHCl_3$

11.28 Problems on Raman Spectroscopy

Example-1. A sample was excited by the 4358Å line of mercury. A Raman line was observed at 4447 Å. Calculate the Raman shift (in cm^{-1})

Solution . Given that $\bar{\nu}_o$ (Frequency of incident photon)

$$\frac{1}{\lambda} = \frac{1}{4358X10^{-8}} = 22946\ cm^{-1}$$

Also $\bar{\nu}_R$ (Frequency of scattered photon giving Raman line)

$$\frac{1}{\lambda} = \frac{1}{4447X10^{-8}} = 22487\ cm^{-1}$$

Hence, the Raman shift $\Delta\,\bar{\nu} = \bar{\nu}_O - \bar{\nu}_R$ = (22946-22487) cm^{-1}=459cm^{-1}

$\Delta\,\bar{\nu}$ = 459cm^{-1}

λ We see the $\bar{\nu}_R < \bar{\nu}_{O.}$ We can say that it is Stokes' line.

Example-2. Using radiation of wavelength 4 x10^3Å, the first Stokes' line appears at a spacing of 350 cm^{-1} from the Rayleigh line. Calculate the frequency of the first anti-Stokes' line in wave number.

Solution. We know that $\bar{\nu}$ (Stoke's line) = $\bar{\nu}_O - \bar{\nu}_R$

Also $\bar{\nu}$ (anti-Stokes line) = $\bar{\nu}_O + \bar{\nu}_R$

Given that, $\Delta\,\bar{\nu}_R$ is the Raman frequency. It is equal to the change in the frequency of incident photon.

Thus $\Delta\,\bar{\nu}_R$= 350cm^{-1}

$$\bar{\nu}_0(incident) = \frac{1}{\lambda} = \frac{1}{4X10^{3}} = \frac{1}{4X10^{-5}} = 2.5X10^{10}\ cm$$

= 25000 cm^{-1}

Hence, we write $\bar{\nu}$ (Stoke's lines) = 25000 -350 =24650cm^{-1}

Also $\bar{\nu}$ (antiStoke's lines) = 25000+350 = 25350 cm^{-1}

Example. 3. The fundamental frequency of a molecule is 8.67 x 10^{13} S^{-1}. Calculated the corresponding Raman lines if the molecule is irradiated with 435.8 mm wave length.

(Ans 498.6 nm Stokes, 387 nm anti-Stokes)

Example. 4. On irradiation of CCI_4 with the 434.8nm mercury line, one of the Raman lines appears at 460 nm. Calculate (i) the Raman frequency of $CC1_4$ in wave number (cm^{-1}) (v) the wavelength in micrometers (um) in the IR region at which the absorption would be expected.

(**Ans**. (i) 1207 cm^{-1}(ii) 8.3 (μm))

11.3 Let us sum up:

In this lesson, we pointed out:

- Raman spectroscopy and properties of Raman lines.
- Difference between Raman and IR spectra
- Application of Raman spectroscopy.

11.4 Key Words:

Raman spectroscopy, Infrared spectroscopy, rotational and vibrational Raman spectra.

11.5 Questions for further study:

1. What is the requirement for a vibration to be Raman active?
2. Why are homonuclear diatomic molecules IR inactive and Raman active?
3. Explain why in Raman spectra the Stokes lines are far more intense than the anti-Stokes' lines which are sometimes too weak to be observed.
4. What are the difference between Raman Spectra and infrared spectra?'

11.6 Reference books:

1. Fundamentals of Molecular Spectroscopy, Third Edition by C N Banwell.
2. Instrumental Methods of Chemical Analysis, by Gurdeep R. Chatwal and Sham K. Anand.
3. Molecular Structure and Spectroscopy, by G.Aruldhas.
4. Modern Spectroscopy, fourth edition by J. Michael, Hollas

Unit: 12 Instrumentation

Structure:

12.0 Objectives

To understand the modern spectroscopic instrumentation like single, double beam colorimeter and modern laser Raman techniques. The instruments and their uses are detailed in this unit. Following are the major objectives:

- Characterization of Raman spectrum in many scientific fields.
- Raman active and IR active inactive modes.
- Advantages of Raman and IR spectroscopy.
- Application of IR and Raman spectroscopy.

12.1 Introduction

This unit contains the basics of optical instruments or components which are used commonly in spectroscopy, simple cell, detector, powder supply are presented. Uses and applications of single and doubled beam photonics colorimeter are given in details. The modern laser Raman spectroscopy & its uses with examples along with IR techniques are compared in detail.

12.2 Instrumentation

All photometers, colorimeters and spectrometers have the following basic components:

1. **Source**. A Continuous source of radiant energy covering the spectral region in which the instrument is designed to work.
2. **Filter or Monochromators.** Both filter and monochromator allow the light of the required wavelength to pass through but absorb the light of other wavelengths.
3. **Sample cells.** All the instruments must contain a container for the sample compartment.
4. **Detector.** It is used for measuring the radiant energy transmitted through the sample. In some instruments, detector will be associated with a read out system for the presentation of the detector response. These instruments are explained one by one.

1.Radiation Sources:

The following are requirements of a radiation source:

i. Radiation source must be stable

ii. Radiation source must be of sufficient intensity for the transmitted energy to be detected at the end of the optical path.

iii. Radiation source must supply continuous radiation over the entire wavelength region which is used.

The tungsten filament lamp is the most common source used for visible radiation.

The wavelength range of visible light lies between 4000 Å to 7500 Å region, a tungsten filament lamp is most widely used and its fabrication is similar to the household lamp. However, it contains a piece of tungsten wire which is heated in a controlled atmosphere. In order to get good experimental data, it is important that the tungsten lamp should emit radiant energy which should be constant over long periods of time. This can only be achieved by supplying a constant power supply.

The major disadvantage of the tungsten lamp is that it emits the portion of its radiant energy in the near-infrared region, i.e., only about 15 percent of the radiant energy falls within the visible region at an operating temperature of about 2725 ^{0}C, and at 1725 ^{0} C it is only 1 percent. If the operating temperature is increased to 2850 ^{0} C, leads to increases the total output energy and shifts to shorter wavelength of maximum intensity. But due to higher temperatures the life of the lamp is too much reduced. To remove the unwanted infrared radiations, a heat absorbing filter is placed between the lamp and sample which absorbs most of the infrared radiation without seriously diminishing radiant energy at other wavelengths. Tungsten is the most efficient material for lamp filaments but the carbon arc is used when a more intense visible light source is required.

The energy of tungsten lamp can be used above 375 nm. In the colorimetric measurement is carried out in the UV or IR region of the spectrum, the hydrogen lamp or a Nernst Glower source can be used (fig 12.1).

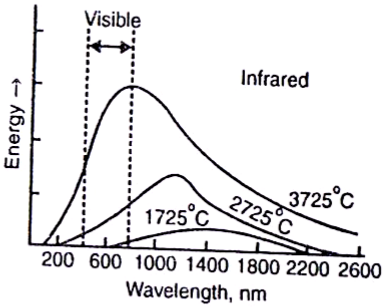


Fig: 12.1 Energy v/s wavelength at visible and IR region for different temperature.

2. Filters and Monochromators: Source is generally emitting continuous spectra; therefore a device is required to be used to select a narrow band wavelength of the continuous spectra. For this reason, filters or monochromators or both are used.

(a) **Filters:** Light filter is a device which allows light of the required wavelength to pass but absorbs light of other wavelengths wholly or partially. Therefore, a suitable filter can select a desired wavelength band. i.e., a particular filter may be used for a specific analysis. If analyses are carried out for several species, a large number of filters have to be used and interchanged. This technique is very useful for many analyses.

There are two types of filters: absorption filters and interference filters. Absorption filters work by selective absorption of unwanted wavelengths. An absorption filter is a solid sheet of glass which is colored by a pigment which is dissolved or dispersed in the glass. Dyed gelatin or similar materials can also be used for absorption filters.

Absorption filters are classified as either cut off or band-pass filters. The table describes the absorption characteristics of common filters (Table 12.1).

Table 12.1: Absorption Characteristics of common Filters

Colour of filters	Approximate range of absorption band in mμ
Yellow	450
Orange	500
Red	575
Purple	450-650
Blue	480
Green	400-475
	575-700

Each instrument contains a set of 12 filters to cover the range from 390 mμ to 700 mμ. In order to get a narrower range, a combination of filters may be employed. But this combination decreases the intensity of light; hence more sensitive detectors are required. Narrower widths are obtained with this interference filters. These filters function on interference phenomena at desired wavelength, thus permitting rejection of unwanted radiation by selective reflection.

To prepare an interference filter, a semitransparent metal film is deposited on a plate of glass, it is coated with a thin layer of some dielectric material (say, MgF_2), followed by another coating of a thin film of metal. Finally, another plate of glass is kept over the films for mechanical protection. A typical interference filter is shown in Fig.12.2.

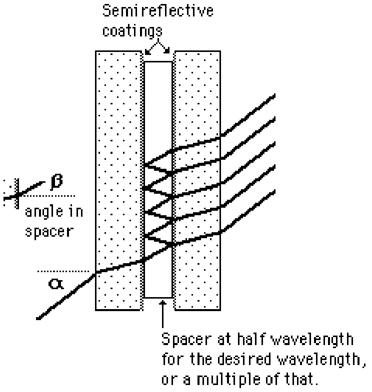


Fig: 12.2 shows typical interference filter

When a light ray is incident upon an interference filter, a part of light reflects back whereas the remaining light is transmitted and this part of the incident radiation is reflected repeatedly by the metal layer but at each reflection, some is transmitted out wards. The different out-going rays undergo constructive interference for those wavelengths which are exactly even multiples of the distance separating the two. For other wavelengths, the beams undergo destructive interference and thus no energy is passed out. By varying the distance between the various filters, the wavelength range can be modified. Interference filters have a band pass of 100-150 Å and peak of 40-60 transmittance per cent.

The net energy efficiency of filters is explained in terms of the width of the radiation band, which corresponds to one-half the maximum transmittance. The relative half-widths and transmission of interference and absorption filters are shown in Fig 12.3. The ideal filter yields maximum transmittance over as narrow a range of wavelengths as required. Both of these ideas are better met with the absorption type. Interference filters are more energy efficient and results in more pure radiation. They show greater transmittances but also possess narrower half-widths than absorption filters. The half-width of an interference filter may be as low as one –tenth that of the absorption unit.

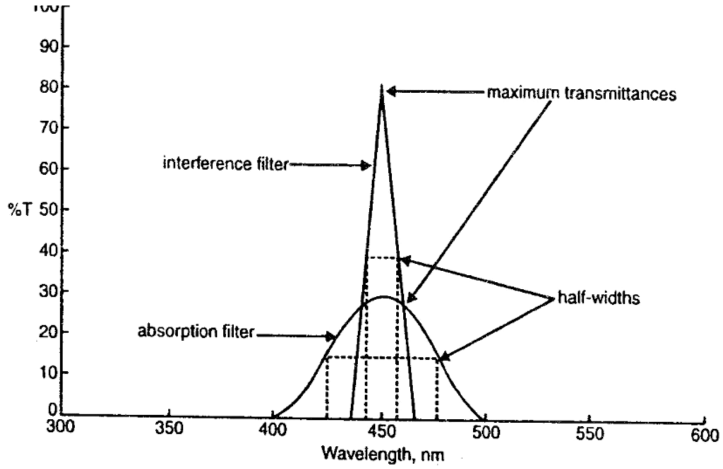


Fig: 12.3: Typical filter characteristics.

(b). **Monochromators:** The monochromator successfully isolates band of wavelengths usually much more than a narrower filter. The required elements of a monochromator are an entrance slit, a dispersing element (a prism or grating) and an exit slit. The function of a prism or a grating is to disperse the heterochromatic radiation into its component wavelengths.

Material construction should be selected with care to match the range in which it has to work. i.e., normal glass for the visual range, quartz for ultraviolet range and alkali halides for infrared region are used.

The replica gratings are of lower cost than prisms; main defect of the gratings is that they produce more than one order of diffraction. For instance, the second order of 400 mμ may interfere with the first order of 800 mμ. This type of interference can be removed by employing filters in front of the entrance slit to absorb interfering radiations. However, one may use two gratings to eliminate stray light.

Grating consists of a large number of parallel lines ruled on a highly polished surface such as alumina, there are, 15,000-30,000 lines per square inch drawn for ultraviolet and visible regions. When light rays are impinged on the grating, its ruled lines act as scattering centers for light rays. Thus, the light is diffracted and is spread out over a range of angles and in certain directions, reinforcement or constructive interference may take place (Fig 12.4).

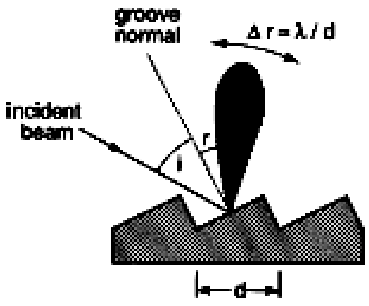


Fig:12.4: shows typical incident beam direction and interference.

Generally, gratings are difficult to prepare; therefore replica gratings are prepared from original grating. This is done by coating the original grating with a film of an epoxy resin which after setting is removed to yield replica. Then, replica is made reflective by aluminizing its surface.

The important advantage of prisms is that - they undergo dispersion, giving wavelengths which do not overlap. But the disadvantage is that they result in non-linear dispersion also. Gratings give linear dispersion but they suffer from an overlap of spectral regions. Due to this cause, filters are employed to reduce the radiation of different orders and stray radiation. In some optical instruments, a prism is used with a grating to sort out the first-order spectrum.

3. Slits. There are two types of slits, entrance slit and exit slit. The main function of the entrance slit is to provide a narrow source of light, so that there should be no overlapping of monochromatic images. The exit slit selects a narrow band of dispersed spectrum for observation by the detector. General practice is that both entrance and exit slits have equal width. Under such conditions the width of a monochromatic image of the entrance slit is such that it will just be passed by the exit slit. Many of the instruments are provided with variable slit widths to give the instrument more flexibility and the entrance and exit slits are adjusted continuously to the same width.

4. Cells. The sample cell holder is usually a solution which should be transparent to the wavelength region to be recorded. For visible region they are generally made of color-corrected fused glass. The thickness of the sample cell is generally 1 cm (internal distance). Cells may be of different shapes i.e., rectangular or cylindrical in shape or cylindrical with flat ends.

Different sample cells are available for the ultraviolet and visible wavelength regions. The choice of a sample cell is based upon the transmission characteristics at the desired wavelength, the path length, shape and size. The transmission characteristics at different wavelengths depend upon the construction materials. For example, Pyrex transmits in the 320-2500 nm range and silica from 170 to 2500 nm. Glass and Plastic may also be used in the visible range whereas KBr or some other such salt like materials is necessary in the infrared region.

The common cell has a rectangular container with a 1 cm path length; however, 5 or 10 cm long path length cells which are constructed of a tube with window of the transmitting material are used with solutions of low solubility or low absorptivity. Circular cells or test tubes are also available in matched sets. Energy cell is etched with a frosted line. The experimental cell holder is marked with a proper alignment guide in order to permit the necessary duplication of sample orientation in the cell holder compartment.

For great accuracy it is necessary to use either the same cell for the blank or all samples, a matched set, or calibrated sample holder cells. They should be diligently cleaned and care should be taken to avoid contamination of the transmitting beam on both side surfaces. The solution level must be considerably above the light beam which is passing through the solution in order to avoid reflections from the upper surface of the liquid. Air bubbles can be removed prior to obtaining experimental measurements.

Each solvent is selected on its ability to transmit light of the desired wavelength and its chemical properties. For example, water may be used at wavelength as low as 180 nm but the lower limit for acetone is 330 nm. More complete information on solvent transmission ranges is available in the manufacture’s specification as well as in the chemical literature.

5. Detection of Radiation: To detect radiations, three types of photosensitive component are photovoltaic cells (also called barrier-layer cells), Phototubes (also called photoemissive tubes) and photomultiplier tubes.

(a) **Photovoltaic Cell**: Photovoltaic cell works without the use of a battery (fig 12.5). Cell consists of a metal base plate like iron or aluminum which acts as one electrode. On its surface, a thin layer of a semiconductor metal like selenium is deposited. Then the surface of selenium is covered by a very thin layer of silver or gold which is collector electrode.

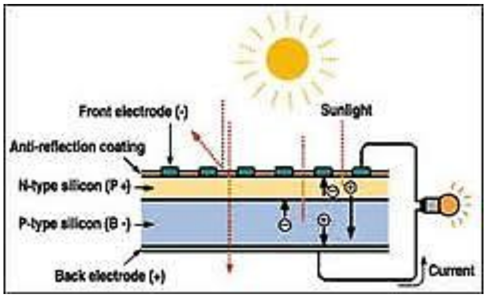


Fig:12.5: typical photovoltaic cell

(b). Phototubes: These cells are also called photo emissive cells. A different of sample cells is useful for the ultraviolet and visible wavelength regions. The choice of a sample cell is based upon these factors namely- the transmission characteristics at the desired wavelength, the path length, shape and size and the relative expense.

This phototube consists of an evacuated glass bulb. Inside the bulb there is a light sensitive cathode in the form of a half-cylinder of metal. The inner surface of cathode is coated with a light sensitive layer such as cesium or potassium oxide and silver oxide. A metal ring placed near the center of the bulb acts as an anode (fig 12.6 depicts a simple phototube circuit.)

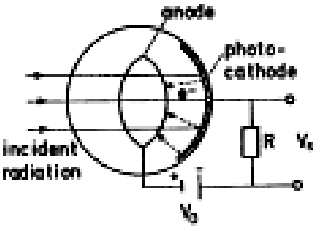
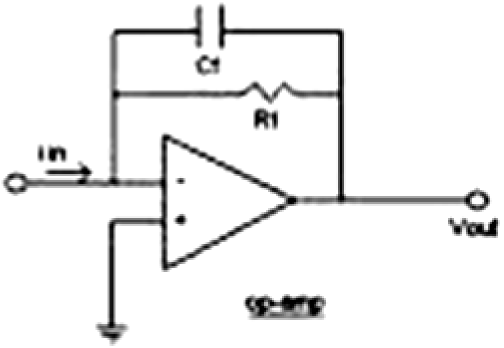


Fig:12.6 Schematic diagram of a photo-emissive cell.

When radiation is incident on the cathode, photoelectrons are emitted. These photoelectrons are attracted and collected by an anode. Then, these are returned via the external circuit. Due to the flow of these electrons, there occurs an IR resulting in drop across the resister R_L which is proportional to the current. This current is amplified by electronic means and is taken as a measure of the amount of light striking the photosensitive surface.

Phototubes are very sensitive than photovoltaic cells, phototubes have high internal resistances, their output currents can be amplified and these are employed for measuring low intensities of illumination. The metal or metal oxide coating on the photoemissive cathode determines the wavelength response because of their sensitivity. For example a sodium coating is utilized in the 350-450 nm region and other coatings result in other wavelengths. For UV, Quartz widows are required on the tube when the radiation is incident on it.

(c)**Photomultiplier Tubes:** The sensitivity of a photoemissive photocell is increased considerably by employing the Photomultiplier tube.



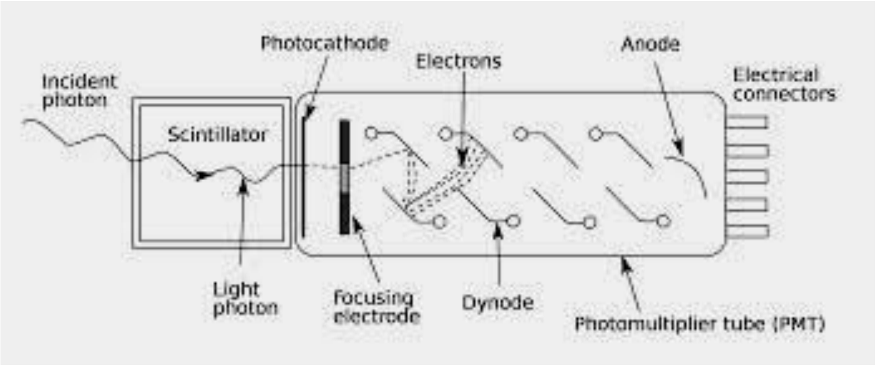


Fig:12.7 Schematic diagram of photomultiplier tube.

Photomultiplier tube consists of an electrode covered with a photo emissive material. This tube also contains a large number of plates called dynodes; each dynode is covered with a material which emits several electrons for each electron striking on its surface. Also, each dynode is charged at a successively higher potential. A typical photomultiplier tube is shown in Fig.12.7.

When radiation is incident upon the cathode surface, electrons are ejected. These are accelerated to the sensitive surface of the dynode where secondary electrons are emitted in greater numbers than the initially striking to the plate. These electrons in turn are accelerated to another dynode maintained at a higher potential, where the number of electrons is again increased by a factor of 3 or 5. This is repeated several times until a large number of electrons arrive at a collector. The number of electrons falling on the collector measures the intensity of light incident on the cathode surface. Most photomultiplier tubes have about 10 dynodes. Each dynode is maintained at 80 to 100 V more positive than the preceding dynode. By a photomultiplier tube, the overall amplification factor of about 10^6 can be achieved.

The output of a photomultipliers tube is only several milliamperes; it can be used to measure intensities about 200 times weaker than those measurable with a photoelectric cell and amplifier. The response time of a photomultiplier tube is 10^{-9} seconds. A photomultiplier tube must be carefully shielded to avoid from the stray light.

6. Power supply: The functions of power supply are-

(i) It reduces the line voltage to the instrument's operating level with a transformer.

(ii) It converts alternating current (AC) to direct current (DC) with a rectifier if DC is required by the instrument.

(iii) It smoothens out any ripple which may occur in the line voltage in order to deliver a constant voltage to the source lamp and instrument.

The recommendations of manufacturers should be followed in the choice and use of power supply for a particular instrument and for a particular source lamp. The precision of the readout in any spectrophotometer can be no greater than the precision of the power supply regulation. If the power supply is batteries (as in field units) they should be checked continuously and charged or change it if it is necessary.

7. Visual Comparators: Before photoelectric devices were generally available, colorimetric analysis was carried out by simple visual comparison methods. In most of these techniques an absolute accuracy of ± 5 percent is attained. However, this can be increased by careful attention to details. There are four major techniques for colour compassion in quantitative visual colorimetry. They are:

(a) Multiple standard methods (b) Duplication method (c) Dilution method, and
(d) Balancing method.

The first three methods are carried out with Nessler tubes and the last method with colorimeters like Klett Bio colorimeter or Dubosque colorimeter technique.

8. Photo-Electric colorimeter. Photo-electric colorimeters are two types:

(a) **Single beam instrument**: The Evelyn Photo–electric colorimeter is as shown in fig.12.8. The main parts of a single beam instrument are. (a) Source of light with a concave reflector (b) an adjustable diaphragm,(c) a colored- glass filter for monochromatic light. (d) Cuvette for holding the absorbing solution. (e) Single photocell to receive the radiation and (f) a directly connected to galvanometer. The output current of the cell is directly proportional to the radiant power falling upon it at a given wavelength.

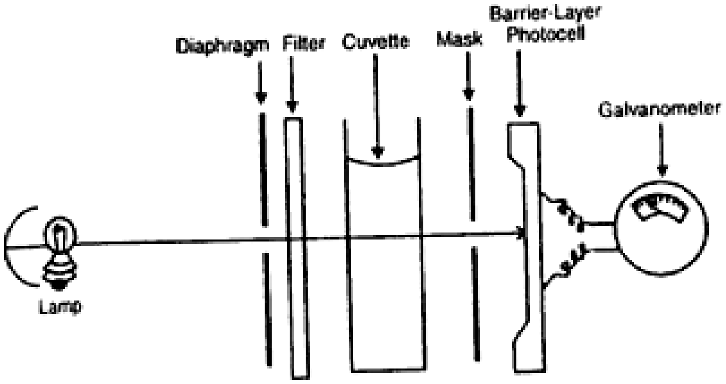


Fig:12.8: Schematic diagram of single cell photometric colorimeter.

To determine the absorbance of a solution, cuvette is filled up with pure solvent. Then, diaphragm is adjusted so that the meter reads full scale (100 percent). Now the solvent is replaced by solution without disturbing diaphragm. Then the meter will recorded the percent transmittance from which the observance of the solution can be recorded.

The single beam colorimeter possesses the fault that the reading fluctuates with variation in the source intensity. This defect can be minimized by using a storage battery as a current supply or by using a more costly constant- voltage transformer. A battery remedy is to use two photocells in a double–beam circuit. In this arrangement, fluctuations, being observed equally by both cells, are cancelled out.

(b) **Double-beam instrument:** Fig 12.9 shows a schematic (combined optical and electrical) diagram of the Fisher Electrophotmeter II. This instrument is employed for a potentiometric null balance measuring system.

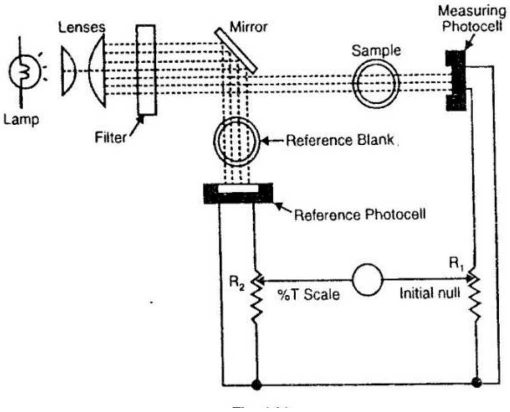


Fig:12.9: Schematic diagram of double-beam photometric colorimeter.

The operation of this instrument: the null-balance galvanometer is adjusted to bring the needle at midscale with the lamp off. Then, the lamp is switched on and blank solution is kept in both light beams. The potentiometer R_2 is adjusted to read 100 % transmittance and then the slide wire contact R_1 is adjusted to null the galvanometer solution of standard and unknown are introduced into the measurement beam and slide-wire contact R_2 is adjusted to renull the meter. The transmittance (linear) or absorbance (non-linear) can then be read off from the potentiometer dial for every sample.

12.2.1 Advantages of Double Beam Instrument:

The double beam instruments are more complicated and expensive, they have the following advantages:

(i) It is not necessary to continually replace the blank with the sample or to zero adjust at each wavelength as in the single beam units.

(ii) The ratio of the powers of the sample and reference beams is constantly obtained and used. Any error due to variation in the intensity of the source and fluctuation in the detector is minimized.

Because of the factors these double beam system lends itself to rapid scanning over a wide wavelength region and to the use of a reader or digital readout

12.2.2 Modern Laser Raman Spectrometer:

Laser Raman spectrometer system consists of four major components:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer)

4. Detector (Photodiode array, CCD or PMT).

A Sample is illuminated with a laser beam in the range of ultraviolet (UV), visible (Vis) or near infrared (NIR), Scattered light is collected with a lens and is sent through spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. The major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect. Researchers use commercially available interference (notch) filters which cut-off spectral range of ± 80-120 cm^{-1} from the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency (range below 100 cm^{-1}) Raman mode.

Stray light is observed in the spectrometer mainly due to light dispersion on gratings and strongly depend on grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure than the ruled once. Stray light generated by holographic gratings are about an order of magnitude less intense than from ruled gratings of the same groove density. Multiple dispersion steps are another method of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In Such systems Raman-active modes with frequencies as low as 3-5 cm^{-1} can be efficiently detected.

In the advancement of technology recently more and more researchers use multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD) are used to detect the Raman scattered light. Sensitivity and performance of modern CCD detectors are rapidly improving. Many researchers use CCD and are fast becoming the detector of choice for Raman spectroscopy.

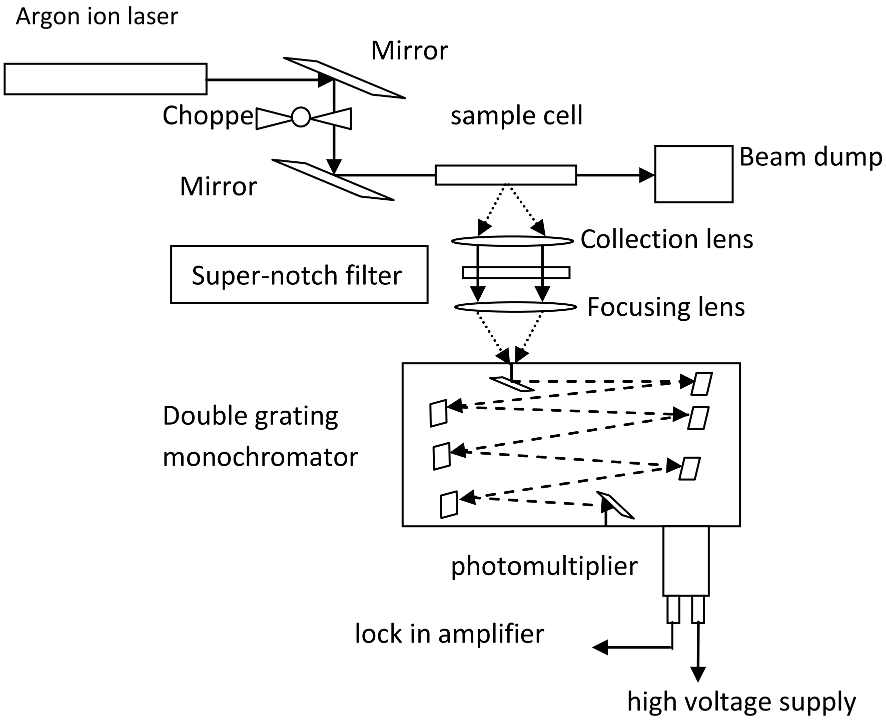


Fig: 12.10 Laser Raman Spectrometer

12.2.2.1 Excitation source.

A Laser source is used to excite Raman spectra because it gives a coherent beam of monochromatic light. This results in sufficient intensity to produce a useful amount of Raman scatters and allows for clean spectra, free of extraneous bands. Lasers used for spectroscopy must exhibit good wavelength stability and low background emission.

12.2.2.2 Probe

The Probe collects the scattered photons, filters out the Rayleigh scattering and any background signal from the fiber optic cables, and sends the Raman scatter to the spectrograph. Different probes also focus and deliver the incident laser beam.

12.2.2.3 The Detector

The commonly used detectors are photomultiplier tube, which provide accurate sensitivity, low noise and large dynamic range. For example single-channel detector requires point-by-point spectral data acquisition and consequently long scan times, multi-channel detectors are more popular, with the obvious advantages for time resolved measurements. Multi-channel detector may be a one dimensional diode-array with 512 or 1024 pixels (each 2.5 mm high by 25 µm wide). Multi-channel detectors offer certain merits over photomultiplier tubes for many applications, as they permit the obtaining of the large portions of a spectrum in few seconds.

12.2.2.4 The computer

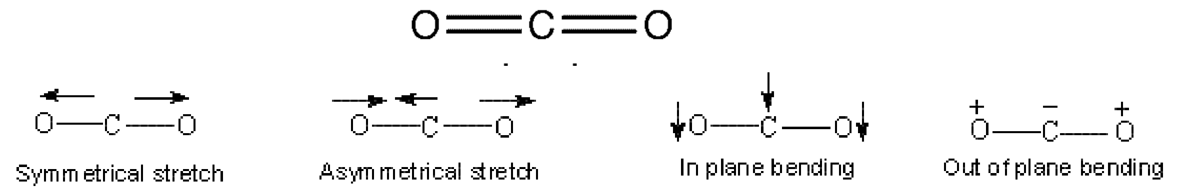
The Computers are incorporated the spectral analysis (addition, subtraction, self-convolution, etc). They are indispensable while using a multi-channel detector and offer an important merit with a single-channel system. Compatible software and graphics facilities for Raman spectroscopy are currently under intensive development. Various new techniques are under development, with a view to increases it’s utility. Recently substantial increase uses of Fourier transform techniques, to collect Raman spectroscopic date and these techniques increasing its applications in future.

12.2.2.5 Spectrograph

When Raman scattered photons enter the spectrograph, passing through a transmission grating to separate them by wavelength and enter to detector, which records the intensity of the Raman signal at each wavelength. These data are used to plot the complete Raman spectrum.

12.2.3 Infra-red and Raman Spectra are Complimentary:

The infra-red spectrum to occur, the molecule must show a change in the dipole moment. In the Raman spectra, there must be a change in the polarizability of the molecule. As these are two different observed results, lines may be formed in one of the spectra or in both. Symmetry stretching of the molecules which are usually not appeared in the infra-red appears prominently in Raman spectra. Also asymmetric vibrations show opposite behavior. Thus, vibrational modes which are missing in infra-red somewhat appear in Raman spectra. Consider the case of carbon dioxide molecule (fig. 12.10).



No change in dipole moment therefore IR inactive
There is change in polarisability therefore Raman active

There is change in dipole moment therefore IR active but Raman inactive

The deformation vibrations of CO_2 are degenerate and appear at the same region (666 cm^{-1}) in the IR spectrum of CO_2. There is no change in polarisability therefore these vibrations are Raman inactive.

Fig: 12.10 observed carbon dioxide molecule stages

In smaller molecules, the less symmetric vibrations often produce intense IR bands where as more symmetric vibrations produce prominent Raman bands.

12.2.4 Structure Determination from Raman and Infra-red Spectroscopy

In this topic we shall explain some examples of the combined use of Raman and infra-red spectroscopy to determine the shape of some simple molecules. The discussion must necessarily be on selected molecules. CO_2 N_2O, SO_2, NO_3^-, ClO_3^-, and ClF_3 have been chosen to explain the principles used; extension to other molecular types should be obvious.

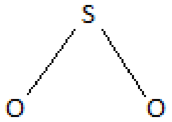
For the tri-atomic AB_2 molecules, the questions to be decided are -whether each molecule is linear or not and, if linear, whether it is symmetrical (B – A – B) or asymmetrical (B– B – A). In the case of carbon dioxide and nitrous oxide, both molecules give rise to some infra-red bands with PR contours, hence, therefore be linear. The mutual exclusion rule shows that CO_2 has a centre of symmetry (O – C – O) while N_2O has not (N – N-O), since only the latter has bands common to both its infra-red and Raman spectra. Thus the structures of these molecules are completely observed.

In the infra-red and Raman absorptions of SO_2 are collected (Table 12.2.) We observed that the molecule has no center of symmetry. Since all three fundamentals are both Raman and infra-red active. In the infra-red all three bands show very complicated rotation fine structure.

Table 12.2 Infra-red and Raman bands of sulphur dioxide

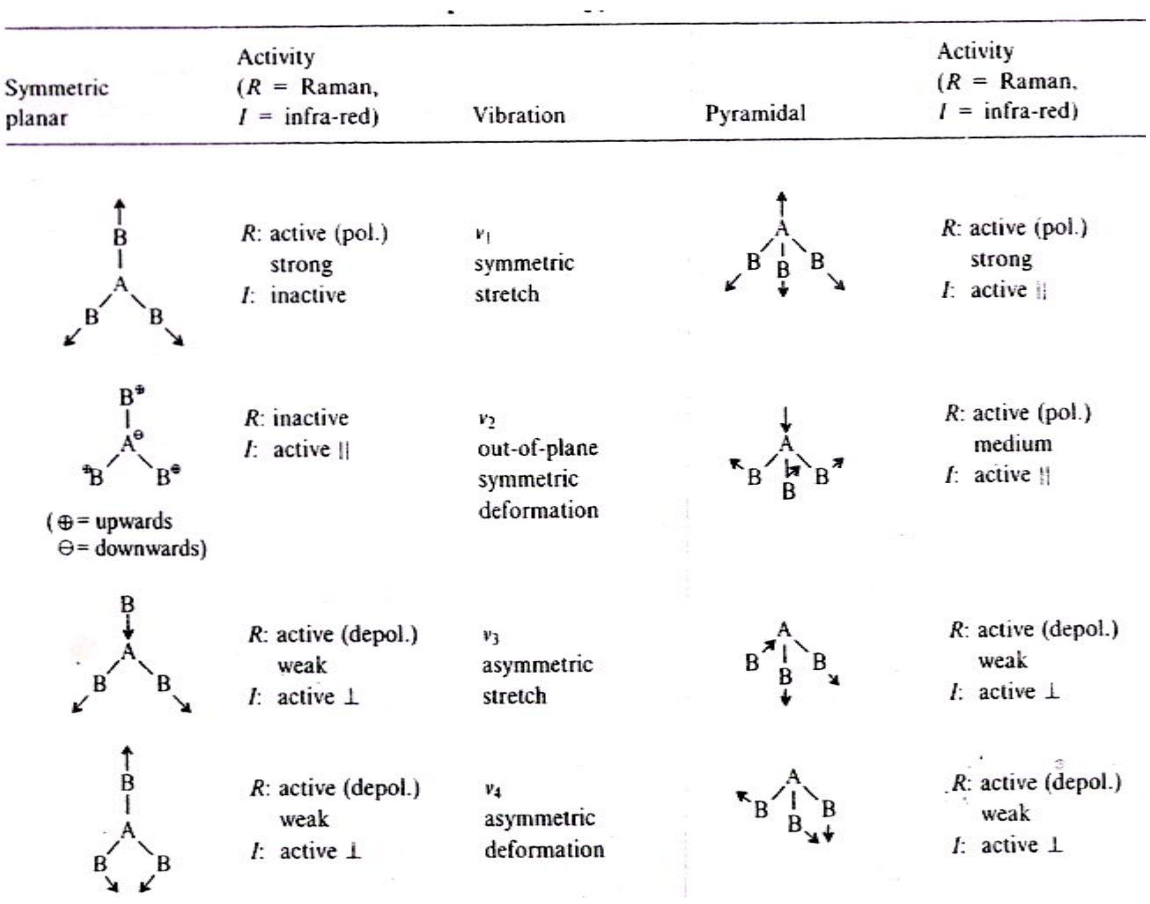
Wave number	Infra-red contours	Raman
519	∥ type band	Polarized
1151	∥type band	Polarized
1361	⊥ type band	Depolarized

It is seen that the molecule is non-linear –no band shows, the simple PR structure say sulphur dioxide the molecule has a bent shape.



The AB_3 type molecules require more discussion. In general we would expect 3N-6=6 fundamental vibrations for these four atomic molecules. However, if the molecular shape has some symmetry this number will be reduced by degeneracy. In particular, for the symmetric planar and symmetric pyramidal shapes, one stretching mode and one angle deformation mode of each double degenerate and so only four different fundamental frequencies should be seen. These are sketched (Table 12.3) where their different activities and band contours or polarizations are also collected. Both molecular shapes are in fact symmetric tops with the main (threefold) axis passing through atom A perpendicular to B_3 plane. It is with respect to this axis that the vibrations can be described as parallel (||) or perpendicular (⊥). The symmetric modes of vibrations are parallel (||) and Raman polarized while the asymmetric are perpendicular (⊥) and depolarized. All the vibrations of the pyramidal molecule change both the dipole moment and the polarizability; results all are both infra-red and Raman active. The symmetric stretching mode (**ν_1**) of the planar molecule, however, leaves the dipole moment unchanged (it remains zero throughout) and so is infra-red missing, while the symmetric bending mode does not change the polarizability and so ν_2 is Raman inactive for planar AB_3.

Table 12.3 Activities of vibrations of planar and pyramidal AB_3 molecules.



Symmetric planar	Activity (R = Raman, I = infra-red)	Vibration	Pyramidal	Activity (R = Raman, I = infra-red)
	R: active (pol.) strong I: inactive	ν_1 symmetric stretch		R: active (pol.) strong I: active ||
(⊕ = upwards ⊖ = downwards)	R: inactive I: active ||	ν_2 out-of-plane symmetric deformation		R: active (pol.) medium I: active ||
	R: active (depol.) weak I: active ⊥	ν_3 asymmetric stretch		R: active (depol.) weak I: active ⊥
	R: active (depol.) weak I: active ⊥	ν_4 asymmetric deformation		R: active (depol.) weak I: active ⊥

The complete pattern of the spectra, then, should be as follows:

Planner AB_3:	1 Vibration Raman active only (ν_1)
	a) infra-red active only (ν_2)
	b) Vibrations both Raman and infra-red active (ν_3, ν_4)
Pyramidal AB_3:	All four vibrations both Raman and infra –red active
symmetric AB_3:	Non Possibly more four different fundamental frequencies.

With this pattern in mind we can consider the spectra of NO_3^- ions. The spectroscopic data are summarized in Table 12.4. Without considering any assignment of the various absorption bands to particular vibrations, we can see immediately that the nitrate ion fits the expected pattern for a planar system, while the chlorate ion is pyramidal. Complete assignments follow by comparison with table 12.3. Thus for the nitrate ion, the band which is Raman active only is obviously ν_1 while that which appears only in the infra-red is ν_2. If we make the very reasonable assumption that stretching frequencies are larger than bending, then the assignment of ν_3 and ν_4 is self-evident

Table 12.4 IR and Raman spectra of NO_3^-

Nitrate ion (NO_3^-)		
Raman (cm^{-1})	Infra-red (cm^{-1})	Assignment
690(depol.)	680 $\perp$	υ_4
-	830 $\parallel$	υ_2
1049 (pol.)	-	υ_3
1355 (depol.)	1350 $\perp$	υ_1

12.2.5 Structure studies by Raman Spectroscopy

Raman technique is of great tool for molecular vibrations that are inactive in the infrared due to molecular symmetry. For centro-symmetric molecules like H_2, CO_2, C_2H_2 etc, the vibrations which are IR inactive are Raman active in fact, Raman spectroscopy supplements infra-red spectroscopy. It is the major tool for solving many research problems concerning the structure studies of compounds. Following are the few important applications of Raman spectra in structure determination.

(i) **Structure of centro-symmetric molecules.** Carbon dioxide is a centro-symmetric molecule with linear structure (O=C=O). One expects two fundamental modes in the IR and one in the Raman. It is proved experimentally that *(a)* 1337 cm^{-1}(Raman active) and *(b)* 667 cm^{-1}*(c)* 2349 cm^{-1} are infrared active. When the vibration in the structural centrosymmetric is infrared active and Raman inactive and vice versa.

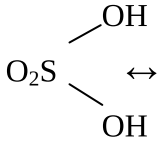
(ii) **Structure of N_2O:** N_2O is similar to CO_2, one should observe similar behavior as seen in carbon dioxide. If it is nonsymmetrical as N-N-O, then the vibration should be active both in IR as well as Raman. Actually, additional fundamental vibration is observed both in IR and Raman technique. This shows that the structure of N_2O is N-N-O.

(iii) **Structure of water:** For water to have bent structure, the fundamental vibrations ν_1,ν_2 and ν_3 should be active both in Raman and in IR. Since it is true experimentally, water has a bent structure.

(vi) **Hydrogen cyanide:** Raman study of hydrogen cyanide shows two lines at 2062 cm^{-1}. It can be attributed to two Isomers in dynamic equilibrium.

(v) **Sulphuric acid:** Raman frequency of 25% sulphuric acid matches with that shown by $KHSO_4$, but on dilution, the Raman frequency corresponds to that of K_2SO_4. It is observed the existence of HSO_4^- ion.

Thus,



$$O_2S(OH)_2 \leftrightarrow H^+ + HSO^-_4 = 2H^+ + SO^{2-}_4$$

(vi) **Inorganic Compounds:** In addition, Raman spectroscopy techniques help in revealing the molecular structures of many organic compounds. Raman spectrum provides information like,

(a) The structure of simple organic compounds.
(b) Shows the presence or absence of specific linkages in a molecule.
(c) Studying of Isomers.
(d) Presence of impurities in the dyes.
(e) Classification of compounds.

It has been observed that Raman lines usually lie in the region 500-350 cm^{-1}

(vii) **Geometrical isomers.** It is known that cis and trans Isomers of 1, 2-dischloroethylene exist in equilibrium proportions. Out of these, trans configuration has centre of symmetry. Thus, the coincident frequencies observed in IR and Raman spectra of the sample can be assigned to cis-configuration. In this way, the analysis of cis and trans Isomers can be carried out.

Note. Raman spectroscopy technique also uses visible and ultra-violet radiations rather than IR radiations; the walls of the sample cell and the other units of the optical system can be made of glass or quartz rather than of special material which are transparent to IR radiations. Also experiment can be conducted conveniently with aqueous media as water is more transparent in the visible and UV regions than in IR region. Raman technique can be utilized for the study of biological systems such as proteins in aqueous solutions.

12.2.6 Advantages of Raman Spectroscopy over Infrared Spectroscopy

Raman technique offers distinct advantages over the more direct infrared absorption measurement.

(i) First Raman spectroscopy can be used to detect and analyze molecules with infrared inactive spectra, such as homonuclear diatomic molecules. For complex molecules whose low symmetry does not forbid both Raman and infrared activity, certain vibrational modes are inherently stronger in the Raman Effect and weaker in, or absent from, the infrared spectrum. Raman activity tends to be a function of the covalent character of bonds. Hence Raman spectra give that information regarding the backbone structure of the molecule, whereas the strong infrared features are indicative of polar segments.

(ii) Raman spectra can be used to study materials in aqueous solutions, a medium that transmits infrared very poorly.

(iii) A third advantage is the ability to study the entire vibrational spectrum with one instrument, unlike infrared spectroscopy in which the for-infrared is usually scanned separately from the mid-infrared.

(iv) Sample preparation for Raman is generally considerably simpler than for the infrared.

(v) Overtone and combination bands are usually weak in the Raman spectrum so that Raman spectrum appears simpler than infrared spectrum, where this band tends to complicate the spectrum.

(vi) The linear relationship between intensity vs concentration in the Raman technique makes study of major components of a mixture easier than in infrared, intensity is logarithmically related to concentration of the sample.

Biological Applications

Spectrum peak overlap is low concentration in Raman spectroscopy mixtures can easily be analysed and environmental Pollution studies. Radiation can be scattered form the pollutant molecules and led to the spectrometer. This technique helps to analysis of pollutants at a low concentration and also it give pollutants as a function of distance. A remote Raman spectrometer permits three dimensional mapping of air pollutants in great level. The Raman has important advantage is continuous monitoring of the quality of air.

12.3 Lets Sum up:

The instrumentation unit gives the idea about Raman spectroscopy with modern laser Raman spectrometer. Detailed study of instruments used in spectrometer, components explained in detailed. Single and double beam spectrometers presented for studying the structural details using IR and Raman with examples explained which can be use full for many applications. Advantages of Raman over IR detailed explained with some examples mentioned in this section. This unit very important to get more information about laser Raman and etc.

12.4 Key Words:

Single and double beam instrument, Laser Raman spectrometer, structural studies and advantages of Raman spectroscopy.

12.5 Questions for self study:

1. Explain the Modern Laser Raman spectrometer.
2. Mentions the advantages of CARS over normal Raman spectroscopy.
3. What are the components in Raman spectrometer?
4. Write shorts notes on Raman spectrometer
    a. Sample holder
    b. Monochromators
5. What are the applications of Raman spectroscopy?
6. Which crystals are used in infrared instruments?
7. Why a laser used to excite Raman Effect?
8. Outline the advantages of using laser as Raman source.

12.6 Reference books:

1. Fundamentals of Molecular Spectroscopy, Third Edition by C N Banwell.
2. Instrumental Methods of Chemical Analysis, by Gurdeep R. Chatwal and Sham K. Anand.
3. Molecular Structure and Spectroscopy, by G.Aruldhas.
4. Modern Spectroscopy, fourth edition by J. Michael, Hollas

Unit: 13 Principles of spectral Analysis

Structure:

13.0 Objectives.

After going through the unit you would be in position

- The Practice of Gas Chromatography
- Applications of Digital Electronic Systems to Gas Chromatography
- Gas Liquid Chromatography (GLC)
- Paper chromatography
- Gel chromatography
- Applications of paper chromatography and gel chromatography.

13.1 Introduction

The basic aim of various methods of chromatography is separating two or more substances. The purity of what is thought to be a single sample is only demonstrated by observing that possible impurities are absent. For this reason, the reference impurity standards must run in a separate position from that of pure compound. Chromatographic method of separations are made by the distribution of components in a mixture (compound) between a fixed and a moving phase, referred to as the stationary and the mobile phase respectively. Separation between two or many substances begins to occur when one is held more strongly by the stationary phase than the other, which results to move on faster in the mobile phase.

The word chromatography takes from the Greek term Khromatos-colour, and graphy–written was the first used in 1906, by Michael Tswett, a Russian botanist, to expalin the separations of plant pigments into different coloured zones. Tswett used a glass column filled with calcium carbonate adsorbent, down which he passed a plant extract dissolved in petroleum ether, to get green and yellow bands of pigment. In 1930s adsorption chromatography attracted popularity, when it was used, for example, as a preparative technique of carotene into its components. Although most separations now concern colorless compounds, the original term chromatography has been retained.

The second broad method of chromatography gives partition between two liquids rather than adsorption by a solid from a liquid was explained in 1941 by Martin and Synge, award in 1952 of a Nobel Prize for his contribution. Their work was done on columns of silica gel with water as the stationery phase. In 1944, Consden, Gordon, and Martin demonstrated a new method of applying this idea of partition chromatography, with filter paper replaced for columns of adsorbent impregnated with a liquid.

The technique was termed paper partition chromatography. It achieved many applications because column chromatography is a helpful for preparative method; paper chromatography is far more convenient for the analysis of mixtures. It allows to the simultaneous comparison under similar material separation conditions of a series of compounds with useful standard references standards. Column chromatography is useful on a scale from grams to milligrams, whereas paper chromatography has the additional advantages of working in the milligram to microgram range. The beginning work followed column procedure by having the advancement solvent flow down the filter paper where as the paper chromatography an ascending method is an alternative possibility.

13.2 The Practice of Gas Chromatography

A diagram of a typical gas chromatograph is shown in Figure 13.1, A suitable source of moving gas phase, or carrier, such as a

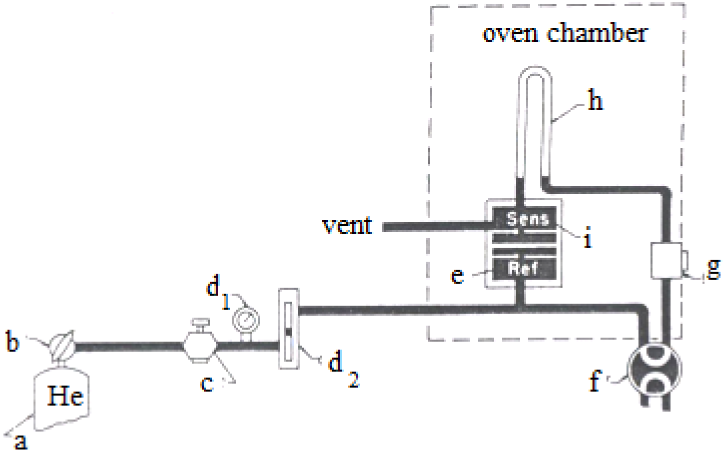


Fig 13.1 Flow schematic of a typical gas chromatography:

(a- helium filled tank; b- tank regular; c, pressure measure regulator in the gas chromatograph; d_1- pressure gauge, d_2 - gas flow meter; e- reference cell of the thermal conductivity detector; f- gas and g liquid sample injection block; h-column; i-sensing side of the thermal conductivity detector).

Pressure tank of helium (a) is connected via regulators and lines to the instrument, into which the constant gas flows. There the pressure and flow of the gas are regulated observed and measured (d_1, d_2) respectively.

Then the gas flow passes the entrance to the chamber of a thermal conductive cell (e). Within this chamber is a small filament or wire-supported bead which is heated electrically to a temperature above that of the oven ambient. The filament having thermal coefficient resistance of materials chosen i.e., small temperature changes will cause their electrical resistance to change markedly. Then the filament is constantly being electrically heated by an outside source, this excess heat is continuously being liberated though conductivity to the surrounding carrier gas. The carrier gases usually applied have very high thermal conductive; helium, hydrogen, and nitrogen are commonly used in this method. After passing through the entrance of conductivity cell, the carrier gas flows through a gas sampling area (f) at which point samples which are vapors at normal operating are metered into the method by means of suitable valves. The sample gas (vapour) volume normally required is of the order of 0.1-5 ml.

The gas flow then enters into the oven area which is heated to a temperature with the requirement that all sample components must be kept in the vapor state during the process. In the oven, the carrier gas passes through a liquid sample injection area (g) where, in the event that the sample can be analysed in a liquid under normal conditions, a small volume i.e., 0.001-0.010 *ml* of material is injected into the stream by the method of a hypodermic syringe which can be passes through a self-sealing rubber septum. The liquid sample injection area is normally well equipped with a separate heating component which result rises in the temperature somewhat above that of the general over ambient. This leads to the rapid vaporization of the liquid sample, a prime requirement for efficient processes.

The sample mixed with the carrier gas, is now sent to the column entrance (h), column is generally the tube, i.e., 1-4 meters in length and 2-4 mm in diameter, of straight, looped, (or coiled metal or glass tubing) which has been placed with a granular material upon the area of which a thin coating of a nonvolatile liquid has been deposited. In this system, the stationary phase is a solid, and an analysis involving gas chromatography with a column may be termed gas-solid adsorption chromatography or, gas solid chromatography.

In many cases, the granular packing method consists of inert solids such as diatomaceous earth (Celite or kieselguhr) with a liquid coating. In these method, the solid or support serves no active purposes in the chromatographic process technique but merely gives an inert base of high surface area and porosity for the effective distribution of the liquid layer. The liquid material is formed the stationary phase, and determined by gas chromatography involving such a column may be named as gas –liquid partition chromatography or gas-liquid chromatography.

13.2.1 Applications of Digital Electronic Systems to Gas Chromatography

The rapid rate of acceptance of gas chromatography as a quantitative analyzing tool quickly led to a need for improved data processing method. The standard presentation technique for analysis results has utilized by using a strip chart recorder, with interpretation accomplished by manual methods. The technician measure which peaks were significant and computed the height or the area of the peaks by various simple technique. Several of semiautomatic instruments also were applied, which include the analog electronic integrators and mechanical disc integrators. These techniques were time-consuming in the application and often unsatisfactory in terms of accuracy and repeatability of results obtained. The heavy work load, with the several other factors, indicated a clear need for a fast, automatic, instrumental technique of data reduction. Large use of capillary column chromatography, with its consequent sharp, closely spaced peaks, accentuated the requirements. Accurate measurements could not be made on the very sharp peaks either by manual techniques or by the existing semiautomatic instrument. Another influence was the trend away from measurement of peak height toward measurement of peak area. The requirement was for automatic equipment capable of analyzing the peaks automatically, computing areas, and reporting the results in simple easy-to-interpret form.

13.2.2 Gas Liquid Chromatography (GLC)

In GLC the liquid stationery phase is having as a thin coating on a finely divided, inert solid support which is in turn, packed with small diameter tube 1/16 - 1/4 in of moderate 4-15ft. The moving phase and inert helium gas is allowed to flow through the column, generally placed in a oven so that it can be heated to facilitate the separation of high-boiling materials. The mixture of sample is injected, with the help of microsyringe, through a rubber septum into the column, and then the components of the mixture will flow through the column at varying rates and are observed as they emerge by a detector which transmits a signal to the recorder.

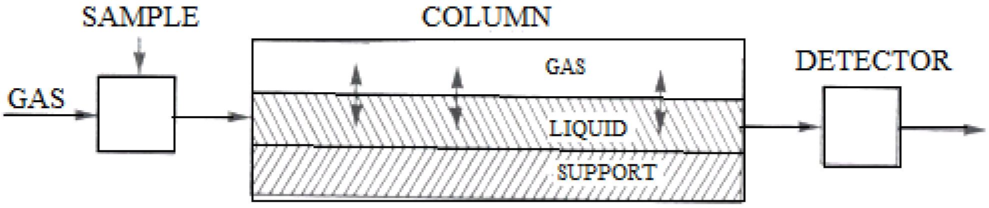


Fig:13.2 A schematic GLC apparatus.

The sample is introduce into the gas stream and allowed to flow into the column where it can be separation between the gas phase and the liquid-coated support. The sample is separated and emerges from the column into the sensors. Figure. 13.2 Schematically describes a GLC apparatus which contains (i) a high pressure carrier gas supply with a pressure regulator, (ii) a sample inlet system, (iii) a packed column of coated support, (iv) a sensor, and (v) a recording device for the sensor describes what occurs when a two-component liquid mixture is injected into the column for the study.

The observing of a specific sample on a particular column at a certain temperature and gas flow will be quite characteristic; thus the appearance of the compound at the sensor will occur after a consistent length of time interval, the retention time. This retention time permits the qualitative analysis of a compound in a sample mixture of others and, depending on the recording (measuring) device, its quantitative determination. Identification can also be carried out on a component which has been kept as it leaves the column.

13.2.3 Qualitative Applications of gas liquid chromatography

i. Qualitative applications of chromatography describe the presence or absence of a specific compound in a component. This is done by comparing the pure compound with the mixture on a single chromatogram (TLC)

ii. Qualitative chromatography gives data on the complexity of a mixture. The mixture Sample is chromatographed under various conditions and the number of spots or peaks (GLC) gives the minimum number of components. If some of the spots or peaks observed contain more than one substance, the mixture sample may be much more complex than it observed to be. Due to this, the purity of a compound can be studied. In this condition, the compound is chromatographed under several steps, conditions and concentration of the sample.

iii. Qualitative chromatography helps to establish a component or mixture or “fingerprint” pattern for a given tissue or for given crude chemical or drug or element. Samples to be analysed can then be verified with this pattern to learn something about abnormalities of tissues or about impurities of chemicals or other impurities in pure one.

13.3 Paper chromatography

The paper chromatography method possessed for separation of compounds from one another, although now combined with thin layer chromatography, were observed to be small sample size, high resolution case of detections, and simplicity of technique. Presently it is true that the thin layer method is generally preferred for non-polar substance, paper chromatography remains the more accurate method for polar compounds such as water soluble antibiotics.

At first the separation of components was brought thought to place by partition between solvent and water held in the paper, then the known partition paper chromatography was given to the phenomenon analysis observed that simple portion could not always accurately explain the effects observed.

The method observed some part it is necessary examining the paper structure in adequate explanation detail. Cellulose has 2000 or more anhydroglucose units linked in chains through oxygen atoms, and polar solvents show great affinity for the hydroxyl groups in every glucose unit either through weak secondary forces (hydrogen bonds), and this take place between separate chains forming a crystalline structure at these points; thus the paper is considered to consist of crystalline and amorphous regions which various in their capacity to absorb water to get further outer layer of the crystallite.

13.3.1 Applications of paper chromatography.

The quantitative method applied for measuring the coloured impurities in hydroxocobalmin, it is light sensitive. It is not recommend letting the coloured sample dry on the paper at stage step wise, as this makes them much harder to elute and increases breakdown. The blank paper absorption should contribute (less than 1%) at a wavelength of 361 mµ.

Due these processes recoveries of all components from the paper absorption observed an average loss of 2%. This loss to be observed with paper chromatography method, and is caused through irreversible absorption on the paper. Thus, it is acceptable to measure impurities, which have nearly the same proportionate but neglible compared to net loss, rather than the main component. However, the losses of varies from compounds to compound might be very different and strictly quantitative results can be observed only by using control standards that have been treated in exactly the same way as the compound.

13.3.2 By method of internal standardization

If A standard E is selected, that result a peak which does not matches with the other substance is added to the mixture. A preliminary characterization is carried out, by evaluating the weights w_1', w_2' and w_3' in relation to the standard, w_E , assuming that $K_1 = K_2 = K_3 + K_E = 1$.

$$w_i = w_E \frac{A_i}{A_E} \qquad (1)$$

Using each of the selected substance of the mixture, another mixture is prepared, called the standard, containing, therefore, w_1', w_2', w_3' and w_E g,.

Analysis of the chromatogram corresponding to this standard mixture sample enables the following calculations to be made always taking K_E arbitrarily as 1.

$$K_1 = w_1 A_E/w_E A_1,\ K_2 = w_2/ w_E A_2,\ K_3 = w_3 A_E / w_E A_3$$

These proportionality coefficients which are only the coefficients related to the response coefficients of the standard K_E can be applied to the first chromatogram. This implies more exact values.

$$w_i = w_E K_{i(E)} \frac{A_i}{A_E} \qquad (2)$$

where $Ki(_E)$ means K_i relative to K_E.

13.3.3 By method of internal normalization

Without taking the supplementary standard substance in this method, a first analysis is carried out as above, measuring the percentage of each solute by means of the equation.

$$x_i' = \frac{A_i}{\Sigma A_i} X\ 100 \qquad (3)$$

It can be assumed that equality of all the K_i-values. Then a standard mixture is taken with the percentage x_i' calculated from the respective pure substances.

The chromatogram found with this mixture then enables each of the K_i coefficients to be evaluated and they are then used to obtain the first chromatogram. But a relative technique is often preferred in which the value 1 is given to the coefficient of one of the peaks, which has been carefully selected from the observation.

The relative coefficient for any of the other peaks is then calculated on the standard chromatogram:

$$K_{i(T)} = \frac{x_i'}{A_i A_T}\frac{1}{100} \tag{4}$$

Hence A_T is the area of the peak selected as the basis of evaluation with the use of $K_T = 1$.
Returig to the initial chromatogram gives the relation:

$$x_i = \frac{K_{i(T)}A_i}{K_{i(T)}A_i + A_T}\ 100 \tag{5}$$

And for the peak that has been used as a base:

$$x_i = \frac{A_T}{K_{i(T)}A_i + A_T}\ 100 \tag{6}$$

13.3.4 An important observation on the calculation of the coefficient K_i

Among of the two procedures explained above may be used to find the coefficient of proportionality with the help standard mixtures which are similar in composition to the mixtures being analyzed. It is necessary, however, for accurate that this condition be fulfilled. Serious errors may occur if a coefficient with a standard containing 20% of a solute is used for the analysis of a mixture having only 1-2 percentage of that solute.

13.3.5 Trace Analysis technique

The quantitative analysis by using of gas chromatography method having a number of problems but these are most dominates in trace analysis. The analysis purpose a “trace” is a substance which is observed in a mixture at a concentration < 1.0 % which means that the problem is one of finding an impurity in a solvent (or a mixture) of solvents used as sample. Some of the major factors in such a case will be evaluated.

13.3.6 Effected of the position of the respective peaks

The trace analysis is most accurate in this when the peak of the impurity is higher steam from the principal peak and when it has a small retention volume; the obtained peak is then sharp and well defined from the major peak. However, this give rise to difficulties because it is often necessary to inject rather large quantities which results in some tailing of the principal peak making the evaluating the peak area a more difficult method. This is, due to overloading of the column, will be more troublesome if the peak of the impurity is downstream of the principal peak in the observation, because it may interfere with the trace (or even mask). Now it is known that the separation factor must be higher than a certain number if the quantitative analysis is to be valid and the distance separating the two peaks should be increased apart, but the second peak (mentioned impurity) will then be agency and the precision of measurement further diminished is the result.

This type of problems increasing the sensitivity of the detector. One must be emphasized that the accuracy of the analysis does not increase in the same ratio of the observation. If conditions are favorable for a bigger response from the analysis of trace, the getting of the principal peak also increases unless the weight of the compound is deceased, when the impurity peak of the analysed will have the same dimensions as it would due to less sensitive detector. Nevertheless, the experimental result is effective on the whole, because the lessening of making enables the trace to be analysed more precisely. An increased accuracy means that a better separation can be results without the risk of complete disappearance of the secondary peak.

Some times it is important to realize that the emergence of two different peaks can be reversed, even in the case of solutes that have apparently very close behavior. This is obtaining by a small change of stationary phase. In the analysed peak is such that it is strongly favorable result that this should be tried for all new analyses even when the chances of success do not appear to be very accuracy.

13.3.7 Analysis of methane

This analysis is a permanent gas and is a special case which relies on adsorption chromatography technique, on molecular sieve, i.e,, if a question of separating it from air (or carbon monoxide). Gas from mains is analysed in this way. The modern technique of ultra-rapid analyses of permanent gases may be usefully applied for the analysis of methane.

13.3.8 Analysis of petrol

It is a present in it complex problem, No one column is designed found to separate all the hydrocarbons present in it. Many authors describe preliminary fractionations either by distillations of cuts containing compounds having the same number of carbon atoms (or by liquid – phase) chromatography according to the standard method described F.I.A. which operators on the principle of separation of hydrocarbons in the presence of fluorescent indicators in the new methods. Adsorptions by molecular sieves and insertion in crystals such as urea have also been used in the analysis system.

13.4 Gel chromatography or Gel permeation chromatography

Gel permeation chromatography (GPC), or exclusion chromatography, extensively uses porous material as the stationary phase and a liquid as a mobile phase. The diameters of the pores of the porous material range from 50-3000 Å, which are of the size as that of many molecules. The liquid penetrates in to the pores according to pore size. The penetration of small molecules are more faster than larger molecules, which frequently are excluded from the smaller pores present, resulting in a difference to the rate at which the molecules pass down the column, the smaller molecules travelling faster than the larger molecules.

Selectivity based of steric factors between the adsorbent and adsorbate is in principle used in achieving specific separation through gel chromatography. This technique is known as gel filtration or molecular sieve filtration or exclusion chromatography.

Gel chromatography is a simple and most reliable technique used for separating molecules according to its size, which makes it generally more applicable approach to the purification of all classes of biological substances, including giant macromolecules which couldn’t readily fractionated by other technique. Good separation and high activity yield are easily obtained.

13.4.1 Principle

The principle of exclusion chromatography is: A column of gel particles or porous glass granules is in equilibrium with a suitable solvent for the molecules to be separated. Large molecules which are completely excluded from the pores will pass through the interstitial spaces, while smaller molecules will be distributed between the solvent inside and outside the molecular sieve and will then pass though the column at a lower rate. Three stages in such a column are represented diagrammatically fig 13.3

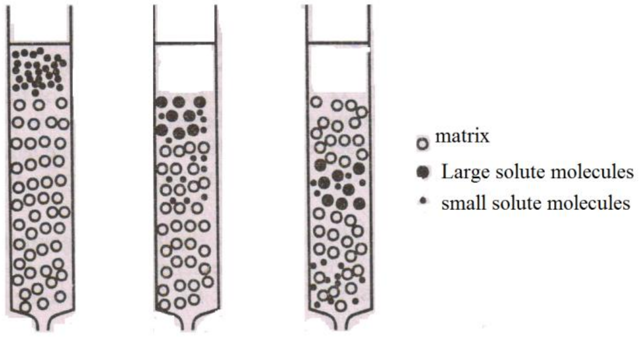


Fig 13.3: Diagrammatic representation of separation by Exclusion chromatography

13.4.2 Materials

Gel which is most commonly used includes the following cross-linked, 1. agarose, 2.polyacrylamide, 3.dextrants, 4. polyacrylmorphine and 5. polystyrenes.

The dextran gels are the products that are obtained by cross-linking between polysaccharide dextran and epichorhyrin. By this way the water soluble dextran is made water insoluble, retaining its hydrophilic character and swells rapidly in aqueous media, forming gel particles suitable for gel filtration. By varying the degree of cross-linking several types of sephadex could be obtained accordingly.

Agarose gel, which are produced from agar, are linear polysaccharides of altering residues of D-galactose and 3,6-anhydro L-galactose units. Its gelling properties are due to hydrogen bonding of both inter-and intra-molecular type. Due to its hydrophilic nature and the nearly complete absence of charged groups, agarose gel, like dextran gel, cause very little denaturation and adsorption of sensitive biochemical substances.

Polyacrylamide gels are prepared by the polymerization of polyacrylamide and methylene bisacrylamide. By changing any of the relative proportions of the two monomers, a wide range of gels with differing porosities can be obtained. There characteristics are quite similar to that of dextran and agarose gels.

13.4.3 Gel preparation, column packing and Detectors

The methods given below are more generally used for the preparation of gel:

I. The dry powder of the gel is allowed to swell in the solvent which is to be used as eluant. In practice a weighed measured of the dry of the gel is mixed in solvents and allowed to swell. The mixture is kept until the equilibrium is established.
II. In the second method gel slurry is warmed of about 100^0 C in a water bath. As a result the gel swells in few days. The slurry is cooled and packed in the column.

There are basically two types of column packing; porous glasses (or silica) and porous cross-linked organic gel such as dextran, methacrylate-based gel, polyvinyl alcohol-based gel and hydroxethyl cellulose gels. The detectors used are based on UV fluorescence, UV absorption, or changes in refractive index.

13.4.4 Applications

The main applications of gel chromatography are the separation and characterization of molecules or different molecular weights.

1. Purification: Purification of biological macromolecules. Viruses, proteins, enzymes, hormones, antibodies, nucleic acids polysaccharides have all been separated and purified by the use of appropriate gels or glass granules.
2. Molecular weight determination: The effluent volumes of globular proteins are largely determined by their molecular weight.
3. Solution concentration: Solution of high molecular weight substances can be concentrated by the addition of dry gel sephadex G-25(coarse)
4. Desalting: By use of a column of sephdex G-25, solution of high molecular weight compounds may be desalted
5. Protein-Building Studies: Excusion chromatography is one of a number of methods commonly used to study the reversible binding of a ligand to a macromolecule such as protein including receptor proteins.

13.5 Let us sum up

In this lesson, we pointed out:

- The Practice of Gas Chromatography
- Applications of Digital Electronic Systems to Gas Chromatography

- Gas Liquid Chromatography (GLC)
- Paper chromatography
- Applications of paper chromatography.
- Gel chromatography.

13.6 Key Words

Chromatography, Gas Chromatography, Gas-Liquid Chromatography, Paper Chromatography, Gel Chromatography

13.7 Review Questions

1. What is the literal meaning of chromatography in Greek words?
2. What is the principle of gas chromatography?
3. Write short notes on paper chromatography.
4. What are the main applications of gel chromatography?
5. Discuss the Principle of gel permeation chromatography.

13.8 Reference Books

1. Introduction to Chromatography, by James M. Bobbitt, Arthur E. Schwarting and Roy J. Gritter.
2. Chromatography, Edited by D.R. Browning.
3. Chromatography, by L. Savidan.
4. Practical manual of Gas chromatography, by J. Buzon, N.Guichare, J.Lebbe, A. Prevot, J. Serpinet, J. Tranchant.
5. The practice of gas Chromatography, Edited by Leslie S. Ettre and Albert Zlatkis.
6. Instrumental methods of chemical Analysis, by Gurdeep R. Chatwal and Sham K. Anand.

Unit: 14 Techniques and applications of Spectroscopy

Structure:

14.0 Objectives.

After going through the unit you would be in position

- to Understand the basic techniques of spectroscopy
- Know about the importance of spectroscopy
- To learn about elements of practical spectroscopy
- Getting the basic concepts of spectroscopic instruments like absorption and emission spectroscopic techniques
- know about physical basis and steps in AES
- To know the important applications of various techniques.

14.1 Introduction to Spectroscopy:

The Spectroscopic techniques form the wide range and most important techniques used in Chemistry and Physics. These techniques provide a large range of qualitative and quantitative data. Most of the spectroscopic techniques are more or less depending on the emission or absorption of electromagnetic radiation of certain energy changes within an atomic or molecular system. The changes in energy are associated with a complex series of discrete or quantized energy levels in which atoms or molecules are assumed to exist. The use of spectroscopic techniques in analytical chemistry is in the determination atomic and molecular structure, including functional groups' photochemical process and stereochemical arrangements. Various spectroscopic techniques are used currently because they require a very small amount of material and short interval of time for analysis.

Modern spectroscopy and its advantages form a significant part of modern chemistry, physics and technology. The word 'spectroscopy' means 'the watching of images', but the modern subject covers the interaction of electromagnetic radiations with matter. The very important effect of such interaction is that energy is absorbed or emitted by the matter in discrete value called quanta. The absorption or emission processes of the electromagnetic spectrum range from the gamma region (nuclear resonance absorption or the Mossbauer Effect) to the radio region (nuclear magnetic resonance). When the measurement radiation frequency is done experimentally, its gives a value for the change of energy involved and one can draw the conclusion of studied about the set of possible discrete energy levels of the matter. The experimental measurements of radiation frequency (emitted or absorbed) and the energy levels derived from these comprise the practice of spectroscopic techniques.

In many spectroscopy branches the system interacts with the electric field, but, in case of magnetic resonance spectroscopy it interacts with the magnetic field.

Spectroscopy is powerful technique available for the study of atomic and molecular structure and is used in the study of a wide range of samples to get the data. The study of spectroscopy technique can be carried out as follows:

(a) **Atomic Spectroscopy:** The interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state called the ground state.

Monoatomic substance normally exists in the gaseous state and is able to absorb electromagnetic radiation, leads to transitions of electrons from one electron energy level to another. The electronic absorption of electromagnetic energy can occur only if the photon has an energy which is equal to the energy difference between two quantized energy levels, i.e., $\Delta E = h\nu$, where 'ΔE' is the energy different between two levels and 'ν' is the frequency of photon which can results in the electronic excitation. Applications of atomic spectroscopy in the field of physics and chemistry are few. However its demand has increased by the development of lasers.

(b) **Molecular Spectroscopy:** The interaction of electromagnetic radiation with molecules, these results in transitions between rotational and vibrational energy levels in addition to electronic transitions. Which gives, the spectra of molecules are much more completed than those of atoms.

Molecular information may be obtained about molecular vibrations and rotations that reveal a great deal about molecular structure.

The detailed information regarding molecular structure (molecular symmetry, bond distances and bond angles) and physicochemicals properties like electronic distribution, bond strength and intra-and inter-molecular processes are obtained from the atomic and molecular spectroscopy.

The spectroscopic investigation find were first carried out by Sir Issac Newton in the seventeenth century; the quantitative analysis was possible only after the intervesion of quantum mechanics. Initially, it was atomic spectra that provided the empirical evidence for the various quantum mechanical ideas.

Range of the spectrum

We have observed the regions into which electromagnetic radiations have been divided in and boundaries are not precise. The molecular process associated with each region is quite different and are noted along with the corresponding regions the brief explanation of the following few lines:

(i) Radio frequency range $3x10^6$ to $3x10^{10}$ c/s; 10 cm to 1 cm wavelength, Nuclear magnetic resonance and electron spin resonance spectroscopy, reversal of spin of a nucleus or electron is the cause of energy change.

(ii) Microwave region: $3x10^{10}$ to $3x10^{12}$ c/s; 1 cm to 100 µm wavelength (Rotational spectroscopy).

(iii) Infrared region: $3x10^{12}$ to $3x10^{14}$ c/s; 100 µ to 1 µ wavelength (Vibrational spectroscopy).

(iv) Visible and ultra-violet region: $3x10^{14}$ to $3x10^{16}$ c/s; 1 µ to 100 Å wavelengths (Electron spectroscopy).

(v) X-ray region: $3x10^{16}$ c/s; and above; 100 Å wavelength.

(c) **Near Infra-red Spectra.** In the absence of any of the electronic transition (no change in electronic state) vibrational transition can occur, i.e. there is a possibility of a transition from one vibrational energy level to another with the same electronic (ground) state of the molecules involving in energy changes of about 0.1 eV ($1.6X10^{-20}$erg/mole) ; frequency of radiation will be

$$\nu = \frac{1.6X10^{-20}}{3X10^{8}6.6X10^{-34}} = 8X10^{4}\ \mathrm{m}^{-1} \qquad \text{or} \qquad \lambda = 125000\text{Å} = 12.5\mu$$

This observation shows these radiations accompanying vibrational changes within the electronic ground state, should appear in near infra-red portion of the spectrum.

The vibrational transition within particular electronic state would be associated with different possible rotational changes which results to the presence of a number of closely spaced spectral lines (vibration rotation bands). These are observed in absorption in the wavelength region of about 1 to 20µ. For a diatomic molecule, the mode of vibration is only one hence only one vibration-rotation band for each vibrational transition.

(d) Far infra-red Spectra. In the far infra-red region, transitions occur that are purely rotational in character, unaccompanied by changes in electronic and vibrational energies. Such a transition involves an energy change of 0.005 eV and thus frequency of radiation is

$$\nu = \frac{0.005x1.6x10^{-19}}{6.6x10^{-34}x3x10^{8}} \qquad \nu = \frac{8x10^{-22}}{3x6.6x10^{-28}} = \frac{8x10^{4}}{19.8}\ \mathrm{m}^{-1}$$

or $\lambda = \frac{19.8}{800}$ cm. =247x10^{-2} cm= 2470000 Å = 247 μ.

It is observed that these radiations will lie in far infra-red region. The bands in the far infra-red regions are therefore called rotational spectra.

14.2 Importance of Spectroscopy

The electromagnetic spectrum is one of the most widely used techniques of analysis. It is used in all branches of chemistry and environmental laboratories because many substances can be selectively converted to a colored derivative. The technique is readily available and generally fairly easy to study.

(i) it will explain the absorption of radiation by molecules and its relation to molecular structure; (ii) make accurate calculations, relating the amount of energy absorbed to the concentration of an absorbing analyze; and (iii) explain the instrumentation required for making data. Data can be made in the infrared, visible, and ultraviolet regions of the spectrum. The radiation energy region of choice will depend upon the availability of instruments, whether the analyte is coloured or can be converted to a coloured derivative, whether it contains functional group that absorbs the ultraviolet or infrared region and whether other absorbing species are present in the solution. IR technique is generally less suited for quantitative measurements but better suited for qualitative or fingerprinting information than are ultraviolet and visible technique. Visible optical technique is generally less expensive and more available than UV spectroscopy.

Table 14.1: Spectroscopic techniques, their principle and applications.

Name of Technique	**Principle**	**Applications**
arc /spark spectroscopy or spectrography plasma emission spectrometry flame photometry	Atomic emission	Qualitative and quantitative determination of metals, largely as minor or trace constituents quantitative determination of metals as minor or trace constituents
X-ray fluorescence Spectroscopy	atomic fluorescence emission	Qualitative and quantitative Determination of elements heavier than nitrogen as trace to major constituents.
atomic fluorescence spectroscopy	atomic fluorescence emission	Quantitative determination of metals as minor or trace constituents

atomic absorption spectroscopy γ-spectroscopy	atomic absorption nuclear emission	qualitative and quantitative determination of elements at trace levels
ultraviolet spectroscopy Visible spectroscopy Infrared spectroscopy	molecular absorption	Quantitative determination of elements and compounds, mainly at trace levels quantitative determination of elements and compounds mainly as trace minor constitutes.
Nuclear magnetic resonance spectroscopy mass spectroscopy	nuclear absorption structural fragmentation	Identification and structural analysis of organic compounds identification and structural analysis of organic compounds.

14.2.1 Elements of Empirical Spectroscopy:

The spectroscopic methods used in various regions of the spectrum naturally differ widely from each other in construction. These experimentally observed differences will be discussed, but here it will probably be helpful to indicate the basic ideas which are common to all types of spectroscopic techniques separately.

1. Absorption techniques: The block diagram [Figure 14.1] shows the components of an absorption spectrometer which might be used in the IR, visible, and ultra-violet regions. The radiation energy from a white source is incident on the sample, and then it is connected to analyzer. This leads to the required frequency reaching the detector at the time interval. The signal later pass to a recorder which is connected to analyzer so as to get a trace of the absorbance as the frequency (energy) varies.

The sample and the analyzer is placed in between a modulator; this electronic device interrupts the radiation beam a certain number of times per second, usually fixed somewhere between 10 and 1000 times, and this detector sends an alternating current signal to the recorder with a fixed frequency of 10-1000 Hz. The two main advantages of this techniques are (a) the amplifier in the recorder can be of a.c type i.e, simpler to construct and more reliable in operation than a d.c amplifier and (b) the amplifier can be tuned to select only that frequency which the modulator imposes on the signal, neglecting all other signals. By this method other extraneous signals are removed from the spectral trace and a better, accurate spectrum results.

In the microwave and radiofrequency ranges the monochromatic sources whose emission frequency can be varied over a range are to be selected. Fig 1.12(b) shows, no analyzer is necessary, the source being, in a sense, its own analyzer. Now it is necessary for the recorder to be synchronized with the source – scanning device in order that a spectral trace be obtained.

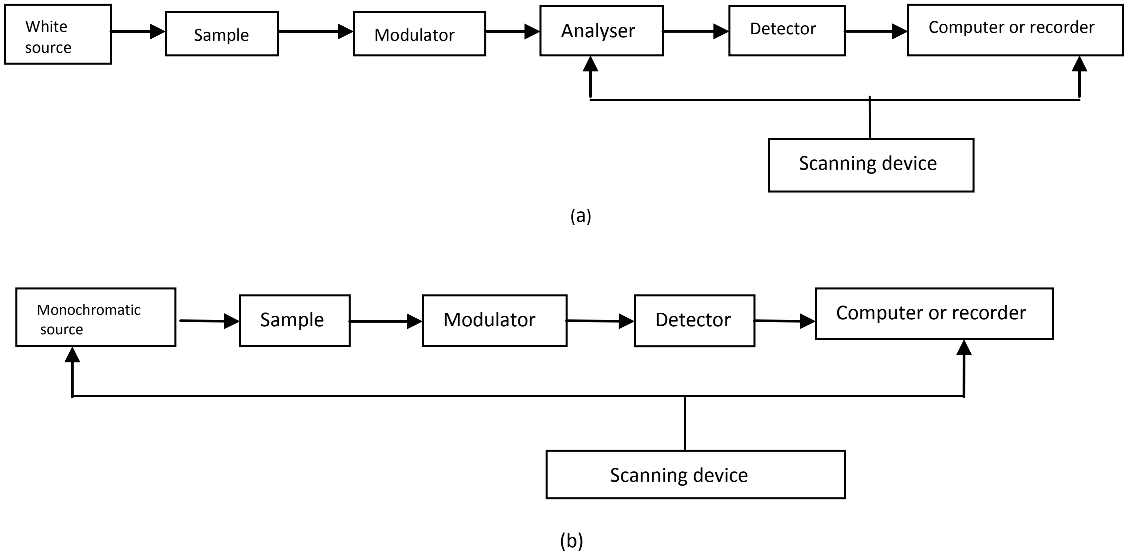


Fig:14.1 Typical diagram of scanning absorption spectrophotometer.

(a) Infrared, visible and ultraviolet regions where polychromatic source is used.
(b) Microwave and radiofrequency regions whose source can be varied over the range of frequencies.

2. Emission instruments: Figure 14.2 shows schematically, a typical spectrometer. The excitation can be thermal or electrical, but usually takes form of electromagnetic radiation. In the latter stage it is essential that the detector does not collect radiation directly from the exciting beam and the two are placed at right angles as shown (Figure 14.2). A modulator fixed between the source and the sample, together with a tuned detector-amplifier, ensures that the only emission recorded from the sample arises directly from excitation by neglecting other emission.

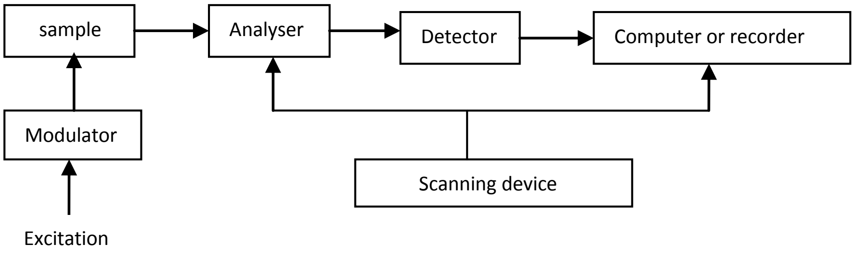


Fig:14.2 Block diagram of a typical emission spectrophotometer.

14.2.2 Electromagnetic Spectrum and Absorption of Radiations

The types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies are known as complete electromagnetic spectrum. The visible spectrum represents only a small part of the electromagnetic spectrum. If all types of electromagnetic radiations in order of their increasing wavelengths, then the portion above the visible region is called Infrared while that lower it is the ultra-violet region. Infra-red have higher wavelength (less energetic). Cosmic rays carry high energy while radio waves (least energetic). Microwaves have larger wavelengths and are used in telephone transmission (higher range energy).

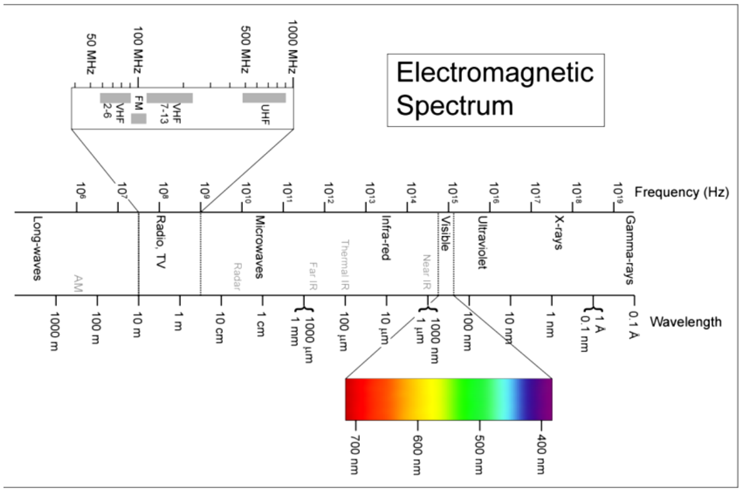


Fig 14.3: Typical Electromagnetic spectrum.

All types of radiations travel as waves with the same velocity but differ in their properties, example X-rays can pass through glass and muscle tissues. Radio waves can pass through air. Visible, Ultraviolet and Infra-red radiations can be bent by reflection or diffraction in a prism. When light radiation is penetrated through an organic sample, some of the wavelengths are absorbed while others belonging to that radiation remain unaffected. A molecule can absorb radiation of certain frequencies, if there exists within a molecule an energy transition of magnitude $\Delta E = h\nu$. It is observed that when light radiations are passed through an organic sample, then electrons of the sample's atoms are excited to higher level. Also, the vibrational and the rotational energies of the molecules are completely quantized. Therefore the wavelength of light absorb by molecule will be due to the changes in the electronic, vibrational or rotational energy levels allowed for the atoms. The wavelengths' absorption can be measured by using spectrometer. If we plot the changes in absorption v/s wavelength, then we get some absorption band which is highly characteristic of a sample and the experiment provides a tool to measure the molecular structure of an unknown compound.

The electromagnetic spectrum can explain the followings:

(i) The visible and ultra-violet region radiations' wavelength (200-800 mµ): the absorption of radiation in this region results the excitation of π electron in a conjugated or an unconjugated system. In the conjugated system, the separation between the ground state and the excited energy level will be less and hence absorption occurs at a longer wavelength. In the case of carbonyl group, an aldehyde or a ketone absorbs some characteristic wavelength. Hence, an UV or visible spectrum is useful for the determination of conjugation, carbonyl group and will not give any other information about the remaining part of the molecule.

(ii) Infra-red radiations covers the wavelength (from 0.8 to 2.5 μ) is called near IR region (15 to 25 μ) is called far IR region and 2.5 to 15 μ is useful region for IR spectroscopy. Hence these radiations are of higher wavelengths and less energetic. The absorption of radiation by an organic sample in 2.5 to 15 μ range causes the changes in the vibrational levels are resulted by the changes in rotational levels. Thus, certain bands appear which characteristically absorb for the stretching vibrations and are very useful in structure determination. The absorptions at higher wavelength in the IR region are the characteristic of a compound and also help in distinguishing one compound from the other (Finger print region). Although, more helpful than ultra-violet method, it does not give complete information about the environmental effects in a molecule.

(iii) NMR spectroscopy gives a complete insight into the environment and the arrangement of atoms within a molecule. For this method, radiations of longest wavelength range- Radio waves are useful. A simple under finding is placed in strong magnetic field and irradiated with radio waves. By using the strength of the magnetic field applied, radiations of definite wavelength (or frequency) will be absorbed which gives the nuclear magnets specific orientations with respect to the applied magnetic field.

14.2.3 Application of UV absorption Spectroscopy to Organic Compounds

1. **Detection of conjugation:** It gives the relationships between different groups, particularly with respect to conjugation; the conjugation may be (a) relation between two or more carbon-carbon double (or triple) bonds, (b) relation between carbon-carbon and carbon-oxygen double bonds or (c) relation between double bonds and an aromatic ring. It can observe the presence of an aromatic ring itself and the number and locations of substitutes attached to the carbons of the conjugated system.

2. **Detection of geometrical isomers:** In the geometrically isomeric compounds, the Trans isomers exhibit λ_{max} at slightly longer wavelengths and have larger extinction coefficients than cis isomers.
3. **Detection of functional groups:** It is possible to determine the presence of some functional groups using UV spectrum. Even the absence of any absorption above 200 nm is of some utility since it shows the absence of conjugation, carbonyl group and benzene rings in the compound.
4. **Qualitative Analysis:** UV absorption spectroscopy can give the information about those types of compounds which absorb UV radiation. These compounds are with unbonded electrons (n electron) or those with the conjugated double-beam system (π electron) and aromatic compounds. Determination is done by using the absorption spectrum with the spectra of known compounds.

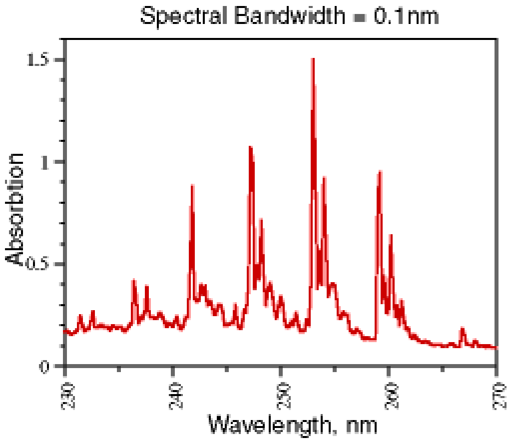


Fig: 14.4 Typical UV absorption spectrum of benzene.

To record UV absorption spectrum, the amount of radiation absorbed at various wavelengths by moving the slit across the dispersed beam of light from the monochromatic source. A typical UV absorption spectrum of benzene vapour is shown in fig. 14.4. In UV absorption spectroscopy, the absorption curve is influenced by the whole molecule as well as by the particular group that contains the absorbing electrons. UV absorption method is useful for characterizing aromatic compounds and conjugated olefins.

5. **Determination of Impurities:** UV absorption spectroscopy method is used for detecting impurities in organic compounds. The main aims of the superiority of this method are, (i) the bands due to impurities are very intense. i.e, an impurity having an amount of 0.05% has a ε value of 2000. Therefore, such an impurity can be observed in a transparent major

component. (ii) The organic compounds can be classified into saturated compounds having little absorption and unsaturated compounds having strong absorption bands. The common impurity in cyclohexane is benzene. Its presence can be easily detected by its absorption at 255nm.

In nylon producing company, the basic materials like adiponitrile and hexamethylendiamine should be very pure. If these materials are not pure, the nylon obtained will be of very low quality. The purity of these materials can be determined by UV absorption method. Traces of unsaturated and aromatic impurities can be determined because the starting materials are transparent in the near ultraviolet region.

6. **Quantitative Analysis. Q**uantitative determination of compound that absorbs UV. This determination is based on Beer's law which is as follows.

$$A= - \log T = \mathrm{Log}\ I_0 /I_t = \varepsilon c l$$

Where 'ε', the extinction coefficient is a constant at any given wavelength for a given species and is independent of the concentration of the absorbing species. 'c' is the concentration and 'l' the length of the sample cell used in UV spectrometer. The optical densities concentration of a substance, wavelength of maximum absorption of the solution of the compound are measured for different concentrations of the solutions, optical density is plotted against concentration of solute over a range of concentrations. A straight line result indicates if Beer's law holds good or not. This plot determines the unknown concentration of solute.

7. **Molecular Weight Determination**. Molecular weights of compounds can be measured using UV-Visible spectrometer provided suitable derivate of these compounds could be prepared. This technique is based upon the formation of a derivative such as a picrate and this is determining from the molecular weight of any amine. First it is converted into amines picrate. Then, a known concentration of the amine picrate is dissolved in a liter of solution and its optical density is measured at λ_{max}=380nm. After, the concentration can be calculated for the solution in gram moles per liter by using the formula

$$c = \frac{log I_{o/I_t}}{\varepsilon_{max}\ \mathrm{X}\ l}$$

From the above formula, concentration can be calculated. The weight *w* of the amine is also known. By knowing *c* and *w*, the molecular weight of the amine picrate can picrate be determined. From the molecular weight of the amine picrate, one can calculate the molecular weight of the parent molecule or compound.

14.2.4 Spectrofluorimeter.

There are two types of instruments mainly (i) those consisting of fluorescence attachment for a spectrophotometer. (ii) Self-contained instruments usually with two monchromators.

A symmetric septrofluorimeter consists of an exciting source, usually mercury or xenon lamp from illumination of the sample at a 90^0 angle. The source is dispersed by a prism or grating blazed for high efficiency at shorter wavelengths and another prism or grating blazed at somewhat greater wavelengths to disperse the emitted fluorescence. The fluorescent intensity can be obtained with help of photo tube attached to a micro photometer and a recorder or an oscilloscope.

Two types of information may be made available with the help of spectrometer. (i) The wavelength of best excitation. (ii) Wavelength of the strongest emission. There are two curves, (i) excitation curve and (ii) emission curve, which are generally plotted or the recorded for each fluorescent material.

The excitation spectrum is obtained by plotting wavelength of the exciting source versus the intensity of emission. The exciting wavelength producing the higher intensity of emission would observe to best exciting wavelength for a light source and grating. To get the spectrum, the curve may be corrected for certain intensity of light source for each wavelength. The data for obtaining such a correction may be obtained by the intensity of the excitation source, at the sample compartment with a thermopile or by fluorescent solution for the study.

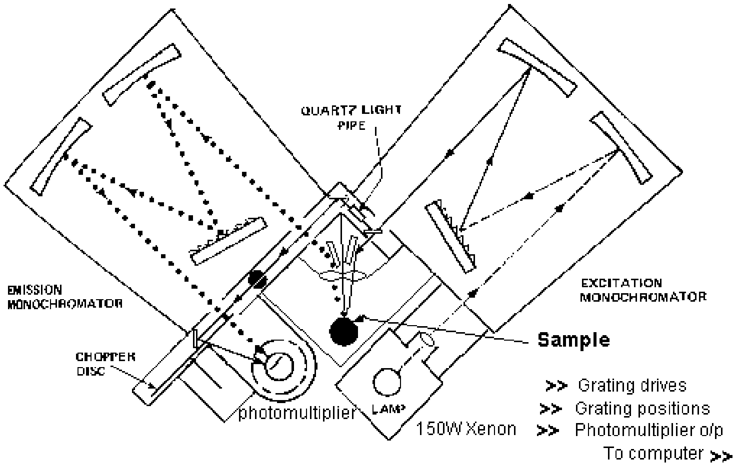


Fig: 14.7 Fluorescence spectrophotometer (Spectrofluorimeter.)

Thus a fluorescence spectrometer can be operated by the following steps.

1. A suitable wavelength in the emission spectrum is chosen with the help of preliminary studies.
2. Second monochromator is set at this point.
3. An excitation spectrum is plotted by scanning the first monochrmator.
4. An emission spectrum is resulted by scanning the second monochromator with the first set a suitable observed value.

14.2.4.1Advantages

i. The spectrophotometer technique is sensitive, about one part in 10^8 or 1.0 µg/ml in many determinations.

ii. Flurometric techniques possess greater specificity than spectrophotometric technique, because there is selection wavelength not only for the radiation emitted, but also for the light which excites the sample.

iii. The fluorometer results affected not only the sensitivity, but also the precision (accuracy).

14.2.4.2. General Applications

i. Finding the Chemical Structures and Processes.

ii. Analysis i.e, determining of Impurity. Estimation of single component-Vitamin, investigation of Fluorescent Intensity of the sample compound.

iii. Finding of 3-4 Benzpyrene.

iv. Finding of Rare earth Terbium.

v. Investigation of Bismuth.

14.2.4.3 Applications of Fluorimetry

Fluorimetry is a well established analytical method. We will describe some of these as follows.

(a) The determination of uranium in salts by fluorimetry: This is used extensively in the field of nuclear physics. The uranium sample is evaporated with nitric acid to bring about oxidation. After, the sample is fused with sodium fluoride to a melt having fluorides of sodium and uranium. On cooling, this solidifies to a glass which is examined in a specially designed fluorimeter.

(b) Some of inorganic ions do not exhibit fluorescence. However, some of these inorganic ions from fluorescent chalets with non-fluorescent organic molecules. This result has provided the basis for very sensitive analysis of many elements.

(c) Fluorescent Indicators**-** The intensity and colour of the fluorescence of many samples depend upon the pH of the solution. These are shown as fluorescent indicators. These are mainly used in acid base titrations. These can be useful in the titration of coloured solutions in which the changes in colour of indicators get masked. Some examples of fluorescent indicators are shown in table 14.3

Table 14.3 Various Fluorescent Indicators

Name of compound	Approx. pH Range	Change in colour
Eosin	3.0 – 4.0	Colourless to green
Fluroescein	4.0 – 6.0	Colourless to green
Quinine sulphate	3.0 – 5.0	Blue to violet
Acridine	5.2 – 6.6	Green to violet-blue

(d) Organic analysis Fluorimetry has been used to carry out qualitative as well quantitative analysis in many aromatic compounds observed in cigarette smoke, air-pollutant, concentrates and automobile exhausts gases. Specific example is the determination of benzopyrene in the nanogram range.

(f) Pharmaceutical chemistry: Aneurine hydrochloride in pharmaceutical preparation such as medicines and elixirs and in foodstuffs such as flour is relatively easily obtained by oxidation to the highly fluorescent thiochrome. The obtained product is soluble in isobutyl alcohol and result easily extracted from the reaction mixture from measurement.

14.3 Solved Problems.

1. Example Calculate the energy in joules per quantum calories per mole and electron volts of photons of wavelength 3000Å.

Solution: We known $E = h\nu$

$$E = h\frac{C}{\lambda} \tag{1}$$

Also we know $h = 6.62\text{x}10^{-34}$ Joules-second

λ=3000Å=$3000\text{x}10^{-8}$cm=$3000\text{x}10^{-10}$m

Substitute the values of h, c and λ in Eq (1), we get

$$E = \frac{6.62x10^{-34}Joule\ -secx\,3x10^{8}meter\ /sec}{3000\,x\,10^{-10}m}$$

$$=6.62\text{x}10^{-19} \text{ Joule}$$

Energy per mole = $Nh\nu$

Where N = Avogadro's number = $6.02\text{x}10^{23}$/mol

Energy per mole = $6.02\text{x}10^{23}$/mol x $6.62\text{x}10^{-19}$ Joule

= $3.98\text{x}10^{5}$ Joule/mol

$$\text{Energy per mol} = \frac{3.98\text{x}105 \text{ Joule /mol}}{4.184\ Joule\ \ /Cal}$$

14.4 Let us sum up

The important technique of spectroscopy unit explains the techniques of spectroscopy with modern spectrometer. The study of these instruments used in spectroscopy to explain in detail for various uses of UV and fluorescence spectrometers presented properly for studying detail usage of UV and fluorescence with examples explained which can be important role for many applications. Detailed advantages of UV and fluorescence with examples are given in this unit.

14.5 Key Word

Atomic and Molecular spectroscopy, Electromagnetic spectrum, Absorption and Fluorescence spectroscopy.

14.6 Review Questions

1. Describe important characteristics of Electromagnetic radiations.
2. (a) Write a note on Electromagnetic spectrum and the absorption of radiations.
   (b) Explain Emission and Absorption spectra.

3. (a) If the energy difference between the two electronic states is 46.12 Kcal mole^{-1}, what will be the frequency of the light emitted when the electron jumps from the higher energy state to the lower energy state?

   (b) The wavelength associated with a ultra-violet radiation is 285 µm. Determine the energy associated with it in kcal mole^{-1}.

4. (a) Describe the range of the Electromagnetic radiations useful for ultraviolet and Infra-red spectroscopy.

5. Compare absorption and fluorescence procedures as to sensitivity and selectivity.

6. Explain the spectrofluorimeter and its applications.

7. Explain the principles of the double focusing and time of flight spectrometers.

8. (a) Distinguish fluorescence from phosphorescence in terms of the mechanism by which an excited molecule is deactivated?

   (b) How would you distinguish the two experimentally?

9. Compare absorption and fluorescence procedures as to a) sensitivity b) selectivity.

10. What are two basic differences in the construction of a fluorimeter as compared to an absorption spectrophotometer?

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UNIT: 15 Equipments and their uses in Different Fields:

Structure:

15.0 Objectives.

After some through the unit you would be in position

- Basic principle of mass spectroscopy.
- Spectroscopic equipments and their uses.
- Application of mass spectroscopy and microwave spectroscopy.

15.1 Introduction:

The different equipments used in various fields of science and in the technological era to study the different parameters of the sample selected by the researcher. Many studies used the methods of interaction of some energy with sample chosen. For example, absorption or emission of atomic, molecular, nuclear energies, etc, below listed some of the equipments, their principle and uses in different fields as given in Table.15.1.

Table: 15.1 Spectroscopic Equipments, principle and uses.

Equipments Name	Principle	Important uses
Arc / park spectroscopy or spectrograph plasma emission spectrometry flame photometry	Atomic emission	Qualitative and quantitative determination of metallic, largely as metals, largely, as minor or trace elements quantitative observation of metals as minor or trace parameters
X-ray fluorescence Spectroscopy atomic fluorescence spectroscopy	atomic fluorescence emission	Quantitative and qualitative determination of elements heavier than nitrogen as trace to major constitutent.
atomic absorption spectroscopy γ-spectroscopy	atomic absorption nuclear emission	Quantitative analysis of metals as minor or trace contains qualitative and quantitative determination of elements at trace levels

ultraviolet spectroscopy Visible spectroscopy Infrared spectroscopy	molecular absorption	Quantitative analysis of elements and compounds, mainly at trace levels quantitative analysis of elements and compounds mainly as trace minor constitutes.
NMR spectroscopy mass spectroscopy	Nuclear absorption structural fragmentation	Determination and structural analysis of organic compounds identification and structural finding of organic compounds.

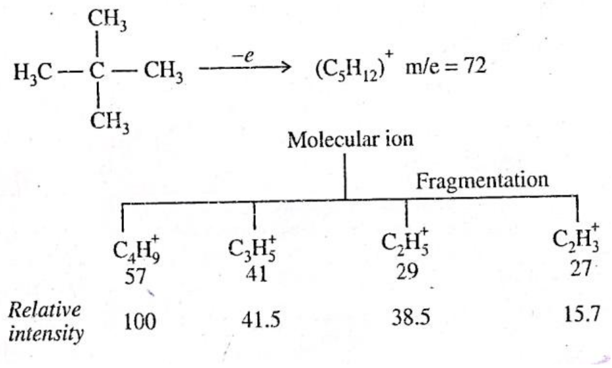
Among above equipments here selected namely, (a) mass spectrometry, (b) microwave spectrometry, (c) Infrared and (d) Raman spectroscopic equipments and their uses in different fields are discussed (IR and Raman spectroscopy see earlier chapters) in this unit.

15.2 Principles of Mass spectrometry:

The mass spectrometry technique is the most accurate method for analysis the molecular mass of the compound and its elemental composition. In this method, molecules are bombarded with a beam of energetic electrons then molecules are ionized and broken up into many fragments, some of which are positive ions. Every kind of ion has a particular ratio of mass to charge, i.e. m/e ratio (value). For most ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

Thus for Neopentane

Neopentene



The molecular ion (here $C_5H_{12}^{+}$) is known parent ion and is usually represented as $M^{+\cdot}$ It is positively charged molecule with an unpaired electron.

The set of ions (fragment ions or daughter ions) are determined such a way that a signal is obtained for each value of m/e that is represented. The intensity of the entire signal indicates the relative abundance of the ion producing the signal. The highest peak in the structure is called the base peak and its intensity is taken as 100, and intensities of other peak represents relative to base peak.

15.2.1 Theory:

A parent ion gives when one electron is removed from the parent molecule of the substance is given by

$$M\,(g) + e \rightarrow M^{+}\,(g) + 2e$$

The m/e parameter of the parent ion is equal to the molecular mass of the compound. In some cases, the parent ion peak may be the base peak and can be identified. In most of the cases, parent ion peak is not the base peak and is often of very small abundance. The mass spectrometer is designed to perform three basic functions. These are: (i) To vapourise compounds of varying volatility. (ii) To get the ions from the neutral compounds in the vapour phase. (iii) To distinguish ions according to their mass over charge ratio and to record them. The graph of m/e values taken along abscissa and their relative intensities along the ordinate is known as the mass spectrum.

$$M^{+}\,(g) \rightarrow m_1^{+} + m_2$$

or $$m_1 + m_2^{+}$$

Neutral particles, produced in the process of fragmentation (whether neutral molecules or radicals) cannot be detected in the mass spectrometer. The mass spectrum of Neopentane presented in Fig 15.1

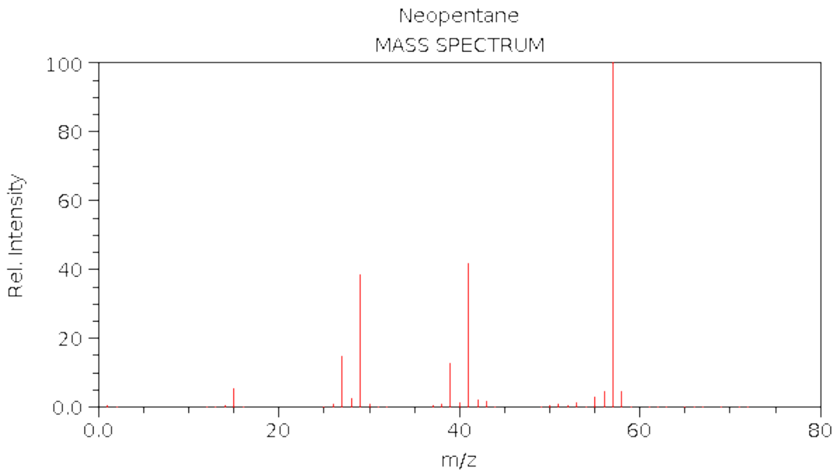


Fig: 15.1 Mass spectrum of Neopentane

15.2.2 Applications of Mass Spectrometry:

The some of the applications of mass spectrometry as given below:

(i) Molecular Mass Determination. Mass spectroscopy is one of the best techniques to determine the molecular mass accurately. When a substance is bombarded with moving electrons and the mass spectrum is obtained, so the mass of the peak at the highest m/e reveals the molecular mass accurately. This technique is only accurate when no ions heavier than the parent ion are formed.

It is seen that mass spectra of a few types of molecules do not give molecular ion peaks in spectra at all even if the energy of bombarding electrons is about 70 eV or so. But molecular masses of such molecules can be deduced from a study of fragment ions which are produced as a result of dissociation of the unstable molecular ions.

(ii) Isotopic Abundance. The presence of isotopic abundance of easily vaporizable elements can be observed using a mass spectroscopy. When this information is coupled with the isotopic mass determination, values of the atomic weights of the elements may be obtained. Example: interested in determining the abundance of isotopes in oxygen gas. This having following steps, (a) Scan a blank spectrum over the mass ranges appropriate to oxygen. (b) Admit the oxygen gas sample in the spectrometer compartment and scan the peaks at m/e 32,33 and 34. Then, correct the peak heights by subtracting contributions from the background. Analyse the mean values of the isotopic ratios as follows: Oxygen 11.17 and 16:18 and 16:18 is equal to [(2xm/e 32):34]. Lastly convert the ratio of the peak heights into percentage abundance of the isotopes of oxygen. And also, one can determine the isotopic abundances of other elements present in it.

(iii) Isotopic Dilution Method. This technique is used to determine the amount of component of a complicated mixture from which it not possible separated quantitatively.

In one is interested in analysing the amount of glycine in a protein hydrolysate, and the weight of glycine in the protein hydrolysate is ‘x’gm and the natural ^{14}N to ^{15}N ratio in it is ‘p’. When ‘y’gm of a ^{15}N enriched synthetic sample of glycine having ^{15}N to ^{14}N ration q is added the mixed sample will getting a new isotope ratio r, which can be analysed by mass spectroscopic method. We know that the two separate weights if ^{15}N containing glycine mixed both together are equal to the weight in the resultant mixture. Therefore, this can be written as

$$\frac{x+b}{r+1} = \frac{x}{p+1} + \frac{b}{q+1}$$

where the value of p and r can be measured by the mass spectrometer from the rations of peak heights of ^{14}N to ^{15}N obtained in mass spectra. As b,p, q and r are known; the value of x can be analysed by using the above relation.

This technique is also useful in analyzing the percentage of caffeine in coffee. In this technique, analysed of isotope ratio in caffeine present in the coffee by the mass spectroscopy requires the sample to be converted in to a suitable form.

(iv)Determination of Ionisation Potential: The ionization potential of molecule (or atom) may be defined as the energy required removing an electron from the molecule (or atom).

$$AB \rightarrow AB^{+} + e^{-}$$

$$A \rightarrow A^{+} + e^{-}$$

$$B \rightarrow B^{+} + e^{-}$$

where AB is the molecule, and A and B are atoms. If ionisation occurs in accordance to the Frank Condon principle so that the molecular separations in the ionized species remain the same as in the neutral atom or molecule.

The minimum energy that the bombarding electrons must possess in order to produce a molecular ion from the neutral molecule is said to as the ionization potential. Mass spectroscopic technique helps to determine this value with ease by applying ionization efficiency curves, (from plots of the ion-current (or peak height) against electron-beam energy eV).

(v)Bonding: Bonding ideas can be interpreted from fracture patterns. A few of the methods used in this regard are given below.

(a) Branched compounds tend to rupture at the branched carbon atom. The + ve charge remains with the branched fragments. The higher the degree of branching the higher is the probability of rupture.
(b) Beta position cleavage is the most probable rupture for the double and hetero bonding.
(c) Ring samples generally exhibit mass numbers which are analysis of the ring.
(d) Side chains are generally ruptured saturated ring compounds at the alpha position.
(e) Carbonyl compounds break in to the carbonyl bond and positive charge remains with the carbonyl group.

(vi) Latent Heat of Vaporisation of Liquids: Mass spectroscopy is used for the analysis of latent heat of vaporization of liquids with the help of Clausius-Clapeyron relation which gives the saturated vapour pressure of a liquid as a function of the absolute temperature.

$$logp = -\frac{\Delta H}{RT} + constant$$

From the above relation one can determine ΔH if the value of p at the given temperature T is known. The peak height of mass spectrum of that liquid whose ΔH value is to be calculated is directly proportional to the saturation vapor pressure, p at the temperature T. and the values of p are measured from the height of peaks in the mass spectrum at different temperatures. The obtained value is from the slope of the plot of log p against 1/T.

The main merit of measure of latent heat of vaporization by mass spectrometry is that the chosen material need not be pure as determination are made at one peak only, generally the molecular-ion peak.

(vii) Impurity Detection: The mass spectrometry method is one of the important methods to detect impurities. The determination of impurities in parts per million is only possible if their structures differ considerably from those of the main components.

If the molecular weights of the impurities are much higher than main components their determination is more easy because their higher mass peaks are free from contributions by those of the main components. If the molecular weights of the impurities present are much lower than the main components, their determination are not an easy finding because of the formation of common fragment ions.

(xii) Characterisation of Polymers: this spectrum is used for the analyseis of polymers. At the beginning, the polymer is pyrolized and then the pyrolized outputs are fed into the inlet of a mass spectrometer and analysed. From the above results, one may obtain much information about the structure of the polymer.

15.23 Introduction to Microwave Spectroscopy

In recent year microwave spectroscopy is great asset in the study of various problems in physics, chemistry, electronics and even astronomy. Mainly, it has been found to be very useful in the detection of the structures of those molecules which do not give reliable results with the help of Raman and infrared spectroscopy techniques. The ability to analyse the frequencies more precisely in the microwave region allows very precise findings, than in the infrared-visible-ultraviolet region and accuracy of the order of 0.001 to 0.005 Å are possible for analysis.

The observed spectra results from spectral transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region. These spectral analysis shown by molecules which possess a permanent dipole moment, (e.g., HCl, CO, H_2O vapour, NO,etc). The diatomic molecules like homonuclear such as H_2, Cl_2, etc. and linear polyatomic molecules such as (CO_2), which do not having a dipole moment, do not show microwave spectra.

15.23.1 Microwave Spectroscopy

The microwave spectroscopy gives, that part of the electromagnetic spectrum which is extending from 100µm ($3x10^{13}$ Hz) to 1 centimeter ($3x10^{10}$ Hz). This region of electromagnetic spectrum is designated as the microwave region. This lies between the far infrared and conventional radio frequency regions. Spectroscopic applications of microwave consist almost exclusively of absorption works, rather than of the emission type. In most of the cases, absorption of microwave energy represents changes of the absorbing molecule from one rotational level to another. Therefore, the microwave spectroscopy deals with the pure rotational motion of molecules and is also known as rotational spectroscopy. The condition for observing resonance in that region is that a molecule must possess permanent dipole moment. When a molecule having dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During the interaction, energy can be absorbed or emitted and thus the rotation of the molecule gives rise to a spectrum. If molecules are not having dipole moments, interaction is not possible and these molecules are said to be “microwave inactive”. Examples of such molecules are H_2, Cl_2, etc. On the other hand, the molecules like HCl, CH_3, CI etc., are having dipole moments and their interaction will give rise to a spectrum such molecules are said to be “microwave active”.

Generally, the microwave spectra obtained in most of the molecules are absorption spectra. Theoretical considerations reveal that the probability of microwave spectra is only about one per cent of the optical absorption.

15.3 Simplified diagram of Microwave Spectrometer.

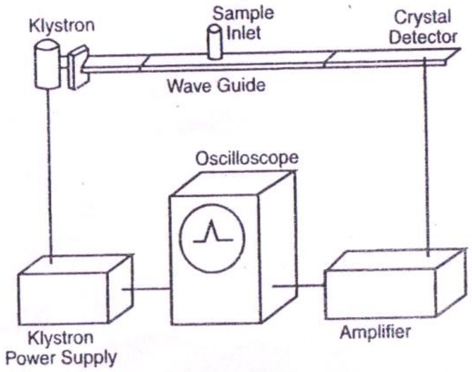


Fig: 15.2. Simplified diagram of Microwave Spectrometer.

15.3.1 Working

Monochromatic radiations of different wavelengths in the microwave region emitted by klystron valve are allowed to pass through the sample space containing the gaseous sample of the substance under investigation. Then, the radiations are made to conduct along a rectangular tube called a waveguide. After this the radiations are received by the quartz crystal detector which is situated at the far end of the waveguide. After receiving the radiations from the wave guide it vibrates and sends an electrical signal which is amplified by amplifier and then displayed as a recording on a screen. The oscillograph obtained on the screen enables one to detect the frequency microwave radiation.

The above microwave spectrometer describes the determination of the highest accuracy because the absorption lines are narrow and fairly faithful in shape and relative intensities. The use of oscilloscope poses a serious problem that the amplifier bandwidth cannot be narrowed to completely remove noise and, thus, the sensitivity is not exceptionally high. At the same time the new lines for unknown substances can be obtained very difficulty unless their frequencies are known within narrow limits.

By observing the intensity of transmitted beam changing the frequency of the oscillator, moment of inertia and internuclear distances up to $\pm$ 0002Å can be determined data obtained values for bond lengths and bond angles determined for linear molecules and symmetrical top molecules by microwave spectroscopy technique are mentioned in following table (Table. 15.2)

Table 15.2: Bond Angles for Some Molecule

S.No	Molecules	Bond Angle	Value of Bond Angle in degrees
1	$CHCl_3$	CI – C –CI	$110^0 24'$
2	CH_3 CI	H – C – H	$108^0 0'$
3	CH_3 F	H – C –H	$110^0 0'$
4	SiH_3 Br	H – Si – H	$111^0 20'$

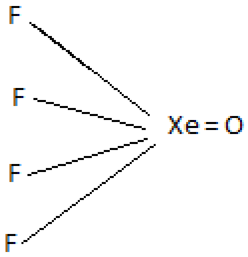
By observing the table it is clear that microwave spectroscopy technique can also be used for determines the nuclear spin.

15.4 Applications of Microwave Spectroscopy

(i) Structural Determination: After studied of microwave spectroscopy we can trap the information regarding molecular symmetry and molecular parameters. This can be explain by considering the following examples.

(a) Structure of xenon oxyfluoride molecule.

The microwave spectrum of this sample is as characteristic of a symmetric top and is consistent with the C_4v symmetry of the sample.



(b) Structure of OCS molecules.

The Problems of structural determination is of such importance in case of carbon oxysulphide that is worth a more detailed discussion. This sample is linear and has two various interatomic distances and is confronted with the difficulty of calculating two unknowns in a single equation.

(c) The Inversion Spectrum of Ammonia.

Bleaney and Townes was the first sample to be studied by microwave spectroscopy. In the spectrum of ammonia sample, each of the lines is split into a doublet due to the inversion of the sample.

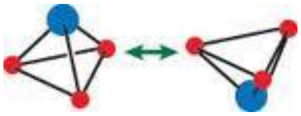


Fig. 15.2: Inversion of ammonia molecule.

The Microwave spectrum of ammonia sample is concerned with the motion of the nitrogen atom between the centers of three hydrogen atoms as given in Fig. 15.2. When a graph is plotted between potential energy and position of nitrogen atom, the spectrum obtained is of the double minimum type shown with a central barrier of 2070 cm^{-1} (6 Kcal). The curvature of each minimum lies near 1000 cm^{-1} which is described as a NH bending fundamental. The splitting of the lower rotational levels (Fig. 15.3) occurs due to quantum mechanical tunnel effect which is due to finite barrier height and the low mass of the hydrogen atoms.

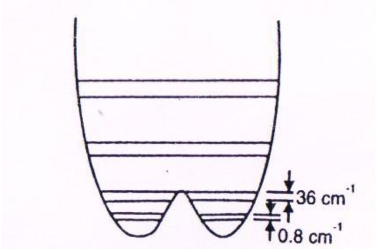


Fig: 15.3 Energy diagram for the Inversion coordinate of Ammonia.

In principle, the inversion of ammonia is a vibrational motion. As the inversion is hindered, the interaction will result in energy difference in microwave region. This interaction will cause the splitting of the vibrational levels. As the transitions are now between the two components of the vibrational levels, this will result in the rotational lines to split.

One may raise the question that the sample such as PH_3 and As H_3 should also show the splitting of the rotational levels. But they do now show such doublings. The main reason for this is that the inversion frequencies in these systems are much slower due to the increase in the barrier height.

(d) Measurement of Barrier Heights.

Microwave spectroscopy can be useful in determine the barrier heights of certain sample. If a part of a sample can rotate about a single bond the internal potential energy of the sample will depend on the orientation of this part with the rest of the sample.

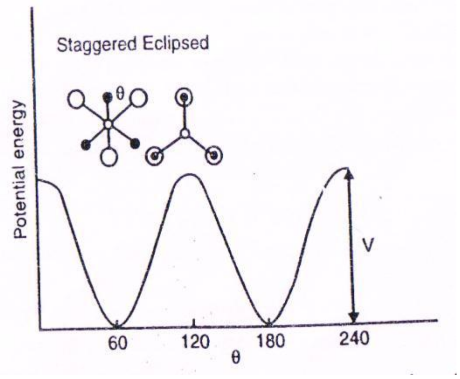


Fig: 15.4 Plot of the potential energy as a function of ɵ.

Let us consider the 1, 1, 1-trifluoroethane sample, Fig 15.4 shows the plot of the potential energy vs. the various orientations of the CF_3 group. The potential energy V(θ) is given by the simple expression. $V(\theta) = \frac{V_3}{2}(1 - cos3\theta)$

For low potential barriers free rotation will take place. On the other hand, for high barriers we will have “tensional vibrations” with quantum mechanical tunneling between equivalent conformations. Table 15.3 lists some of the barrier heights measured by microwave spectroscopy.

Table 15.3 Barrier (K cal mole $^{-1}$)

Molecules	Barrier to rotation
CH_3 OH (C - O)	1.07
CH_3OCH_3 (C - O)	2.72
C_6H_5 CH_3 (C –C)	13.94
CH_3 NO_2 (C –N)	0.006

(e) The structure of ozone molecule.

Microwave spectroscopy technique is successful to deduce the correct triangular structure of the simple ozone molecule. Previously, its correct structure could not be established by optical spectroscopy and electron diffraction technique.

(f) The abundance of isotopes.

The microwave spectroscopy is successful in determining the isotope abundance because each sample possesses a unique moment of inertia depending on the particular nuclei present. From the relative intensity of the spectral lines or from the integrated area, the abundance can be obtained.

Microwave techniques are also useful in locating the position of the isotopic substitution within a sample. An interesting example is that J=0→1 transitions for $^{14}N\ ^{15}N\ ^{16}O$ and $^{15}N^{14}N^{16}O$ sample are 850 MHz apart.

An interesting example of quantitative chemical determined was reported by Southern et al. who in calculated isotopic abundances were able to determine ^{15} N in the range of 0.38 to 4.5 percent within ±3 percent and ^{13} C in the range of 1.1 to 10.0 percent within ±2 percent. Only 0.00015 mol of gas was required for a determination and procedure took only 10 to 15 per sample. In constant to NMR, IR and UV, microwave spectroscopy is not used routinely to identify compounds.

Conclusion: It must be pointed out that microwave spectroscopy is fundamentally not suitable for analysing new compounds. The microwave spectrum is a property of the sample as whole and it is not possible to relate certain parts of the spectrum to certain parts of the molecule.

15.5 Microwave Oven:

In recent past, the microwave oven has become a very useful cooking device in the kitchen. Its mode of operation has been found to depend upon the absorption by the food of the microwave radiation in which it is placed. The water molecules in the food absorb the microwave radiation and are thereby raised to the higher rotational states. The biological molecules in the food, on the other hand, are far too big to be able to rotate. The heating in the microwave oven is mainly internal heating. In internal heating, the water molecules in the food get excited and the excess rotational energy get re-emitted as heat with the help of which the food gets cooked. However, the microwave radiation also affects the human body. Hence, the door seal of microwave oven must be in good condition so that no radiation leaks out.

15.3 Let us sum up.

In this lesson, we pointed out:

- Basic principle of mass spectroscopy.
- Spectroscopic equipments and their uses.
- Application of mass spectroscopy and microwave spectroscopy.

15.4 Key Words

Mass spectroscopy, latent heat, polymers, microwave spectrometer.

15.5 Review Questions

1. Explain the basic principle of mass spectroscopy.
2. Mention the applications of the mass spectroscopy.
3. Explain the brief principle of mass spectroscopy.

15.6 Reference Books

1. Instrumental methods of Chemical analysis by Gurdeep R. Chatwal.

2. Fundamentals of Molecular Spectroscopy, Third Edition by C N Banwell.

3. Modern Spectroscopy, fourth edition by J. Michael, Hollas.
4. Molecular Structure and Spectroscopy, by G.Aruldhas.

Unit 16. Solar stellar Physics and cosmic ray

Structure:

16.0 Objectives.

On successful completion and understand of this unit the students should have:

- Structure of the Sun
- Luminosity of a star
- Stellar Evolution
- Stellar time scale
- Discovery of Cosmic rays
- Cosmic ray Composition
- The Cosmic ray energy spectrum

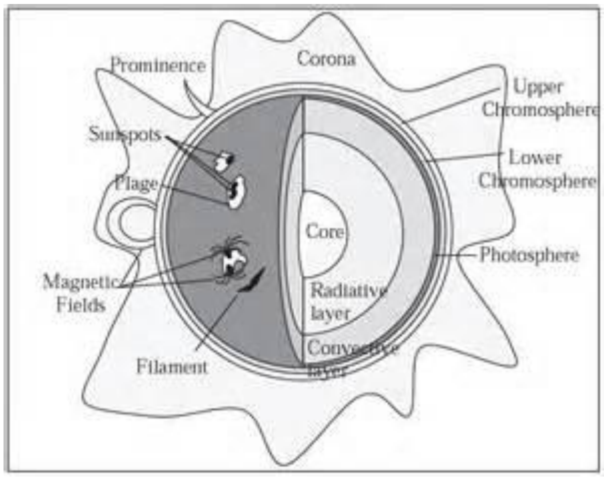
16.1 Introduction.

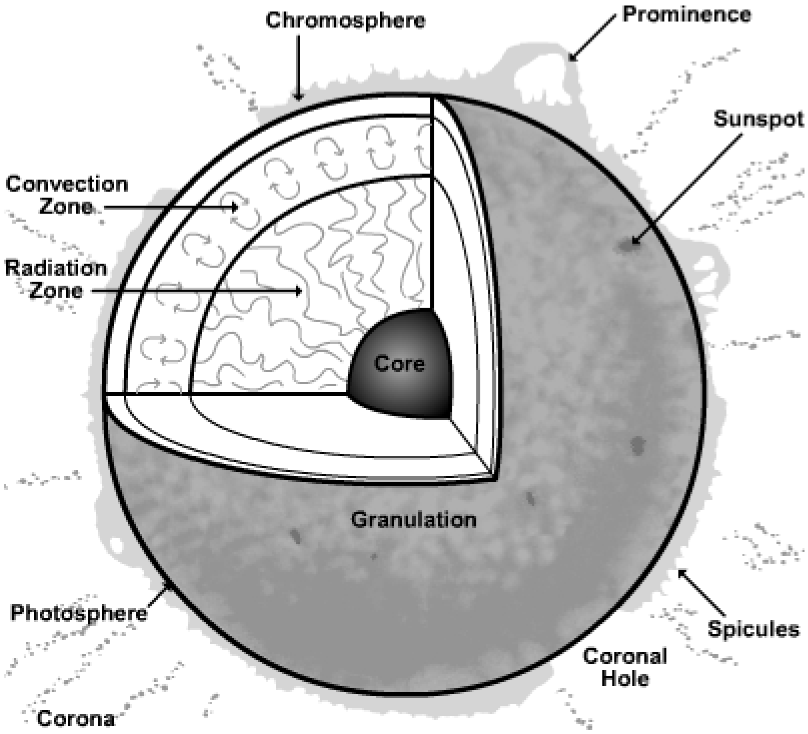
Astronomy is the branch of physics which gives detail study of relative positions of celestial objects and their related phenomena. Astrophysics is the sub branch of astronomy deals major study of the nature of stars. Up to seventeenth century, the astronomical studies were concentrated on the sun, moon planets and the other celestial objects observed around the sun. The relative motion of the objects around solar system was successfully explained detailed by Sir Isaac Newton with his universal law of gravitation. After these studies reveled the existence of counts of fainter and various distant stars which result to the conclusion that the large system of stars, called Milky Way spreading to many thousands of light years leads to existences of a great universe. With the abundances information, astronomers started applying the tested law of physics to the stars and galaxies to understand their nature and properties. The success of the application of the laws of physics to study the nature of the celestial bodies result to a new branch of physics called astrophysics. Astronomy is mainly classified as the study of i) solar system ii) stars iii) stellar clusters and galaxies iv) nebulae v) pulsars vi) quasar etc. and in understanding the behavior of nature and universe in a better way

The solar system includes of the sun, nine planets i.e., Mercury, Venus, Earth, Mars, Jupiter, Saturn, Uranus, Neptune and Pluto their satellites and rings thousands of asteroids which rotate round the sun between the orbits of mars and Jupiter, and about a billion comets which form a cloud extending up to a distance of one light year. The largest body sun is in the solar system; Jupiter second with a mass about one-thousandth that of the sun and radius about one-tenth of the sun. Comparing with other planet the Earth is comparatively small with a mass about $(1/330)^{th}$ that of Jupiter and radius about one-eleventh that of Jupiter.

16.2 Sun Structure.

The sun is a very big sphere of hot gas (radius 6.96×10^5 Km and a mass of 1.99×10^{30} Kg), the pressure, temperature and density goes on increases, from the sun's surface inward to the centre as core, where its energy is librated by thermonuclear fusion. The hydrogen present in it is converted into helium in releases large quantity energy form of photons ($h\upsilon$) and thermal motions. The photons above released diffuses outwards through the radiative zone and reach the outer most zone (convective zone), where most its energy transportation takes place. The visible surface of the sun known as photosphere occurs at the top of the convective zone layer. Photosphere is a thin layer of gases that represents the depth to which we even observe dark sports (sunspots) appear in the photosphere. Above the photosphere layer is chromosphere which is a region of emerging prominence and the spicules. Beyond this region a thin layer called corona where its emerging light is thrown into the outward flouring solar wind and the interplanetary system.





a) **Photosphere:** Is the innermost layer of the solar atmosphere whose thickness ranges to about 330Km. The continuous absorption spectrum of the sun is mainly produced by H^- ion which layer of p hotosphere originates entirely from the photosphere the temperature goes on decreases as we move from lower to upper layer of photosphere and attains a least temperature in the transition layer between the photosphere and chromospheres, the temperature again raises in the chromospheres attaining maximum in the corona. The pressure and density in the photosphere are low of the order of 10^{-2} and 10^{-4} compared to earth atmospheric pressure.

b) **Solar granulation:** The bright irregular grains like structures of the visible disk of the sun are known as photospheric granulation, which is surrounded by darken. It is the top layer of sun's convective zone, where heat energy is transported by convection process. The size of the granules vary from 300-18000 Km with an average value of about their shapes resembling irregular polygons which are separated from one another by narrow and darker of the filamentary. The number of granules on the visible disk of the sun is nearly of about $3.5x10^{16}$. Granules are found to very both in number and size with the 11 year solar cycle.

c) **Chromospheres:** above the photosphere lies the second major layer of the solar atmosphere known as chromospheres. Which extends nearly which is up to 10000 Km is fairly in homogeneous. Above the photosphere with its gas density gradually becomes less but temperature increasing rapidly upwards. The lower layer of the chromospheres is just simply an extension of the photosphere, where strongest absorption line of hydrogen (Balmer) and K-line of Ca-II are formed. The temperature in chromosphere increases to very high temperature in upper layer of chromosphere at a height of about 20000 Km above the photosphere where the chromospheres merge into the corona, the temperature is 10^6 K.

d) **Solar corona;** The corona is natural, smooth extension of the chromospheres. During solar eclipse the corona is visible as a white halo extending from the sun's limb. A brighter inner halo huges of the solar limb, coronal streams extend far in to space. The corona may be divided into K-corona and F-corona.

e) **Solar wind:** The high coronal temperature tends to below away the corona from the sun. The sun's gravitation on this gas is just insufficient to retain in it, resulting in rise to known as solar wind.

f) **Prominences:** During total solar eclipse the solar disk exhibit red flames protruding from the chromospheres through the corona. These flames like structure are called prominence. The typical dimension of prominence is 30000 Km - 200000 Km in height and 5000Km in thickness, yielding a total volume of 3×10^{28} cm^3.

16.3 Luminosity of a star;

All the stars including sun, in the night sky shine due to thermonuclear fusion. But all the stars are not same but are different from one another with their luminosity (L) which is defined as the amount of energy passing normally unit area on its surface in unit time. The luminosity of various stars is measured in terms of the sun's luminosity L_Θ or in terms of watt ($1\ L_\Theta = 3.9 \times 10^{26}$W) most of the stars are less luminous than the sun. Knowledge of stars luminosity is very important to understand the internal structure of stars and their evolution.

16.3.1 Inverse square law relating brightness and luminosity;

The apparent brightness (b) of a star is defined as the ratio of the luminosity L of the star and the surface area of the sphere of radius d.

i.e. $b = \frac{L}{4\pi d^2}$ where d- distance between star and observer (radius)

This is the inverse square law. It can be observed from above equation that the apparent brightness of light coming from a star as seen by an observer is inversely proportional to the square distance between from the star and observer, the apparent brightness of the sun is given by

$$b_{\odot}=\frac{3.9\text{x}10^{26}}{4\pi(1.5\text{x}10^{11})^2} \quad =1370 \text{ Wm}^{-2}$$

$$d=1.5\text{x}10^{11} \text{ m} \quad \text{(sun-earth distance) similarly,}$$

The luminosity of a star, and sun are respectively given by

$$L=4\pi d^2 b$$

$$L_{\odot} = 4\pi d_{\odot}^2 b_{\odot}$$

$$\frac{L}{L_{\odot}} = \left(\frac{d}{d_{\odot}}\right)^2 \frac{b}{b_{\odot}}$$

$$L = \left(\frac{d}{d_{\odot}}\right)^2 \frac{b}{b_{\odot}} L_{\odot}$$

The relative distance $\left(\frac{d}{d_{\odot}}\right)$ and the relative brightness $\frac{b}{b_{\odot}}$ of the stars with respect to sun are the standard values that can be obtained from the tables. The luminosities calculated with above relation range from $10^6 L_{\odot}$ to $10^{-4} L_{\odot}$.

16.4 Stellar evolution;

The experimental and observational studies on sun show that the stars are not permanent. The thermonuclear reaction in the core of the sun on a over consumes about $6\text{x}10^{11}$ kg of hydrogen per second and converts it into helium. Produce huge amount of energy which is radiated by the sun. Sun has large but finite quantity of hydrogen stored in it to sustain thermonuclear reaction for a very long duration. Therefore the sun and the other main sequence stars (HR diagram) cannot shine forever. As the quantity of hydrogen content keeps on decreasing, the star tries to overcome the relentless pull of self gravity and outward radiation of enormous amount of heat energy. Therefore a star’s life is a everlasting continues against gravitational collapse. Therefore, stars do have a beginning as well as an end.

16.4.1 Introduction. Stars are formed when interstellar gas clouded of sufficient mass collapse under the action of their gravitational pull. This collapse converts gravitational pull energy into thermal energy, due to working done in bring the gas molecule close to each other resulting in heating the gas during the stellar formation process, nearly half of the gravitational energy between gas molecules is converted into thermal energy and the remaining energy is emitted in the form of radiation to interstellar space. It should be noted that when a mass collapses, the gravitational binding energy increases and liberates energy with the star. In other words the system becomes more stable. If the mass of the collapsing body is more than $0.08M_{\Theta,}$ necessary for sustained hydrogen fusion, a star is born. A formation in the process of star is commonly called a protostar.

16.5 Global stellar structure;

16.5.1 Stellar time scale;

Stars are holed together by gravity, which is balanced by gas pressure. Stars quasi-steady state follows some characteristic time scale. Which is the time scale of free fall $\widehat{t_{ff}}$ is the time scale for stellar collapse if there were no pressure gradients opposing gravity. Then the only acceleration is by gravity $d^2r/dt^2=-GM/r^2$, where r is the radial distance to the stellar centre, G is the gravitational constant, and M and R are the stellar mass and stellar radius, respectively. This leads to the order of magnitude estimate;

$$\widehat{t_{ff}} \approx \left(\frac{R^3}{GM}\right)^{1/22} = 1600\left(\frac{M}{M_\Theta}\right)^{-1/2}\left(\frac{R}{R_\Theta}\right)^{3/2} \qquad (16.1)$$

Where M_Θ and R_Θ are the solar mass and radius, respectively.

To a star which is in virtually in hydrostatic equilibrium, the local departures from equilibrium are restored at the speed of sound;

$$C_s=[(\gamma p)/\rho]^{1/2} \qquad (16.2)$$

Where ρ is the density, p is the gas pressure, and $\gamma \equiv C_p/C_v$ is the ratio of the specific heats at constant pressure and constant volume. The order of magnitude is estimated by hydrostatic equilibrium is, $\bar{p}/R \approx GM\,\bar{\rho}/R^2$. Then we define the hydrodynamic time scale $\widehat{t_{hy}}$;

$$\widehat{t_{hy}} \equiv \frac{R}{\bar{C}_s} = \left[\frac{R^2\bar{\rho}}{\gamma\bar{p}}\right]^{1/2} \approx \left[\frac{R^3}{\gamma GM}\right]^{1/2} = \gamma^{-1/2}\,\widehat{t_{ff}} \qquad (16.3)$$

Where is of the order of magnitude as the free fall time scale$\widehat{t_{ff}}$.

The Kelvin-Helmholtz time scale $\widehat{t_{KH}}$ estimates how long a star could radiate where there is no further nuclear reactions but the star would emit radiations due to its stored total potential gravitational energy E_g at its present luminosity L;

$$\widehat{t_{KH}} \equiv \frac{|E_g|}{L} \approx \frac{GM^2}{RL} \approx 3\text{x}10^7 \left(\frac{M}{M_\Theta}\right)^2 \left(\frac{R}{R_\Theta}\right)^{-1} \left(\frac{L}{L_\Theta}\right)^{-1} \qquad (yr) \qquad (16.4)$$

According to Virial theorem in hydrostatic equilibrium, it the internal (thermal) energy $E_1$is half $|E_g|$. Hence the Kelvin-Helmholtz time scale is of the order of the thermal time scale, which a star would need to radiate all its internal energy at the rate of its given luminosity L.

The nuclear time scale $\widehat{t_{nf}}$, the time a star can radiate by a specific nuclear fusion process, is estimated from stellar evolution calculations. The time scale for hydrogen fusion is found to be

$$\widehat{t_{nu}} \approx 1\text{x}10^{10} \left(\frac{M}{M_\Theta}\right)\left(\frac{L}{L_\Theta}\right)^{-1} (yr)$$

The comparison of the stellar time scales shows

$$\widehat{t_{ff}} \approx \widehat{t_{hy}} \ll \widehat{t_{KH}} \ll \widehat{t_{nu}}$$

Consequently, a star is nearly in both mechanical and thermal equilibrium during all of its evolutionary phases.

16.6 Discovery of cosmic rays:

Cosmic rays are highly energetic and penetrating radiations which are continuously entering in to the earth's atmosphere in all directions from outer space. It consists of high energy charged particles having energy of the order of 15GeV. Cosmic rays were first detected by Elster and Geitital (1899) and by CTR Wilson (1900). They observed that the charge of a insulated electroscope leaked away slowly in spite of the absence of any ionization agent. At initially, it was through that the loss of charge of electroscope is due to the ionizing radiations are coming from radioactive substance present in earth. If that is case, then the rate of discharge must decrease when the electroscope is taken to a higher altitude. In 1911 Hess, recorded ionization of air at different altitudes by sending electroscopes in balloon and found that the rate of discharge of charges from electroscope increases as we go higher altitudes and, on the other hand, the ionization of air in the electroscope decreases as we go down into mines or the sea of earth.

16.6.1 Cosmic Rays

The existence of cosmic rays (CRs) has been known since 1912 when Victor Hess observed changes in an electrometer (a device for measuring the presence of charge) at a high altitude in a hot air balloon. The electrometer discharged more quickly at higher altitudes, Contrary to what was expected, leading Hess for conclusion that the source of the electrometer reading changes must be from above the atmosphere rather than Earth itself. For this discovery, he shared the Nobel Prize for Physics. it is called as Cosmic rays as they were originally thought to be part of the electromagnetic spectrum. But we know today that these are high energy particles which are coming from space. One to represent, CRs together with meteoritic and meteorites dust are the only known to represent particulate matter reaching the surface of Earth's. But they are more important carriers of cosmic information beyond the information brought by light to us.

16.6.2 Cosmic ray composition

In the composition of cosmic rays near approximately 98% particles are of nucleons (proton and neutron together), and the remaining 2% are electrons and their positive counterparts, positrons. Of the particles energy range, from 10^8 to 10^{10} eV, which is quite different from the elemental abundances of the solar system and interstellar medium (87% are hydrogen nuclei,12% are helium nuclei and 1% are heavier nuclei). CRs are slightly under abundant in hydrogen and over abundant, by several order magnitude, in the light elements, like Li, Be and B. Thus the admixture of CR particles is quite different from what we normally expect to see in the solar system or inter stellar medium (ISM).

Most of the compositional anomalies can be explained only those by models that takes into account the interactions of CRs en route to Earth. For example, the over abundance of lighter elements like Li, Be and B can be understood in terms of spallation the breaking up of heavier nuclei in to smaller particles via collision (interactions). As ISM acts like another atmosphere therefore it, must taken in consideration to understand correctly the original composition of these particles at the location where they were first accelerated. Few abundance anomalies still remain even after the ISM atmosphere is taken into account. These can provide hint to the origin and acceleration mechanism of the particles. One such is the relative under abundance of hydrogen. Supernova ejection, for example, consists of mostly heavier elements in comparison to hydrogen. Also, acceleration mechanisms may be effective for interstellar grains than for particles that are in the gas phase such as hydrogen. The strong under abundance of electrons compared to nucleons can be understood in terms of the relative energies and momenta of the particles, which will be discussed below.

16.6.3 The cosmic ray energy spectrum.

CRs are of at relativistic speeds and resulting in high energies. The total energy of a particle whose rest mass is m_0, moving at a speed, v, is

$$E=m_0c^2 +T = \gamma\, m_0c^2 \qquad (16.5)$$

Where T is the kinetic energy, m_0c^2 is the rest mass energy, and γ is called the Lorentz factor, defined as,

$$\gamma \equiv \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \qquad (16.6)$$

If $v \ll c$, a binomial expansion can be used on eq (16.6) to find.

$$\gamma = 1 + \frac{1}{2}\frac{v^2}{c^2} \tag{16.7}$$

Of which, eq (16.5) reduces to,

$E = m_0c^2 + \frac{1}{2}\, m_0v^2\ (v \ll c)$ For velocity which are less than velocity of light

This is the most familiar expression showing rest mass energy of the particle and its kinetic energy. The electron and proton rest mass energies are 0.51 MeV and 938 MeV, (calculated from $E=mc^2$) respectively, corresponding to γ =1.Note that Electrons with energies greater than that of 0.5MeV or protons with energies greater than about 1GeV are therefore will be dominated by their kinetic energies we consider a relativistic speed to be at least 0.3c, if any particle with γ greater than 1.05 is consider as relativistic.

The cosmic ray energy spectrum is shown in figure 16.1 showing a power law spectrum, with several changes in slope, and 13 orders of magnitude in particle energy. This is a log-log plot; a straight line represents a power law distribution of energies for those particles which can be described by,

$$J(E)= KE\Gamma \tag{16.8}$$

Where Γ is the cosmic ray energy spectral index, E is the energy of a particle and K is a proportionality constant. The quantity, J(E), is a kind of specific intensity for particles and can be integrated to obtain the number of CRs hitting an object per unit time. Its unit of particles s^{-1} $m^{-2}GeV^{-1}$ sr^{-1}A single value of Γ, does not fit the data perfectly (dashed curves). These changes in the slope, are marked at the knee and the ankle at energies of $4x10^{15}$eVand $5x10^{18}$eV, respectively, showing KE dominance. Except for the very lowest and very highest energies, Γ≈2.7 is a good fit to the data at energies lower than the knee and Γ≈3. i.e., changes in the slope have been scrutinized in detail because it is through this it may represent changes in the origin and /or acceleration mechanism of the particles.

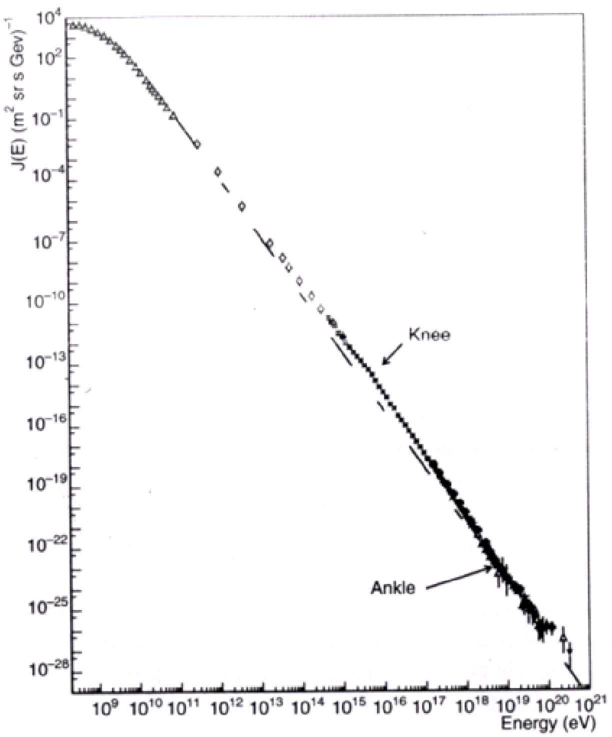


Figure 16.1

Figure 16.1 cosmic ray spectrum for particles from 10^8 to 10^{21} eV. The ordinate represents J(E) and the abscissa represents the kinetic energy per particle for which E≈T over almost the entire energy range plotted. The dashed line shows a power law fit with a single spectral index. Subtle changes in the spectral slope can be seen in two places the knee and, to a lesser extent ankle.

16.6 Let us sum up

In this lesson, we pointed out:

- Structure of the Sun
- Luminosity of a star
- Stellar Evolution
- Stellar time scale
- Discovery of Cosmic rays

- Cosmic ray Composition
- The Cosmic ray energy spectrum

16.7 Key Words

Luminosity of a star, stellar evolution, Cosmic rays.

16.8 Review Questions

1. Explain the structure of the Sun.
2. Briefly explain the stellar evolution.
3. Stars have luminosities ranging from 10^{-6} L_{Θ} to 10^{6} L_{Θ} justify.
4. Write a note on Cosmic ray.

16.9 Reference Books

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