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Tirunelveli - 627 012 Tamilnadu, India

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

II YEAR

M.Sc. Physics

Course Material

Spectroscopy

Prepared

By

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SPECTROSCOPY

UNIT I:

MICROWAVE SPECTROSCOPY

Rotational spectra of diatomic molecules - Rigid Rotor (Diatomic Molecules)- reduced mass – rotational constant - - Effect of isotopic substitution - Non rigid rotator – centrifugal distortion constant- Intensity of Spectral Lines- Polyatomic molecules – linear – symmetric asymmetric top molecules - Instrumentation techniques – block diagram -Information Derived from Rotational Spectra- Stark effect- Problems.

UNIT II:

INFRA-RED SPECTROSCOPY

Vibrations of simple harmonic oscillator – zero-point energy- Anharmonic oscillator – fundamentals, overtones and combinations- Diatomic Vibrating Rotator- PR branch – PQR branch- Fundamental modes of vibration of H_2O and CO_2 -Introduction to application of vibrational spectra- IR Spectrophotometer Instrumentation (Double Beam Spectrometer) – Fourier Transform Infrared Spectroscopy - Interpretation of vibrational spectra–simple applications

UNIT III:

RAMAN SPECTROSCOPY

Theory of Raman Scattering - Classical theory – molecular polarizability – polarizability ellipsoid - Quantum theory of Raman effect - rotational Raman spectra of linear molecule - symmetric top molecule – Stokes and anti-stokes line- SR branch -Raman activity of H_2O and CO_2 -Mutual exclusion principle determination of N_2O structure -Instrumentation technique and block diagram - structure determination of planar and non-planar molecules using IR and Raman techniques - FT Raman spectroscopy- SERS

UNIT IV:

RESONANCE SPECTROSCOPY

Nuclear and Electron spin-Interaction with magnetic field - Population of Energy levels - Larmor precession- Relaxation times - Double resonance- Chemical shift and its measurement - NMR of Hydrogen nuclei - Indirect Spin - Spin Interaction – interpretation of simple organic molecules – Instrumentation techniques of NMR spectroscopy – NMR in Chemical industries- MRI Scan Electron Spin Resonance: Basic principle –Total Hamiltonian (Direct Dipole- Dipole interaction and Fermi Contact Interaction) – Hyperfine Structure (Hydrogen atom) – ESR Spectra of Free radicals –g-factors – Instrumentation - Medical applications of ESR

UNIT V:

UV SPECTROSCOPY

Origin of UV spectra - Laws of absorption – Lambert Bouguer law – Lambert Beer law - molar absorptivity – transmittance and absorbance - Color in organic compounds- Absorption by organic Molecule -Chromophores -Effect of conjugation on chromophores - Choice of Solvent and Solvent effect - Absorption by inorganic systems - Instrumentation - double beam UV Spectro photometer -Simple applications

UNIT I

MICROWAVE SPECTROSCOPY

Rotational spectra of diatomic molecules - Rigid Rotor (Diatomic Molecules)- reduced mass – rotational constant - - Effect of isotopic substitution - Non rigid rotator – centrifugal distortion constant- Intensity of Spectral Lines- Polyatomic molecules – linear – symmetric asymmetric top molecules - Instrumentation techniques – block diagram -Information Derived from Rotational Spectra- Stark effect- Problems.

1.1 Rotational spectra:

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 (any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned.

The permitted energy values so called rotational energy levels may in principle be calculated for any molecule by solving the Schrödinger equation for the system represented by that molecule.

1.2 Rigid Rotor (Diatomic Molecules):

A rigid diatomic molecule means that the distance between the atoms (bond length) does not change during rotation. No vibrational movement is taking place during rotation.

Let us consider a diatomic molecule A—B in which the atoms A and B having masses m_1 and m_2 are joined together by a rigid bond of length $r_0 = r_1 + r_2$ (figure 1). The molecule A—B rotates about a point C, the centre of gravity: this is defined by the moment, or balancing, equation.

$$m_1 r_1 = m_2 r_2 \qquad \text{--------(1)}$$

$$r_0 = r_1 + r_2 \qquad \text{-------(2)}$$

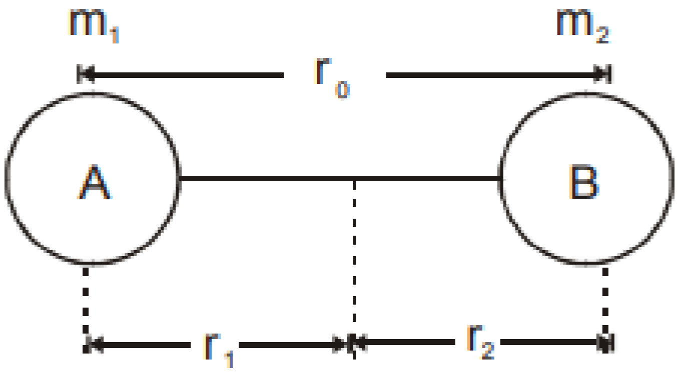

Figure 1.1 Rigid diatomic molecule

The moment of inertia about C is defined by

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$= m_2 r_2 \ r_1 + \ m_1 r_1 \ r_2$$

$$= r_2 \ r_1 (m_1 + m_2) \qquad \text{---------(3)}$$

From equation 2 and 3

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

therefore

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \qquad \text{and} \qquad r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad \text{------(4)}$$

from equation 3 and 4

$$r_1 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$= \mu r_0^2 \qquad \text{------(5)}$$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ and μ is called reduced mass of the system.

The above equation defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

By the use of the Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression

$$E_j = \frac{h^2}{8\pi^2 I} J (J + 1) \text{ Joules when } J = 0, 1, 2 \text{ ......} \qquad \text{----(6)}$$

In this expression h is Planck's constant, are I is the moment of inertia, either I_B or I_C, since both are equal. The quantity J, which can take integral values from zero upwards, is called the rotational quantum number and each level is (2J + 1) fold degenerate. Often it is convenient to analyse the rotational energy spectrum in wave number units. Therefore we may write.

$$\varepsilon_j = \frac{E_j}{hc}$$

$$= \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \qquad J = 0, 1, 2.... \qquad \text{------------(7)}$$

$$= B J(J+1) \text{ cm}^{-1} \qquad J = 0, 1, 2.... \qquad \text{------------(8)}$$

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

Substitute J = 0 ; $E_j = 0$

J = 1 ; $E_j = B(1+1) = 2B$

J = 2 ; $E_j = B\,2\,(2+1) = 6B$

J = 3 ; $E_j = B\,3\,(3+1) = 12B$

J = 4 ; $E_j = B\,4\,(4+1) = 20B$

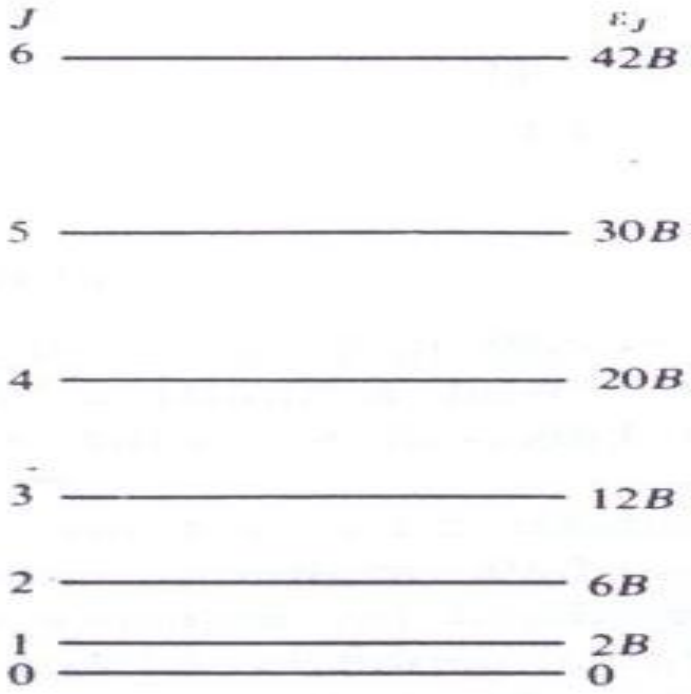

Figure 1.2 Rotational energy Spectrum

Selection rule:

$\Delta J = \pm 1$

$$E_J \rightarrow E_{J+1}$$

$$E_{J \rightarrow E_{J+1}} = B\,(J+1)\,(J+2) - B\,J\,(J+1)$$

$$= 2\,B\,(J+1)$$

Absorption process:

$J = 0 \rightarrow J = 1 \quad = 2\,B$

$J = 1 \rightarrow J = 2 \quad = 4\,B$

$J = 2 \rightarrow J = 3 \quad = 6\,B$

J = 3 → J = 4 = 8 B

Emission process:

J = 1 → J = 0 = 2 B

J = 2 → J = 1 = 4 B

J = 3 → J = 2 = 6 B

J = 4 → J = 3 = 8 B

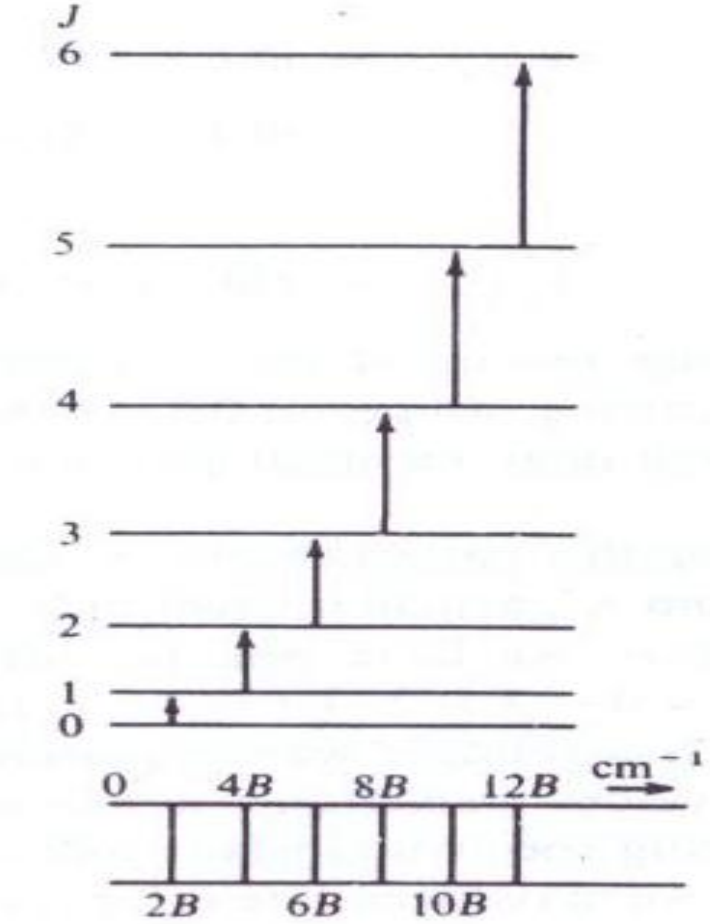

Figure 1.3 Rotational energy levels

1.3 Effect of isotopic substitution:

When a particular atom in a molecule is replaced by its isotope — an element identical in every way except for its atomic mass — the resulting substance is identical chemically with the original.

In particular there is no appreciable change in inter nuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and *B* value for the molecule.

Considering carbon monoxide as an example, we see that on going from $^{12}C^{16}O$ to $^{13}C^{16}O$ there is a mass increase and hence a decrease in the *B* value. If we designate the "C molecule with a prime we have $B > B'$.

This change will be reflected in the rotational energy levels of the molecule and Figure shows, the relative lowering of the "C levels with respect to those of "C. Plainly, as shown in Figure 1.4 , the spectrum of the heavier species will show a smaller separation between the lines ($2B^1$) than that of the lighter one (2B). Again the effect has been much exaggerated for clarity, and the transitions due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam et al., as already stated, found the first rotational absorption of $^{12}C^{16}O$ to be at 3.842 35 cm', while that of $^{13}C^{16}O$ was at 3.673 37 cm '. The values of *B* determined from these figures are:

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

where the prime refers to the heavier molecule**.**

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} . \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12-00, we have

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

from which m', the atomic weight of carbon -13, is found to be 13 - 0007. This is within 0.02 per cent of the best value obtained in other ways.

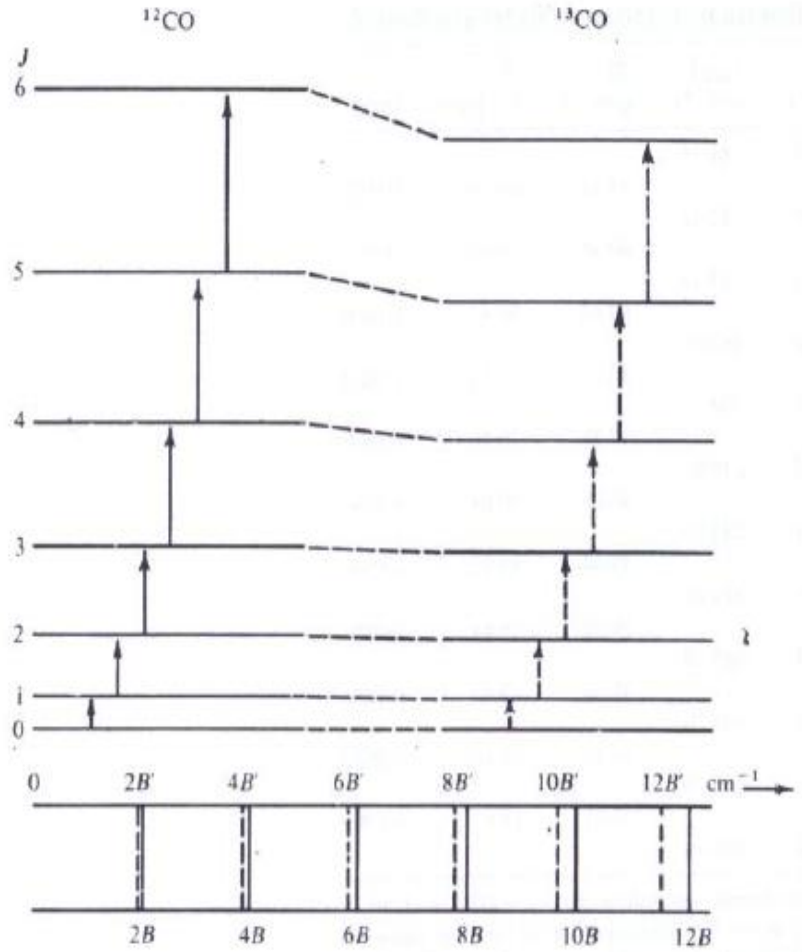

Figure 1.4 Energy Levels

1.4 Intensity of Spectral Lines:

The intensity of a spectral line is proportional to the number of molecules in the initial state. The number of molecules in the energy state E_J at temperature T is given by

$$N_J = N_0 \, e^{\frac{-B\,J\,(J+1)hc}{K_B\,T}}$$

where N_0 is the number of molecules in the state J = 0. The degeneracy of the J t^{h} state is (2J + 1). Taking degeneracy of the J t^{h} state into consideration, above formula for population of J t^{h} state becomes

$$N_J = 2\,J\,(J+1)N_0 \, e^{\frac{-B\,J\,(J+1)hc}{K_B\,T}}$$

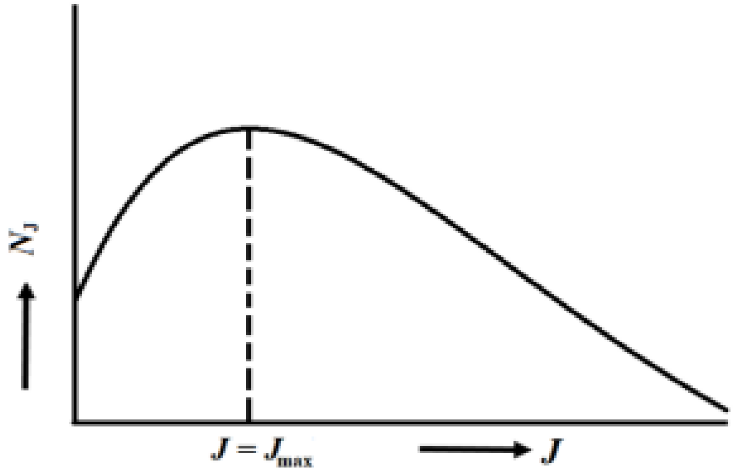

Figure 1.5 Intensity of Spectral Lines

1.5 Non rigid rotator:

The Schrödinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_j = \frac{h^2}{8\pi^2 Ic} \text{ J (J + 1)} - \frac{h}{32\,\pi^4 I\ r^2\,k} \text{ J (J + 1)}^2$$

$$\varepsilon_j = \frac{E_j}{hc}$$

$$= \text{B J (J + 1) – D J}^2 \text{ (J + 1)}^2 \text{ cm}^{-1}$$

where the rotational constant, B, is as defined previously, and the centrifugal distortion constant D, is given by:

$$D = \frac{h^3}{32\,\pi^4\,I^2\ r^2\,k\,c} \text{ cm}^{-1}$$

which is a positive quantity. The above equation applies for a simple harmonic force field only; if the force field is anharmonic, the expression becomes:

$$\varepsilon_j = BJ(J + 1) - DJ^2(J + 1) + H^{J3} (J + 1)^3 + KJ^4(J + 1)^4 \text{--- -----cm}^{-1}$$

where H, K, etc, are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D.

From the defining equations of B and D it may be shown directly that

$$D = \frac{16\,B^3\pi^2\ \mu c^2}{k}$$

$$= \frac{4\,B^3}{\overline{\omega}^2}$$

where $\overline{\omega}^2$ is the vibrational frequency of the bond, Selection rule:

$$E_{J\to J+1} = B(J+1)(J+2) - B\,J\,(J+1) - D[(J+1)^2\,(J+2)^{2\,+} - J^2\,(J+1)^2\,]$$

$$= 2\,B\,(J+1) - 4\,D\,(J+1)^3$$

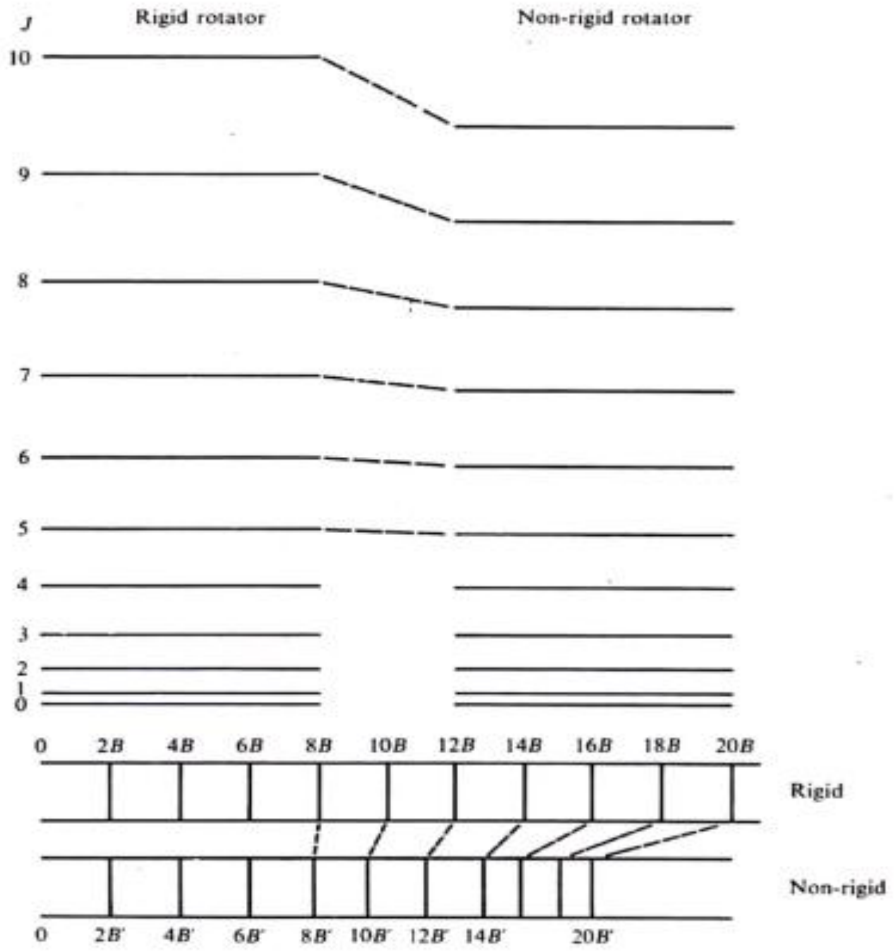

Figure 1.6 Non rigid rotator Energy Levels

1.6 Polyatomic molecules:

The rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular direction through the centre of gravity - the principal axes of rotation. Thus a body has three principal moments of inertia, one about each axis, usually designated I_A , I_B and I_C .

Polyatomic molecules are broadly divided into four classes:

(i) Linear Molecules

(ii) Symmetric Top Molecules

(iii) Asymmetric Top Molecules

Linear molecules

As the name suggests, in this case, all the atoms of the molecules are arranged in a straight line. Some of the molecules of this category are HCl, CO_2, OCS, HCN, C_2H_2 etc. The three directions of rotation may be taken as

(a) about the bond axes

(b) end-over-end rotation in the plane of the paper and

(c) end-over-end rotation at right angles to the plane.

As the nuclei of the atoms which give the main contribution to the mass are situated in the axis A, the moment of inertia about this axis is approximately zero. i.e. $I_A= 0$.

The moments of inertia I_B and I_C correspond to the end- over end rotation of the molecule and therefore they are equal. Thus, for a linear molecule $I_A= 0$ and $I_B = I_C$.

Let us consider the rotation of OCS molecule. Figure1.7 shows the molecule, where r_0 , r_c and r_s represent the distances of the atoms from the centre of gravity.

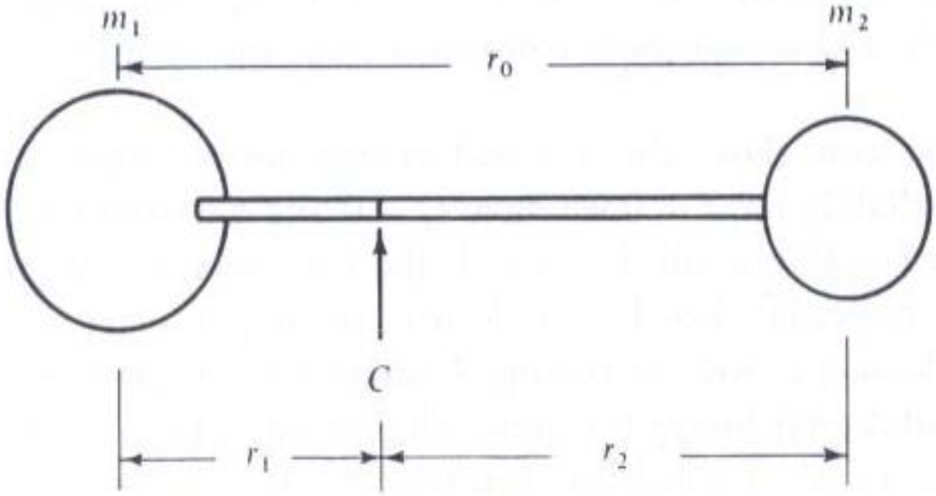

Figure 1.7 **Linear molecule (OCS)**

Consideration of moments gives

$$m_0r_0 + m_cr_c = m_sr_s \quad \text{---------(1)}$$

Where m_i is the mass of atom i. the moment of inertia is:

$$I = m_0{r_0}^2 + m_c{r_c}^2 + m_s{r_s}^2 \quad \text{------(2)}$$

From the figure

$$r_0 = r_{c0} + r_c$$

$$r_s = r_{cs} - r_c \quad \text{-------(3)}$$

r_{c0} and r_{cs} are the bond lengths of the molecules.

Substitute equation (3) in equation (1)

$$(m_c + m_0 + m_s) r_c = m_sr_{cs} - m_or_{co}$$

$$M r_c = m_sr_{cs} - m_or_{co} \quad \text{----------(4)}$$

Where M is the total mass of the molecules. Substituting equation (2) in (1)

$$I = m_0 (r_{c0} + r_c)^2 + m_c{r_c}^2 + m_s(r_{cs} - r_c)^2$$

$$= \mathrm{M\,r_c}^2 + 2\,\mathrm{r_c}(\,\mathrm{m_o r_{co}} - \mathrm{m_s r_{cs}}\,) + \mathrm{m_o r_{co}}^2 + \mathrm{m_s r_{cs}}^2$$

Substituting r_c from equation (4)

$$\mathrm{I} = \mathrm{m_0 r_{co}}^2 + \mathrm{m_s r_{cs}}^2 - \frac{(\,\mathrm{m_o r_{co}} - \mathrm{m_s r_{cs}}\,)^2}{\mathrm{M}} \qquad \text{-------(5)}$$

Considering the isotopic molecule, ^{18}OCS, may writ $m_0{}'$ for m_o throughout equation (5) is

$$\mathrm{I}' = \mathrm{m_0}'\mathrm{r_{co}}^2 + \mathrm{m_s r_{cs}}^2 - \frac{(\,\mathrm{m_0}'\mathrm{r_{co}} - \mathrm{m_s r_{cs}}\,)^2}{\mathrm{M}} \qquad \text{-------(6)}$$

And now solve for r_{co} and r_{cs}, extracted a value for I' from the microwave spectrum of isotopic molecule.

Symmetric top molecule:

The rotational energy levels of this type of molecule are more complicated than those of linear molecule, because of their symmetry; their pure rotational spectra are still relatively simple.

For example, methyl fluoride

$$\mathrm{I_B} = \mathrm{I_C} \neq \mathrm{I_A} \qquad\qquad \mathrm{I_A} \neq 0$$

There are two directions of rotation in which the molecule might absorb or emit energy – that about the amine symmetry axis and that perpendicular to this axis.

Thus need two quantum numbers to describe the degree of rotation, one for I_A and one for $\mathrm{I_B}$ or $\mathrm{I_C}$ however, it turns out to be very convenient mathematically to have a quantum number to represent the total angular momentum of the molecule, which is the sum of the separate angular momenta about the two different axes. This is usually chosen to be the quantum number J. reverting for a moment to linear molecules, there used J to represent the end-over-end rotation of molecules.

However, this was the only sort of rotation allowed, s o it is quite consistent to use J, in general, to represent the angular momentum. It is then conventional to use K to represent the angular momentum about the top axis.

Asymmetric top molecules:

Since spherical tops show no microwave spectrum the only other class of molecule of interest here is the asymmetric top which has all three moments of inertia different.

The best method of attack so far has been to consider the asymmetric top as falling somewhere between the oblate and prolate symmetric top; interpolation between the two sets of energy levels of the latter leads to first approximation of the energy levels and hence spectrum of the asymmetric molecule.

It suffices to say that arbitrary methods such as this have been quite successful.

1.7 Instrumentation techniques:

- Source
- Monochromator
- Beam direction
- Sample
- Detector

Source and monochromator:

The usual source in this region is the klystron valve which, emits radiation of only a very narrow frequency range is called monochromatic and acts as its own monochromator. The actual emission frequency is variable electronically and hence a spectrum may be scanned over a limited range of frequencies using a single klystron.

One disadvantages of this source is that the total energy radiated is very small of the order of milliwatts only. However, since all this is concentrated into a narrow frequency band a sharply tuned detector can be sufficiently activated to produce a strong signal.

Beam direction:

This is achieved by the use of waveguides-hollow tubes of copper or silver usually of rectangular cross section-inside which the radiation is confined. The waveguides may be gently tapered or bent to allow focusing and directing of the radiation. Atmospheric absorption of the beam is considerable, so the system must be efficiently evacuated.

Sample and sample space:

In almost all microwave studies so far the sample has been gaseous. However, pressures of 0.01 mmHg are sufficient to give a reasonable absorption spectrum, so many substances which are usually thought of as solid or liquid may be examined provided their vapour pressures are above this value. The sample is retained by very this mica window in a piece of evacuated waveguide.

Detector:

It is possible to use an ordinary superheterodyne radio receiver as detector, provided this may be tuned to the appropriate high frequency; however, a simple crystal detector is found to be more sensitive and easier to use. This detects the radiation focused upon it by the waveguide and the signal it gives is amplified electronically for display on an oscilloscope or for permanent record on paper.

UNIT II

INFRA-RED SPECTROSCOPY

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Vibrational spectroscopy is due to the interaction of matter with the Infra red region of the electromagnetic spectrum.

Spectral Range of IR Radiation:

- Near IR: 12000 cm^{-1} to 4000 cm^{-1}
- MID IR: 4000 cm^{-1} to 620 cm^{-1}
- Far IR: 300 cm^{-1} to 10 cm^{-1}

The mid IR region is used for the sample analysis in IR spectroscopy.

2.1 Vibrations of simple harmonic oscillator:

The compression and extension of a bond may be like the behaviour of spring and may extend the analogy by assuming that the bond, like a spring, obeys Hook's law. It may be write

$$f = - k (r - r_{eq}) \qquad \text{-------------(1)}$$

where f is the restoring force, k the force constant and r the inter nuclear distance.

In this case the energy cure is parabolic and has the form

$$E = ½ k (r - r_{eq})^2 \qquad \text{----------(2)}$$

Plotting the energy according to equation (2). The zero of curve and equation is found at $r = r_{eq}$ and any energy in excess of this, for example ε_1. arises because of extension or compression of the bond.

An elastic bond, like a spring, has certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion.

Classically, it is easy to show that the oscillation frequency is;

$$\omega_{osc} = \frac{1}{2\,\pi}\sqrt{\frac{k}{\mu}}\ Hz \qquad \text{------(3)}$$

Where μ is the reduced mass of the system.

To convert

$$\overline{\omega}_{osc} = \frac{1}{2\,\pi\,c}\sqrt{\frac{k}{\mu}}\ cm^{-1} \qquad \text{------(4)}$$

Vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the schrodinger equation.

For the simple harmonic oscillator these turn out to be;

$$E_v = \left(v + \frac{1}{2}\right) h\omega_{osc} \quad \text{joule} \qquad \text{------(5)}$$

Where v is the vibrational quantum number. Converting to the spectroscopic units,

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\ \overline{\omega}_{osc} \quad \text{cm}^{-1} \qquad \text{-----(6)}$$

In particular we should notice that the lowest vibrational energy, obtained by putting v= 0 in equation 5 and 6 we get

$$E_0 = \frac{1}{2}\,h\omega_{osc} \quad \text{joule}$$

$$\varepsilon_0 = \frac{1}{2}\ \overline{\omega}_{osc}$$

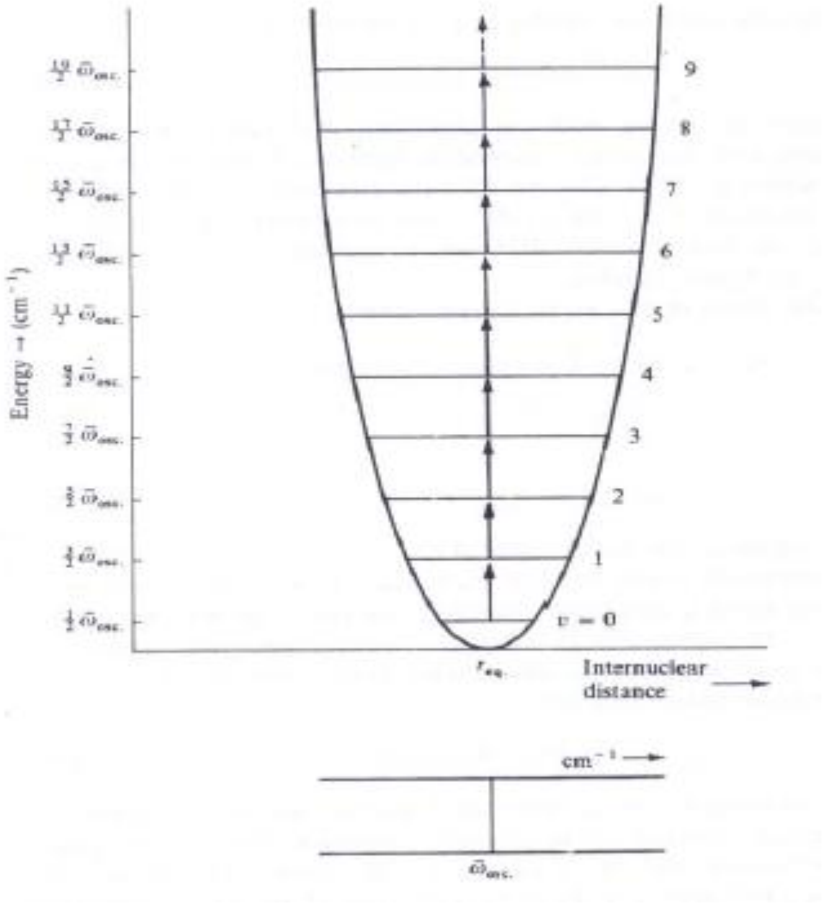


Figure 2.1 Vibrations of simple harmonic oscillator:

The quantity $\frac{1}{2}\ \bar{\omega}_{osc}$ is known as the **zero-point energy**.

2.2 Anharmonic oscillator:

Real molecule do not obey exactly the laws of simple harmonic motion; real bonds, although elastic, are not so homogeneous as to obey Hook's law. If the bond between atoms is stretched, for instance, there comes a point at which it will break – the molecule dissociates into atoms.

Thus although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes - say greater than 10 per cent of the bond length – a much more complicated behaviors must be assumed.

From the Figure 2.2 the shape of the energy curves for typical diatomic molecules, together with (dashed line) the ideal, simple harmonic parabola.

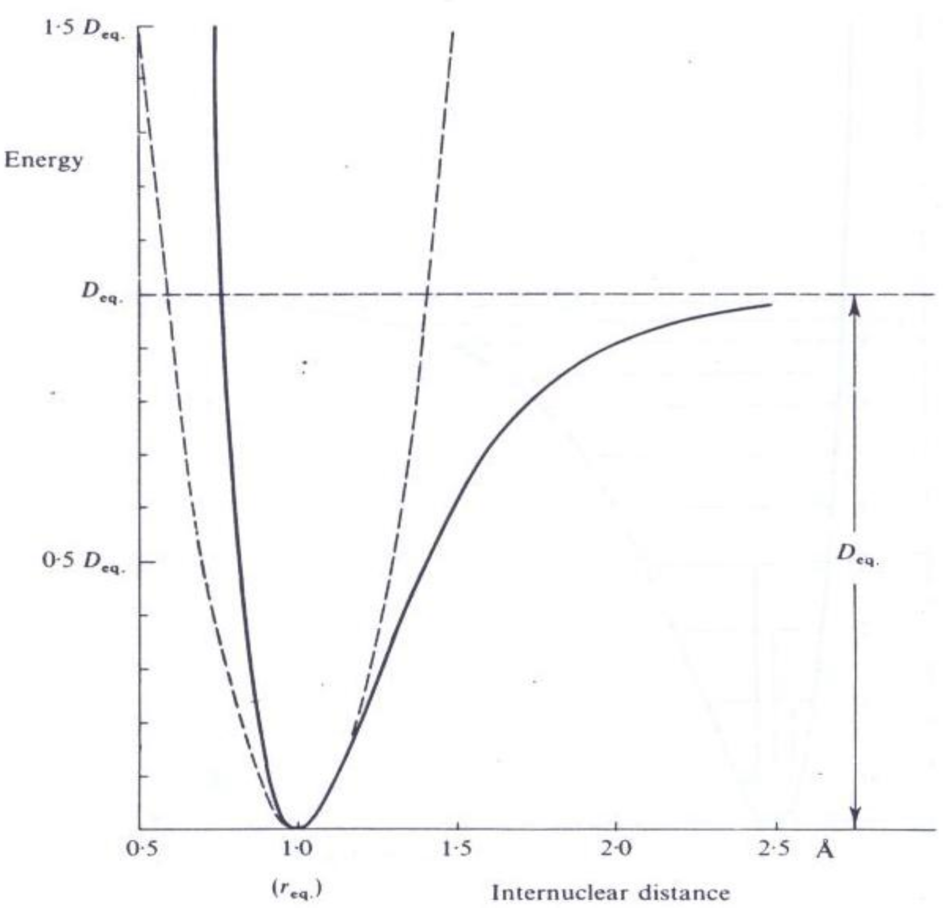


Figure 2.2 Energy curve

A purely empirical expression which fits this curve to a good approximation was derived by P.M. Morse. and is called Morse function:

$$E = D_{eq} [1 - \exp \{a (r_{eq} - r)\}]^2 \qquad \text{----------(1)}$$

a is a constant for particular molecule and D_{eq} is the dissociation energy.

The Schrödinger equation, the pattern of the allowed vibrational energy levels is

$$\varepsilon_v = \left(v + \tfrac{1}{2}\right) \bar{\omega}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{\omega}_e\, x_e \quad \text{cm}^{-1} \qquad \text{-----(2)}$$

$\bar{\omega}_e$ is an oscillation frequency , x_e is the corresponding anharmonicity constant which for bond stretching vibrations, is always small and positive.

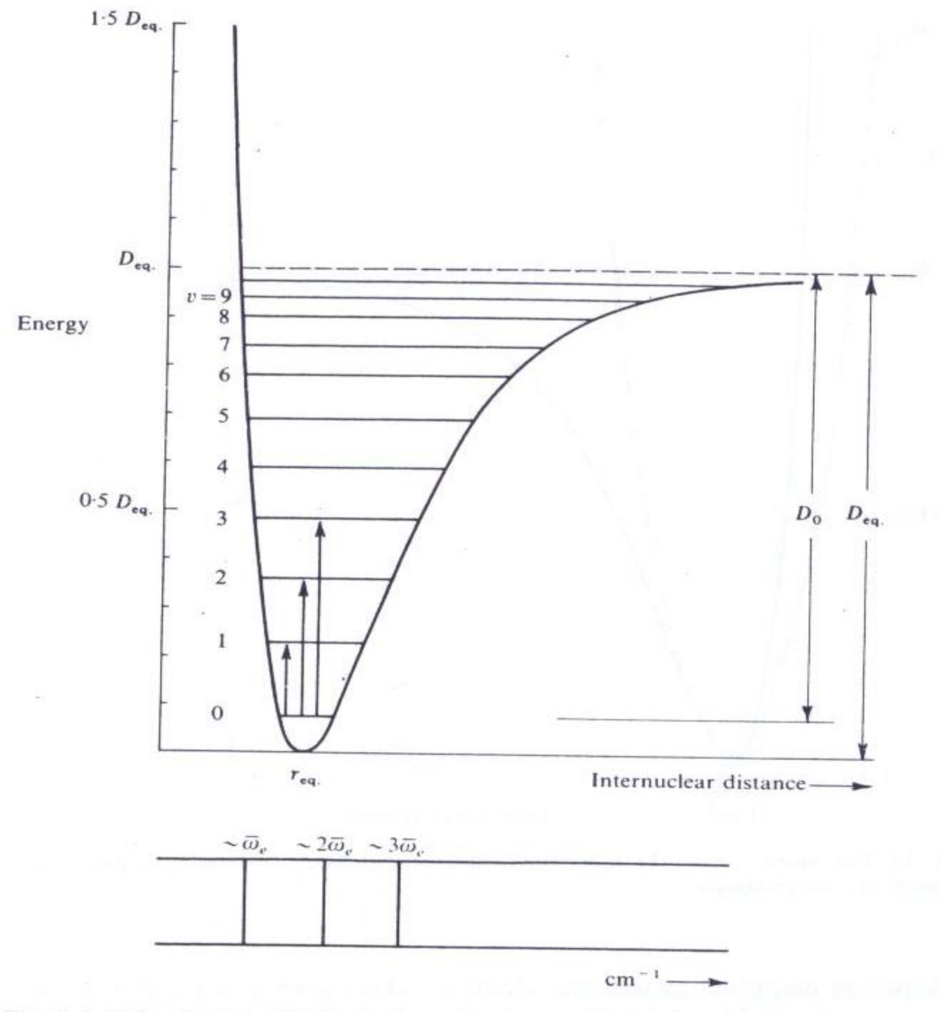


Figure 2.3 ***Anharmonic oscillator***

Rewrite the equation (2) for the anharmonic oscillator:

$$\varepsilon_v = \bar{\omega}_e \left\{1 - \left(v + \tfrac{1}{2}\right) x_e\right\} \left(v + \tfrac{1}{2}\right) \qquad \text{--------(3)}$$

And compare with the energy levels of the harmonic oscillator we have

$$\overline{\omega}_{osc} = \overline{\omega}_e \left\{1 - \left(v + \tfrac{1}{2}\right) x_e\right\} \qquad \text{-----(4)}$$

The anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v.

For hypothetical energy state obtained by putting $v = -\frac{1}{2}$ the molecule would be at the equilibrium point with zero vibrational energy.

Its oscillation frequency would be:

$$\overline{\omega}_{osc} = \overline{\omega}_e$$

$\overline{\omega}_e$ may be defined as the (hypothetical) equilibrium oscillation frequency of the anharmonic system.

For v=0

$$\overline{\omega}_0 = \overline{\omega}_e \left(1 - \frac{1}{2} x_e\right)$$

And $$\varepsilon_0 = \tfrac{1}{2}\, \overline{\omega}_e \left\{1 - \tfrac{1}{2} x_e\right\}$$

The selection rule for the anharmonic oscillator are

$$\Delta v = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \ldots\ldots\ldots\ldots\ldots\ldots$$

Thus they are the same as for the harmonic oscillator, with the additional possibility of larger jumps. However, are predicted by theory and observed in practice to be of rapidly diminishing probability and normally only the lines of $\Delta v = \pm 1, \pm 2, \pm 3$ at the most have observable intensity.

Further, the spacing between the vibrational level is the order of 10^3 cm $^{-1}$ and at room temperature, we use the Boltzmann distribution to show.

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left\{\frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^{3}}{1.38 \times 10^{-23} \times 300}\right\}$$

$$\approx \exp(-4.8)$$

$$\approx 0.008.$$

In other words, the population of the v =1 is nearly 0.01 or one percent of the ground state population.

1. $v = 0 \rightarrow v = 1, \Delta v = +1$

$$\Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$$

$$= \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e\, x_e - \{\frac{1}{2}\, \bar{\omega}_e - \left(\frac{1}{2}\right)^2 \bar{\omega}_e\, x_e\}$$

$$= \bar{\omega}_e\, (1 - 2x_e)\ \text{cm}^{-1}$$

2. $v = 0 \rightarrow v = 1, \Delta v = +2$

$$\Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0}$$

$$= \left(2 + \frac{1}{2}\right) \bar{\omega}_e - \left(2 + \frac{1}{2}\right)^2 \bar{\omega}_e\, x_e - \{\frac{1}{2}\, \bar{\omega}_e - \left(\frac{1}{2}\right)^2 \bar{\omega}_e\, x_e\}$$

$$= \overline{2\omega}_e\, (1 - 3x_e)\ \text{cm}^{-1}$$

3. $= 0 \rightarrow v = 3, \Delta v = +3$

$$\Delta\varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0}$$

$$= \left(3 + \frac{1}{2}\right) \bar{\omega}_e - \left(3 + \frac{1}{2}\right)^2 \bar{\omega}_e\, x_e - \{\frac{1}{2}\, \bar{\omega}_e - \left(\frac{1}{2}\right)^2 \bar{\omega}_e\, x_e\}$$

$$= 3\bar{\omega}_e\, (1 - 4x_e)\ \text{cm}^{-1}$$

These three transitions are shown in above figure. To a good approximation, since $x_e \approx 0.001$ the three spectral lines lie very close to $\bar{\omega}_e, 2\,\bar{\omega}_e, 3\,\bar{\omega}_e$.

The line near $\bar{\omega}_e$ is called the **fundamental absorption** while those near $2\,\bar{\omega}_e\ and\ 3\,\bar{\omega}_e$ are called **first and second overtones** respectively.

2.3 Diatomic Vibrating Rotator:

The combined rotational-vibrational energy is simply the sum of the separate energies;

$$E_{total} = E_{rot} + E_{vib} \qquad \text{(joule)}$$

$$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib} \qquad (\text{cm}^{-1}) \qquad \text{----(1)}$$

Taking the separate expression of $\varepsilon_{rot}, \varepsilon_{vib}$

$$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v$$

$$= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \ldots\ldots + \left(v + \tfrac{1}{2}\right)\bar{\omega}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{\omega}_e x_e \ cm^{-1} \quad \text{------(2)}$$

Ignore the small centrifugal distortion constant D, H etc.

$$\varepsilon_{total} = \varepsilon_{J,v}$$

$$= BJ(J+1) + \left(v + \tfrac{1}{2}\right)\bar{\omega}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{\omega}_e x_e \qquad \text{-----(3)}$$

The rotational levels are sketched in below figure.

For the two lowest vibrational levels, v = 0 and v =1.

The selection rule for the combined motions is same as those for each separately;

$$\Delta v = \pm 1, \pm 2 \ \text{etc.,} \qquad \Delta J = \pm 1, \qquad \text{----------(4)}$$

In below figure drawn some of the relevant energy levels and transitions, designating rotational quantum numbers in the v = 0 state as J ″ and in the v = 1 state as J′. The use of a single prime for the upper state and a double for the lower state is conventional in all branches of spectroscopy.

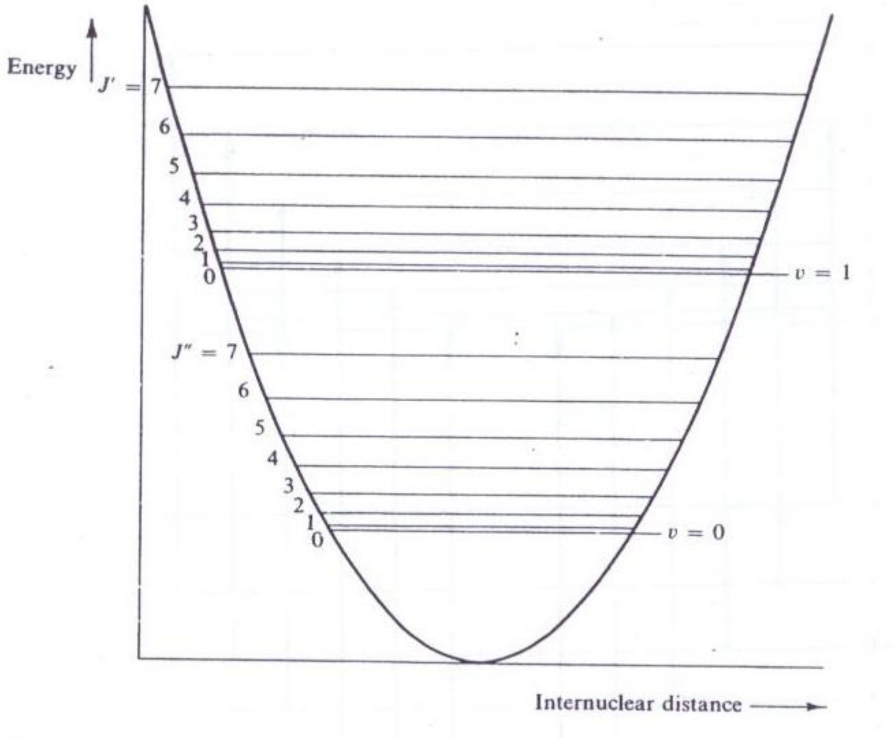


Figure 2.4 Diatomic Vibrating Rotator

An analytical expression for the spectrum may be obtained by applying the selection rule to the energy levels. Considering only the v = 0 → v =1 transition we have in general:

$$\Delta\varepsilon_{J,v} = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0}$$

$$= B\,J''\,(J' + 1\,) + \frac{1}{2}\ \bar{\omega}_e - 2\,\frac{1}{4}\,\bar{\omega}_e x_e - \{BJ(J+1) + \frac{1}{2}\ \bar{\omega}_e - 2\,\frac{1}{4}\,\bar{\omega}_e x_e\}$$

$$= \ \bar{\omega}_0 + B\,(J' - J)\,(J'+J+1)$$

We write $\bar{\omega}_0$ for $\bar{\omega}_e(1 - 2x_e)$.

We should note that taking B to be identical in the upper and lower vibrational states is direct consequence of the Born -Oppenheimer approximation- rotation is unaffected by vibrational changes.

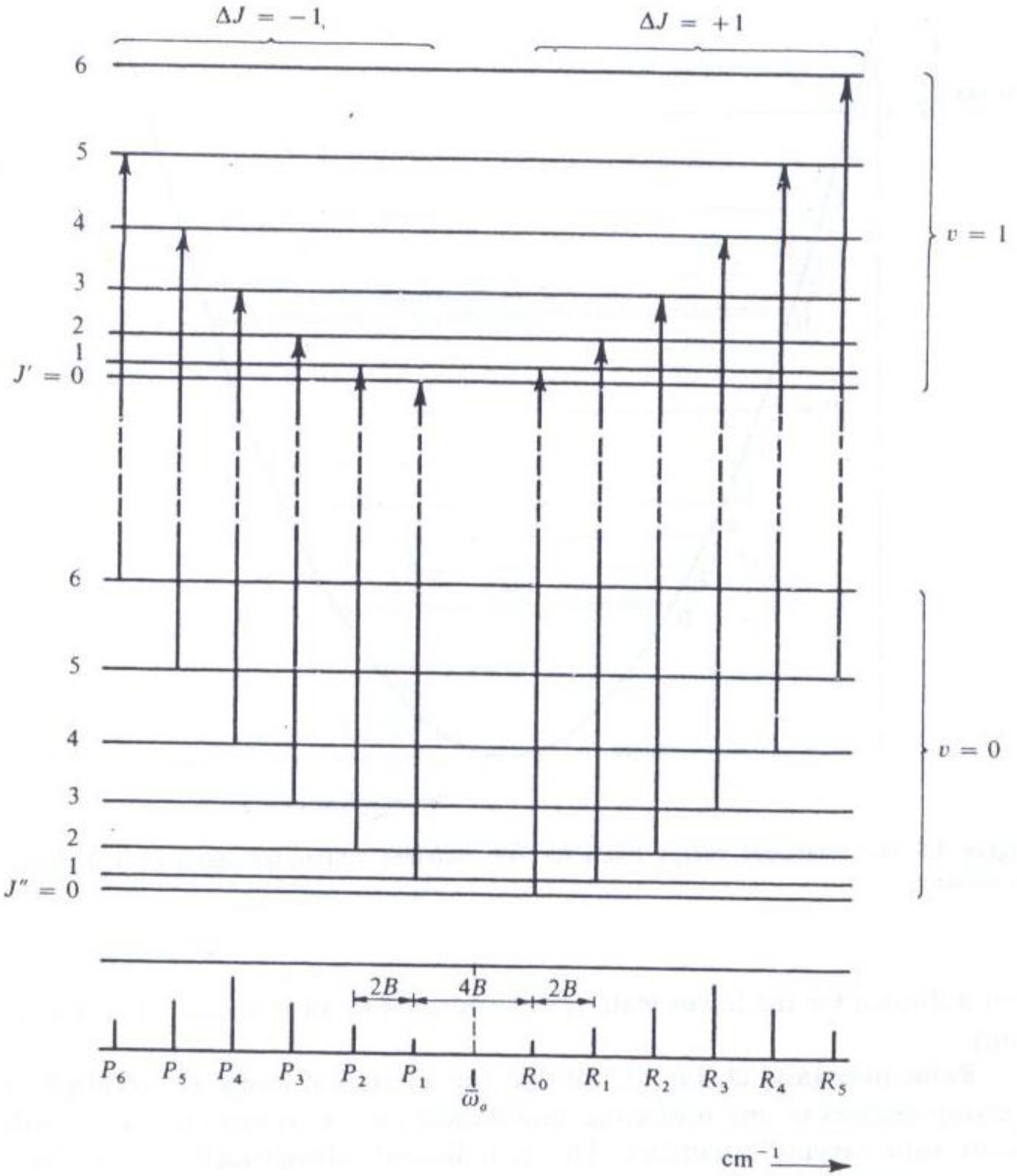


Figure 2.5 **Diatomic Vibrating Rotator** energy levels

1. ΔJ = +1 i.e.,

$$J' = J+1 \text{ or } J - J'' = +1; \text{ hence}$$

$$\Delta\varepsilon_{J,v} = \bar{\omega}_0 + 2B\,(J'' + 1)$$

2. $\Delta J = -1$ i.e.,

$$J'' = J'+1 \text{ or } J' - J'' = -1;\ \text{hence}$$

$$\Delta\varepsilon_{J,v} = \bar{\omega}_0 - 2\,B\,(J'' + 1)$$

These two expressions may conveniently be combined into:

$$\Delta\varepsilon_{J,v} = \bar{\nu}_{spect} = \bar{\omega}_0 + 2\,B\,m$$

Where m replacing $J'' + 1$ in above equation and $J' + 1$ has positive values for $\Delta J = +1$ and is negative if $\Delta J = +1$. Particularly that m cannot be zero since this would imply values of j' and J" to be -1. The frequency $\bar{\omega}_0$ is usually called the band origin or band centre.

ΔJ =	-2	-1	0	+1	+2	
	O	P	Q	R	S	branch

The P and R notation with lower J (J") value as a suffix is illustrated on the diagrammatic spectrum of above figure. This is the conventional notation for such spectra.

2.4 Fundamental modes of vibration of H_2O and CO_2 :

H_2O is non-linear and triatomic. Also 3 N – 6 = 3 allowed vibrational modes, the arrows attached 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 of the molecule; in general a normal vibration is defined as the molecular motion in which all the atoms move in phase and with the same frequency.

The figure shows the nature of dipole changes for the three vibrations of water and justifies the labels parallel or perpendicular attached to them.

Thus the symmetric vibration of H_2O are labelled v_1 for the highest fully symmetric frequency (3651.7 cm^{-1}) and v_2 for the next highest (1595.0 cm^{-1}) . The antisymmetric vibration at 3755.8 cm^{-1} is then labelled v_3.

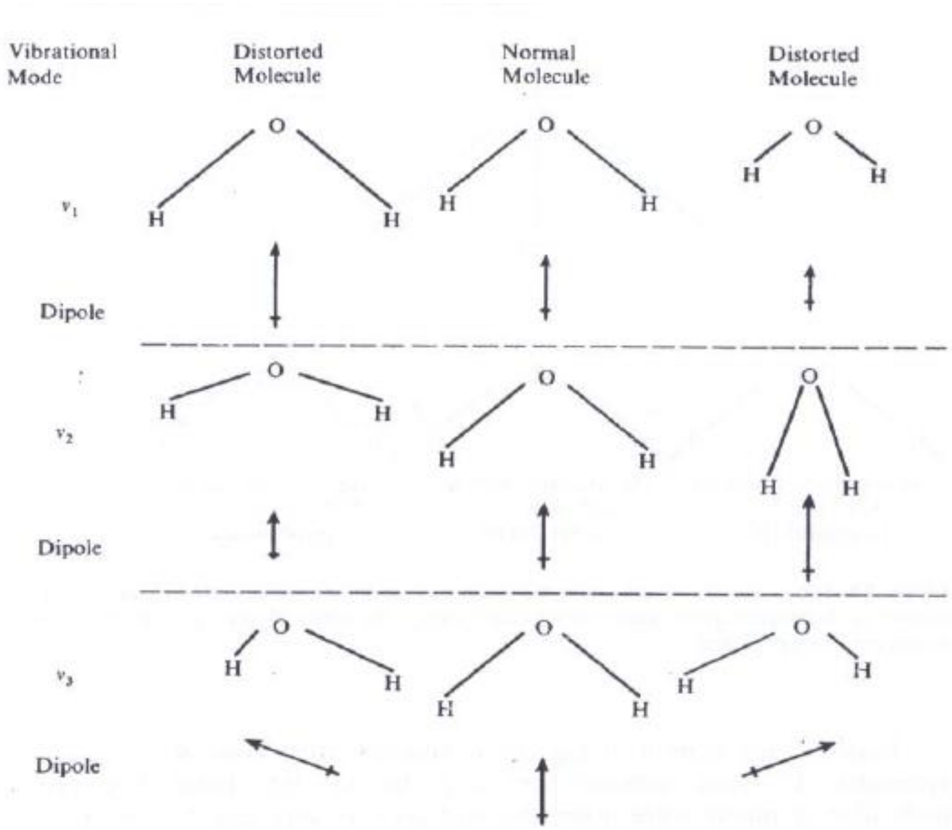
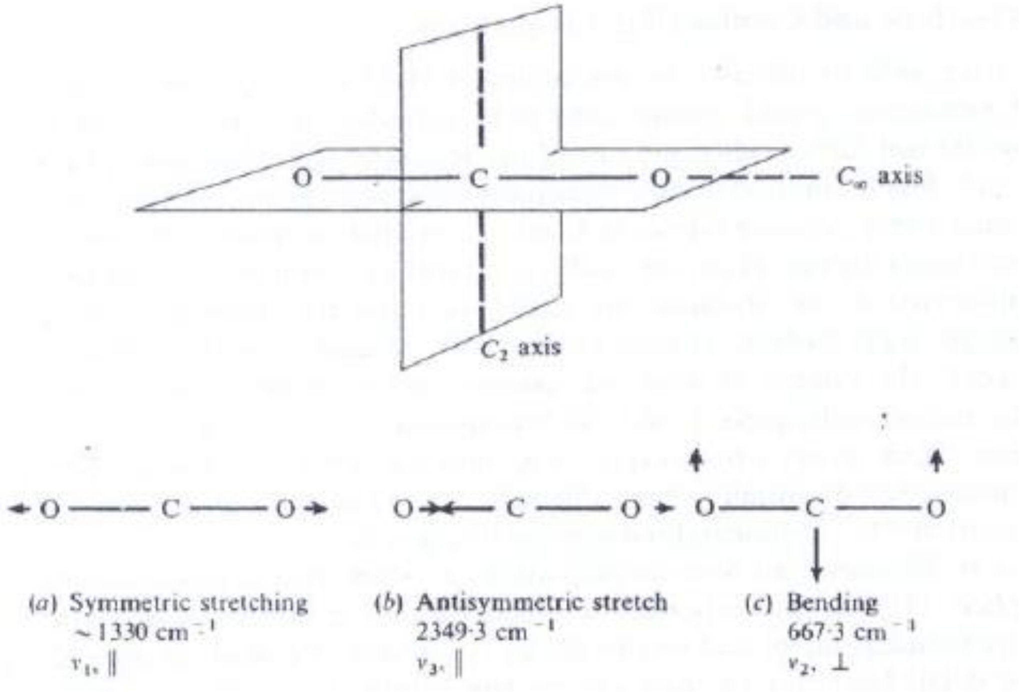


Figure 2.6 Fundamental modes of vibration of H_2O

CO_2 :

For this molecule there are two different sets of symmetry axes. There is an infinite number of two fold axed (C_2) passing through the carbon atom at right angles to the bond direction, and there is an ∞ fold axes(C_∞) passing through the bond axis itself.



(*a*) Symmetric stretching $\sim 1330\ \mathrm{cm}^{-1}$ ν_1, $\parallel$

(*b*) Antisymmetric stretch $2349{\cdot}3\ \mathrm{cm}^{-1}$ ν_3, $\parallel$

(*c*) Bending $667{\cdot}3\ \mathrm{cm}^{-1}$ ν_2, $\perp$

Figure 2.7 Fundamental modes of vibration of CO_2

For linear triatomic molecules 3 N – 5 = 4 and we would expect four vibrational modes. However, consideration shows that v_2 in fact consists of two vibrations – one in the plane of paper as drawn and the other in which the oxygen atoms move simultaneously into and out of the plane. The two sorts of motion are, of course, identical in all respect direction and are termed degenerate;

2.5 IR Spectrophotometer Instrumentation (Double Beam Spectrometer):

The device is referred to as a “double-beam” spectrophotometer due to its utilization of two light beams:

- **Reference beam**: The beam is transmitted through the reference standard for the purpose of monitoring the energy of the lamp.
- **Sample beam**: The aforementioned beam traverses the sample medium in order to reflect the absorption of said sample.

The samples used in IR spectroscopy can be either in the solid, liquid, or gaseous state.

• Solid samples can be prepared by crushing the sample with a mulling agent (KBr) which has an oily texture. A thin layer of this mull can now be applied on a salt plate to be measured.

• Liquid samples are generally kept between two salt (NaCl) plates and measured since the plates are transparent to IR light. Salt plates can be made up of sodium chloride, calcium fluoride, or even potassium bromide.

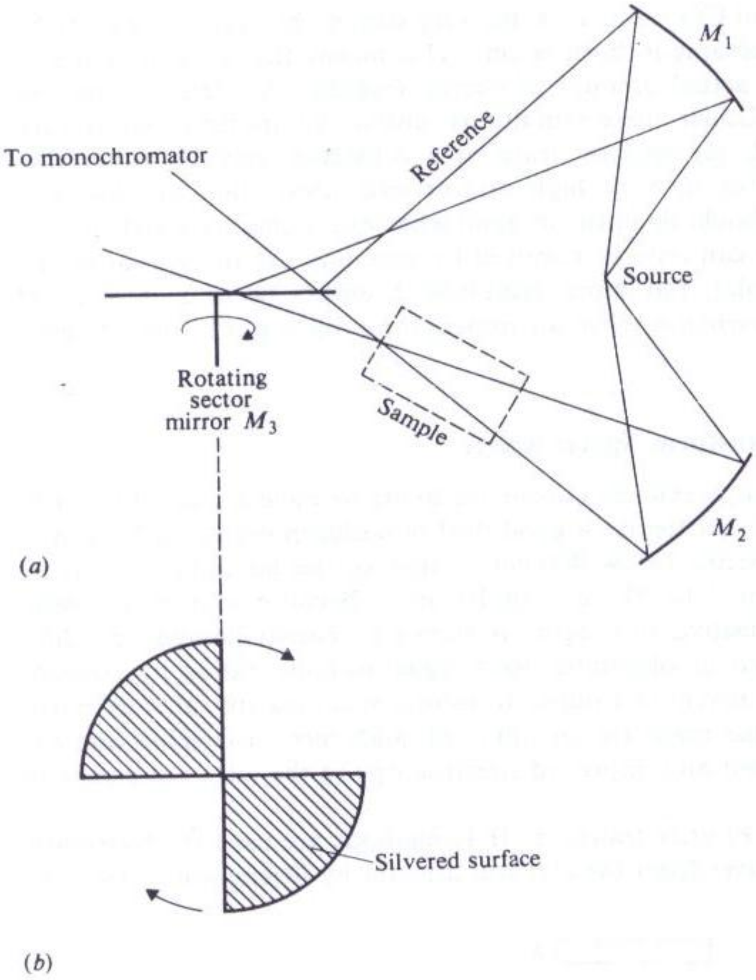


Figure 2.8 IR Spectrophotometer

- Since the concentration of gaseous samples can be in parts per million, the sample cell must have a relatively long path length, i.e. light must travel for a relatively long distance in the sample cell.
- Thus, samples of multiple physical states can be used in Infrared Spectroscopy

A beam of IR light from the source (Nernst Glower / Globar) is split into two and passed through the reference and the sample respectively.

- Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector

2.6 Fourier Transform Infrared Spectroscopy:

Fourier Transform Infrared (FTIR) spectroscopy is the preferred method of infrared spectroscopy. IR radiation is transmitted through a sample in infrared spectroscopy. The sample absorbs some of the infrared energy, and some of it is transferred (passed through). The resulting spectrum gives the sample a molecular fingerprint by displaying the molecule’s absorption and transmission.The instrumentation is given below. (Figure 2.9). It consists of the following

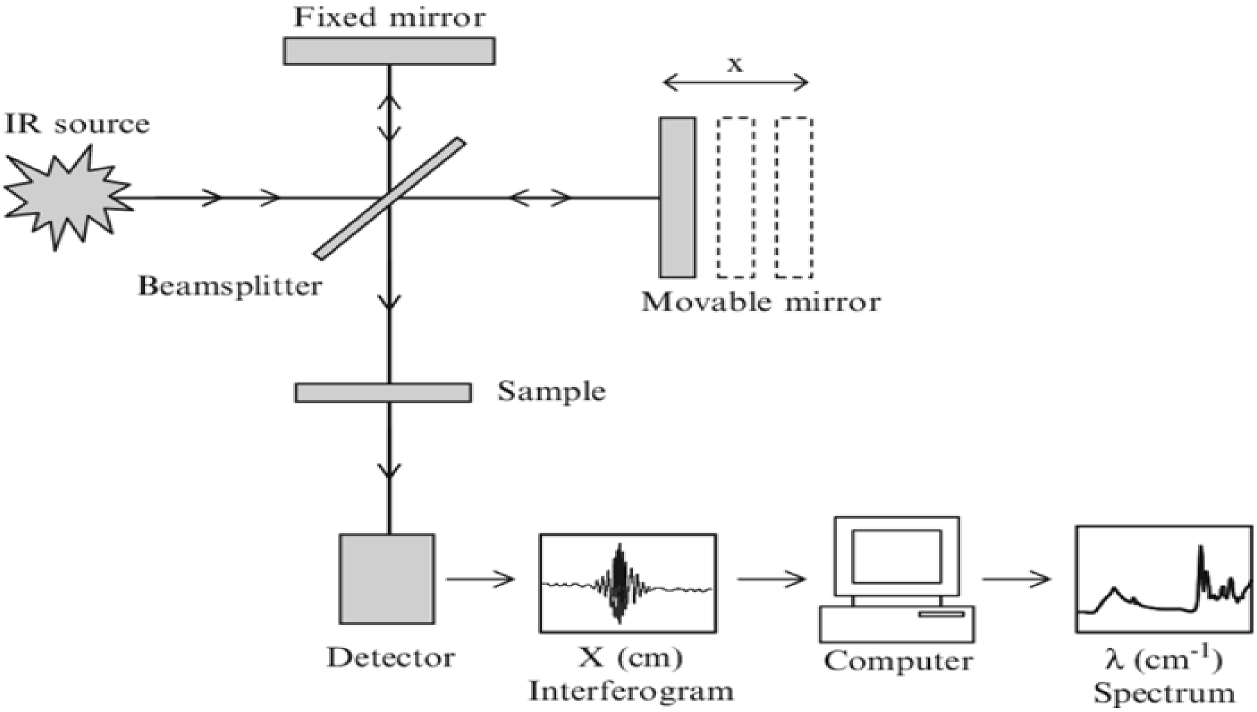


Figure 2.9 Fourier Transform Infrared Spectroscopy

The Source:

A broadband emitter, such as a mid-IR ceramic source, a far-infrared mercury lamp, or a near-infrared halogen lamp, is used as the light source.

The Interferometer

The Michelson interferometer consists of a beam splitter, a moving mirror, and a stationary mirror. The beam splitter divides the light beam into two halves, which are reflected by the moving and fixed mirrors before being recombined by the beam splitter.

As the moving mirror makes reciprocating movements, the optical path difference to the fixed mirror changes, causing the phase difference to shift over time. Interference light is created in the Michelson interferometer by recombining the light beams. An interferogram records the intensity of the interference light, with the optical path difference recorded along the horizontal axis.

The interferometer, which consists of a beam splitter, a stationary mirror, and a moving mirror, is the heart of an FTIR spectrometer. The beam splitter is a semi-transparent mirror that divides a collimated light beam into two optical channels. Half of the light is transferred to the moving mirror and half is reflected to the stationary mirror. The moving and stationary mirrors reflect the two light beams, which are recombined at the beam splitter before going through the sample chamber and onto the detector.

The sample

Depending on the type of analysis being performed, the beam enters the sample compartment and is either transmitted through or reflected off the surface of the sample. This is where certain frequencies of energy that are unique to the sample are absorbed.

Detector

FTIR detectors are used to measure and convert the transmitted or reflected light from a sample into an electrical signal. The sensitivity and wavelength range of the data that can be captured is determined by the type and material of the detector.

The detector converts the beam into photons, which are then translated into measurable electric signals that the computer can read. The following are some examples of common detectors:

- Room temperature DLATGS is a regular analysis tool.
- Cooled liquid nitrogen is employed in sensitive applications.
- Si-photodiodes are employed in near-IR and visible infrared applications.
- Silicon far-infrared bolometers

UNIT III

RAMAN SPECTROSCOPY

Theory of Raman Scattering - Classical theory – molecular polarizability – polarizability ellipsoid - Quantum theory of Raman effect - rotational Raman spectra of linear molecule - symmetric top molecule – Stokes and anti-stokes line- SR branch -Raman activity of H_2O and CO_2 -Mutual exclusion principle determination of N_2O structure -Instrumentation technique and block diagram - structure determination of planar and non-planar molecules using IR and Raman techniques - FT Raman spectroscopy- SERS

Introduction:

Raman spectroscopy is an analytical technique where scattered light is used to measure the vibrational energy modes of a sample.

It is named after the Indian physicist C. V. Raman who, together with his research partner K. S. Krishnan, was the first to observe Raman scattering in 1928.

Raman spectroscopy can provide both chemical and structural information, as well as the identification of substances through their characteristic Raman ‘fingerprint’. Raman spectroscopy extracts this information through the detection of Raman scattering from the sample.

3.1 Theory of Raman Scattering:

When light is scattered by molecule, the oscillating electromagnetic field of a photon induces a polarization of the molecular electron cloud.

This leaves the molecule in a higher energy state with the energy of the photon transferred to the molecule.

This can be considered as the formation of a very short-lived complex between the photon and molecule which is commonly called the virtual state of the molecule.

The virtual state is not stable and the photon is re-emitted almost immediately, as scattered light.

Rayleigh Scattering

• In the vast majority of scattering events, the energy of the molecule is unchanged after its interaction with the photon.

• The energy, and therefore the wavelength, of the scattered photon is equal to that of the incident photon. • This is called elastic (energy of scattering particle is conserved) or Rayleigh scattering and is the dominant process.

Raman Scattering

• In a much rarer event (approximately 1 in 10 million photons) Raman scattering occurs, which is an inelastic scattering process with a transfer of energy between the molecule and scattered photon.

• If the molecule gains energy from the photon during the scattering (excited to a higher vibrational level) then the scattered photon loses energy and its wavelength increases which is called Stokes Raman scattering (after G. G. Stokes).

• Inversely, if the molecule loses energy by relaxing to a lower vibrational level the scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering.

• Quantum mechanically Stokes and Anti-Stokes are equally likely processes.

• However, with an ensemble of molecules, the majority of molecules will be in the ground vibrational level (Boltzmann distribution) and Stokes scatter is the statistically more probable process.

As a result, the Stokes Raman scatter is always more intense than the anti-Stokes and for this reason, it is nearly always the Stokes Raman scatter that is measured in Raman spectroscopy. The wavelength of the Raman scattered light will depend on the wavelength of the excitation light. This makes the Raman scatter wavelength an impractical number for comparison between spectra measured using different lasers.

3.2 Classical theory:

When an electrically neutral molecule is kept in an uniform electrical field, it is polarized. The extent of polarization is given by the induced dipole moment

$$\mu = \alpha . E$$

α – Polarizability of the molecule A second degree tensor

When a radiation of frequency ν is falling on a molecule, the electrical field felt by the molecule is

$$E = E_0 \sin 2\pi\nu\, t$$

This electrical field polarizes the molecule and makes it to oscillate with the same frequency.

The associated induced dipole moment is

$$\mu = \alpha.E$$

$$= \alpha E_0 \sin 2\pi\nu t$$

Such an oscillating dipole emits radiation of its own oscillation frequency, which is called Rayleigh Scattering.

If the molecule undergoes rotation or vibration also, then the polarizability of it changes, hence the emitted frequencies also changes - Raman Scattering.

Lets assume that the polarizability of the molecule α is changed by the vibrational frequency of the molecule ν_{vib}

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{vib}\, t$$

Where

α_0 is the equilibrium polarizability

β is the rate of change of polarizability with vibration

ν_{vib} is the vibrational frequency

$$\mu = \alpha E$$

$$= (\alpha_0 + \beta \sin 2\pi\nu_{vib}\, t) E_0\, sin 2\pi\nu t$$

By expansion and using the relation,

$$\sin A \sin B = \frac{1}{2}[\cos(A-B) - \cos(A+B)]$$

$$\mu = \alpha_0 E_0 \, sin 2\pi \mathrm{vt} + \frac{1}{2} \beta E_0 \, [cos 2\pi(\mathrm{v} - v_{vib})\mathrm{t} - cos 2\pi(\mathrm{v} + v_{vib})\mathrm{t}]$$

Above equation shows that the oscillating dipole has three frequency components namely,

ν Rayleigh Line

$(\nu + \nu_{vib})$ Raman Line (Anti-Stokes)

$(\nu - \nu_{vib})$ Raman Line (Stokes)

The Raman shift is depending on the β value.

If the polarizability change with vibration is zero then the Raman shift is also zero, i.e. the vibration is not Raman active.

3.3 Quantum theory of Raman Effect:

Radiation of frequency v as consisting of a steam of particles (called photons) having energy hv where h is the plank's constant. Photon can be imagined undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged.

A detector placed to collect energy at right angles to an incident beam will thus receive photons of energy hv that is radiation of frequency v.

However, it may happen that energy is exchanged between photon and molecule during the collision such collisions are called inelastic. The molecule can gain or lose amounts of energy only in accordance with the quantal laws: i.e. its energy change must be the difference in energy between two of its allowed state.

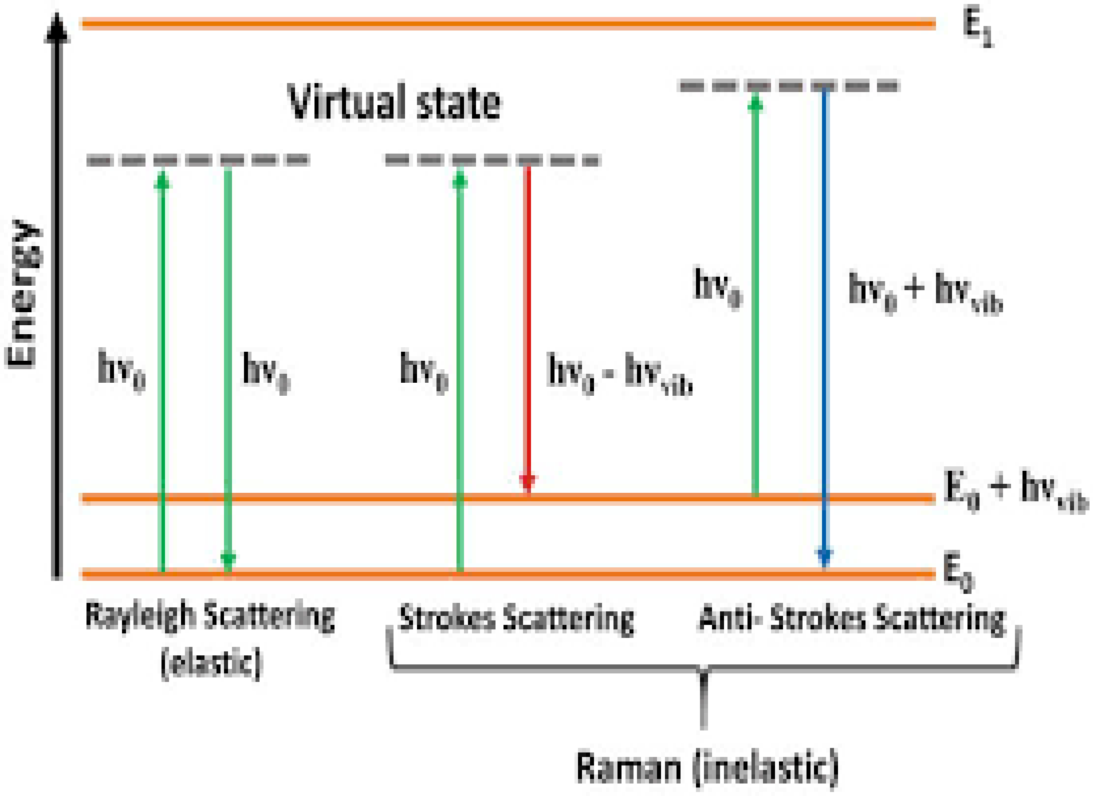


Figure 3.1 Energy Levels

If the molecules gains energy ΔE, the photon will be scattered with energy hv-ΔE and the equivalent radiation will have a frequency v-ΔE/h.

Conversely if the molecule loses the energy ΔE, the scattered frequency will be v+ΔE/h.

3.4 Polarizability ellipsoid:

Consider a diatomic molecule H_2. The polarizability is anisotropic i.e. the electrons forming the bond are more easily displaced by an electric field applied along the bond axis than one across this direction.

This may be confirmed experimentally, for example by a study of the absolute intensity of lines in the Raman spectrum, when it is found that thee induced dipole moment for a given field applied along the axis is approximately twice as large as that induced by the same field applied across the axis: fields in other directions induce intermediate dipole moments. We can represent the polarizability in various directions most conveniently by drawing a polarizability ellipsoid.

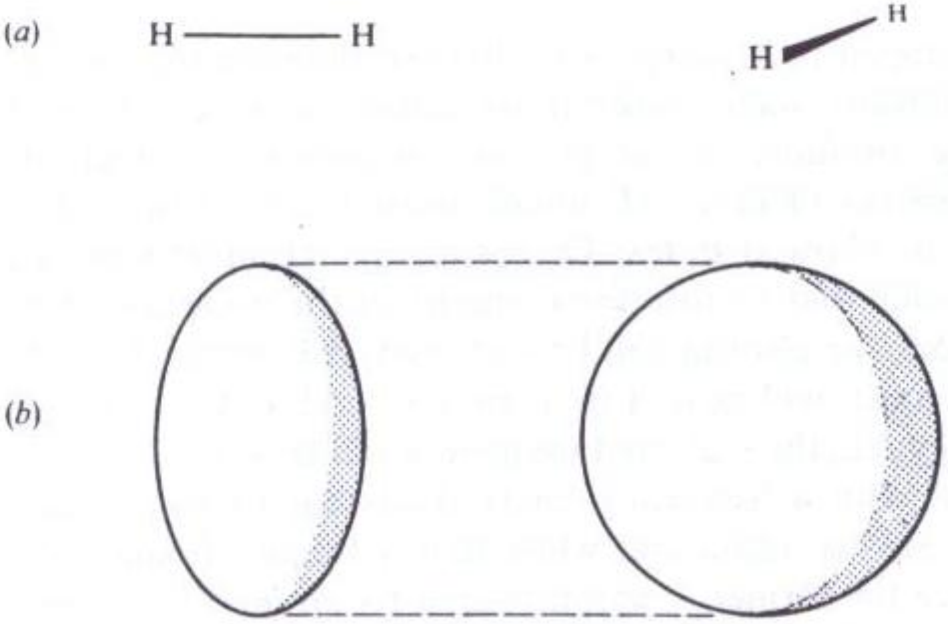


Figure 3.2 ***Diatomic molecule H_2***

3.5 Rotational Raman spectra:

(i) linear molecule

The rotational energy levels of linear molecules have been

$$\varepsilon_J = B\,J\,(J+1) - D\,J^2\,(J+1)^2 \quad \text{cm}^{-1}$$

But in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D, the centrifugal distortion constant.

$$\varepsilon_J = B\,J\,(J+1)$$

Transition between these levels follow the formal selection rule:

$$\Delta\text{J} = 0 \quad \text{or,} \quad \pm 2 \text{ only}$$

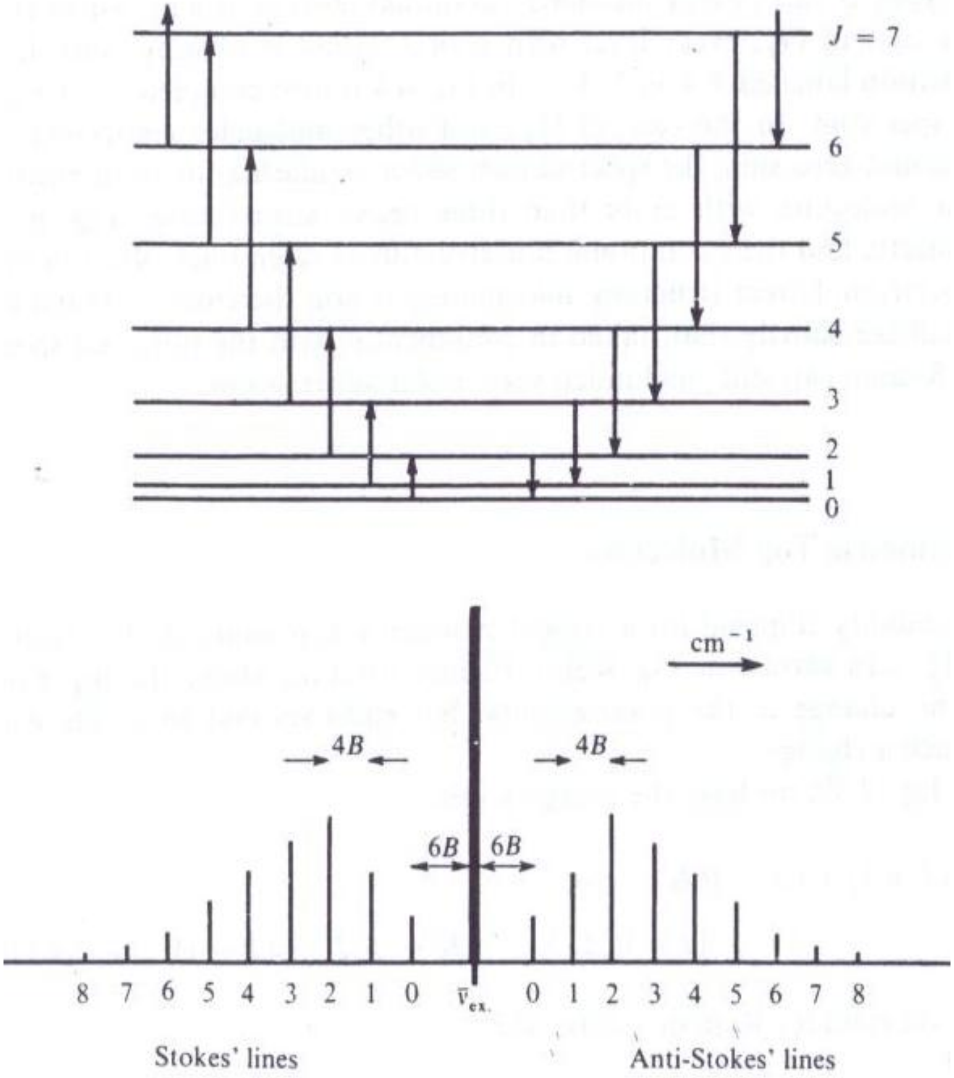


Figure 3.3 Stokes and Anti- Stokes lines

We define ΔJ as ($J_{\text{upper state}} - J_{\text{lower state}}$) then we can ignore the selection rule $\Delta J = -2$. Since for the pure rotational change, the upper state quatum number must necessarily be greater then that in the lower state.

Further transition $\Delta J = 0$ is trivial since this represents no change in the molecular energy and hence Rayleigh scattering only.

$\Delta J = +2$ energy levels

$$\Delta\varepsilon = \varepsilon_{J'=J+2} - \varepsilon_{J'=J}$$

$$= B\,(4J + 6)\ \text{cm}^{-1}$$

Since $\Delta J = +2$ we may label these lines S branch lines and write

$$\Delta\varepsilon_S = B\,(4J + 6)$$

Where J is the rotational quantum number in the lower state

The wave number of the corresponding spectral lines is given by;

$$\bar{v}_S = \overline{v_{ex}} \pm \Delta\varepsilon_S$$

$$= \overline{v_{ex}} \pm B\,(4J + 6)$$

Where the plus sign refers to anti-stokes line, the minus to stokes and $\overline{v_{ex}}$ is the wavenumber of the exciting radiation.

(ii) Symmetric top molecule

Rotation about the top axis produces no change in the polarizability, but end-over-end rotations will produce such a change.

The energy levels are,

$$\varepsilon_{J,K} = B\,J\,(J + 1) + (A - B)K^2$$

(J= 0,1,2,……. K = $\pm J, \pm(J-1), \ldots$..)

The selection rules for Raman spectra are:

$$\Delta K = 0$$

$$\Delta J = 0, \pm 1, \pm 2$$

K is the rotational quantum number for axial rotation, so the selection rule$\Delta K = 0$ implies that changes in the angular momentum about the top axis will not give rise to a Raman spectrum.

Positive ΔJ have two cases:

1. ΔJ = +1 (R branch lines)

$$\Delta\varepsilon_R = \varepsilon_{J'=J+1} - \varepsilon_{J'=J}$$

$$= 2B\,(J+1)$$

2. ΔJ = +2 (S branch lines)

$$\Delta\varepsilon_S = \varepsilon_{J'=J+2} - \varepsilon_{J'=J}$$

$$= B\,(4J + 6)$$

Thus we have two series of lines in the Raman spectrum:

1. $\overline{v_R} = \overline{v_{ex}} \pm \Delta\varepsilon_R$

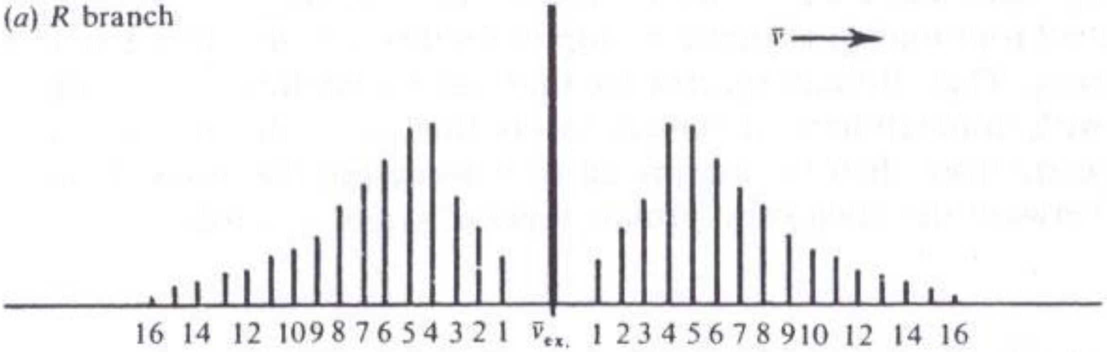
$$= \overline{v_{ex}} \pm 2B\,(J + 1)$$

2. $\overline{v_s} = \overline{v_{ex}} \pm \Delta\varepsilon_s$

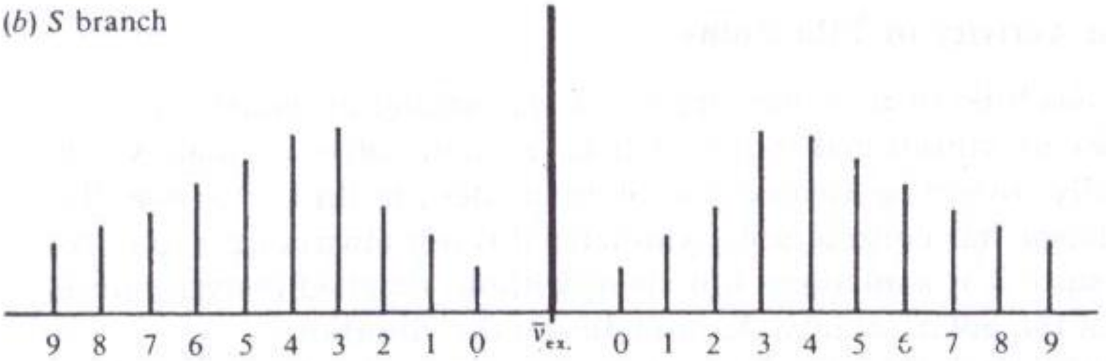
$$= \overline{v_{ex}} \pm B\,(4J + 6)$$

These series are shown in below Figure3.4

(*a*) *R* branch



(*b*) *S* branch



(*c*) Complete spectrum

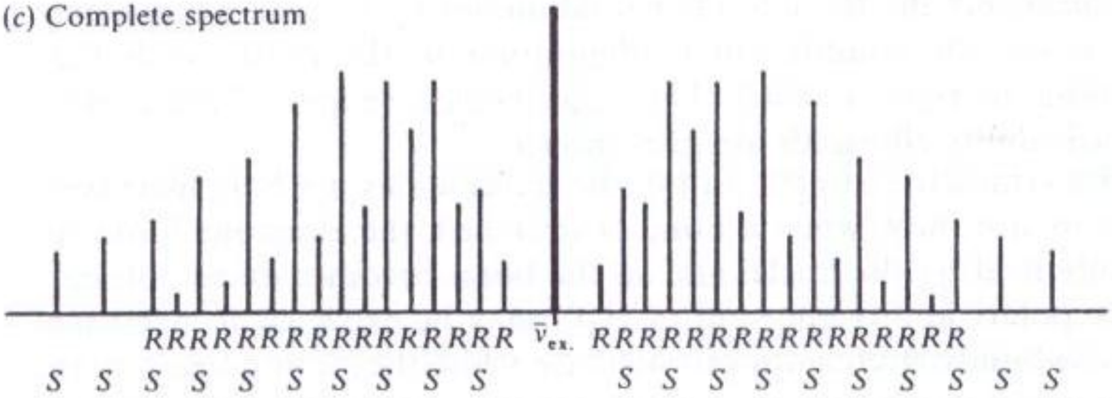
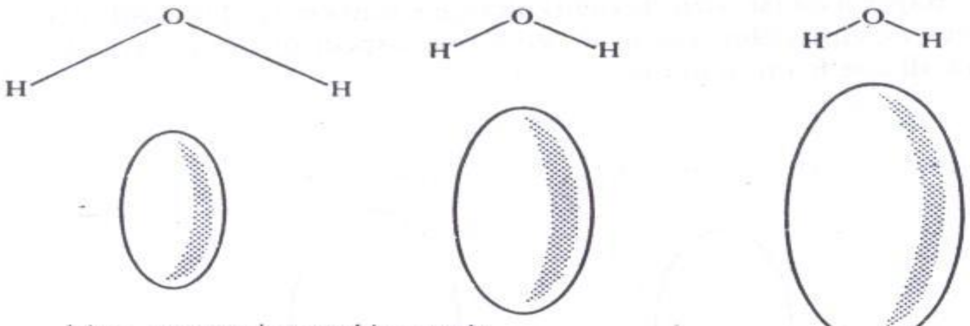


Figure 3.4 Spectrum

3.6 Raman activity of

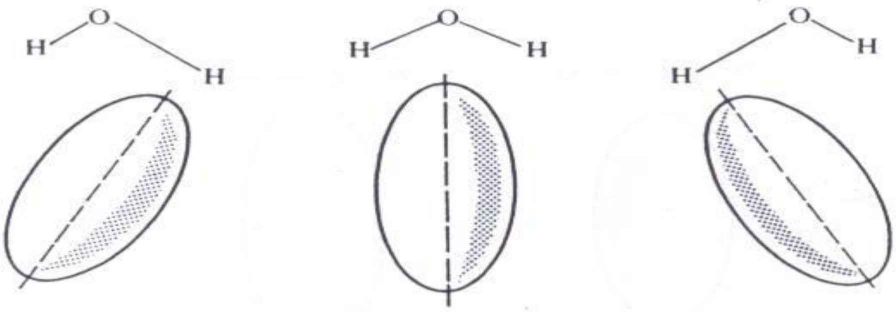
(i) H_2O:

The figure 3.5 illustrates at a, b, and c respectively the three fundamental modes v_1, v_2, v_3 sketching for each mode the equilibrium configuration in the center with the extreme positions to right and left.



(*a*) v_1, symmetric stretching mode

(*b*) v_2, bending mode



(*c*) v_3, asymmetric stretching mode

Figure 3.5 Fundamental modes of vibration of H_2O

The approximate shapes of the corresponding polarizability ellipsoids are also shown.

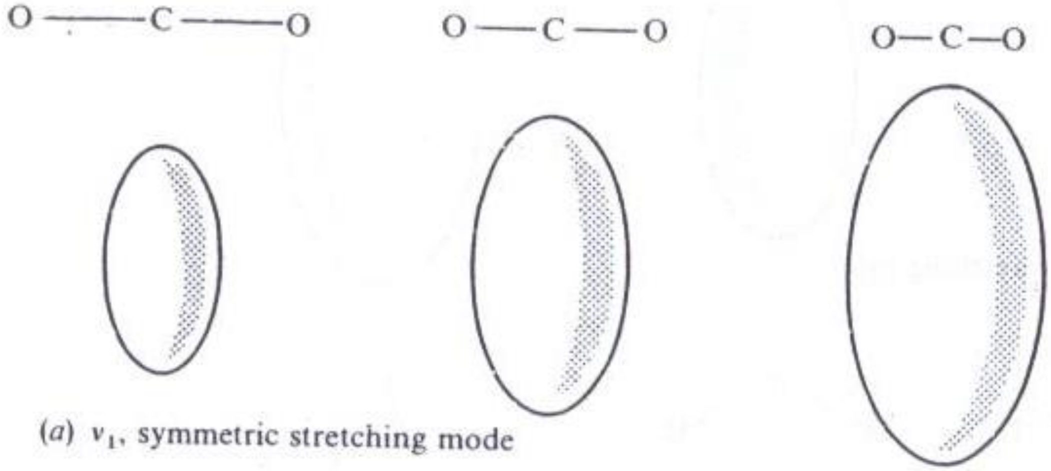
During the symmetric stretch in (a), the molecule as a whole increases and decreases in size; now when a bond is stretched, the electrons forming it are less firmly held by the nuclei and so the bond becomes more polarizable. Thus the polarizability ellipsoid of H_2O may be expected to decrease in size while the bonds stretch and to increase while they compress, but to maintain an approximately constant shape.

On the other hand while undergoing the bending motion, in (b) it is the shape of ellipsoid which changes most; thus if we imagine vibrations of very large amplitude, at one extreme (on the left) the molecule approaches the linear configuration with a horizontal axis, while at the other extreme (on the right) it approximates to a diatomic molecule with a vertical axis.

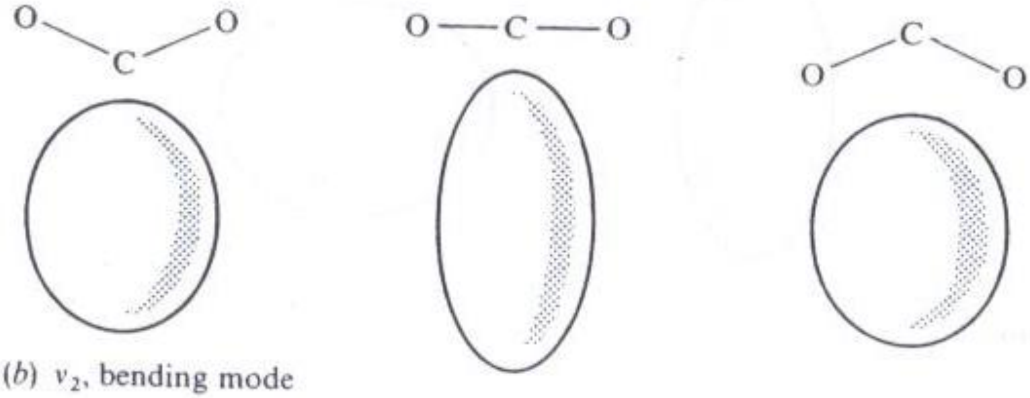
Finally in (c) we have the asymmetric stretching motion, v_3, direction of the major axis (shown dashed) changes markedly. Thus all three vibrations involve obvious changes in at least on aspect of the polarizability ellipsoid, and all are Raman active.

(ii) CO_2

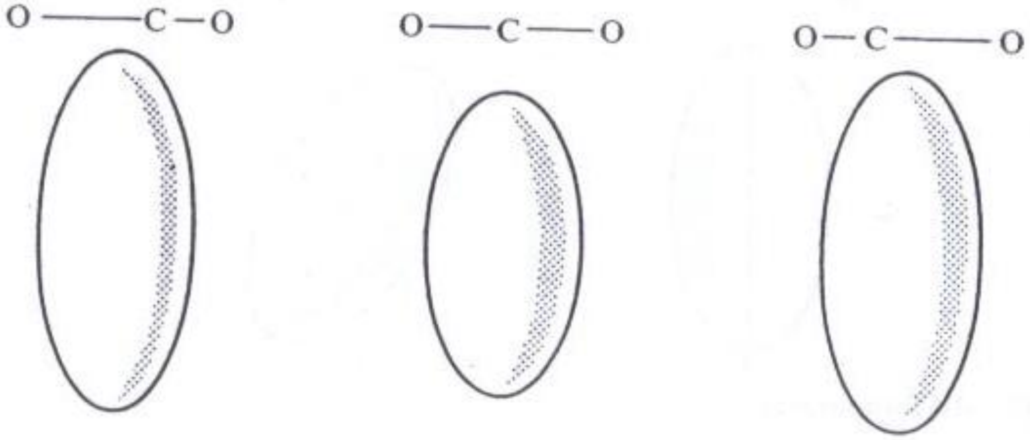
The symmetric stretching mode v_1, is easily decided during the motion the molecule changes size and so there is a corresponding fluctuation is the size of ellipsoid; the motion is thus Raman active. It might be thought that the v_2 and v_3 vibrations are also Raman active, because the molecule changes shape during each vibration and hence presumably so does the ellipsoid; however, both these modes are observed to be Raman inactive.



(*a*) ν_1, symmetric stretching mode



(*b*) ν_2, bending mode



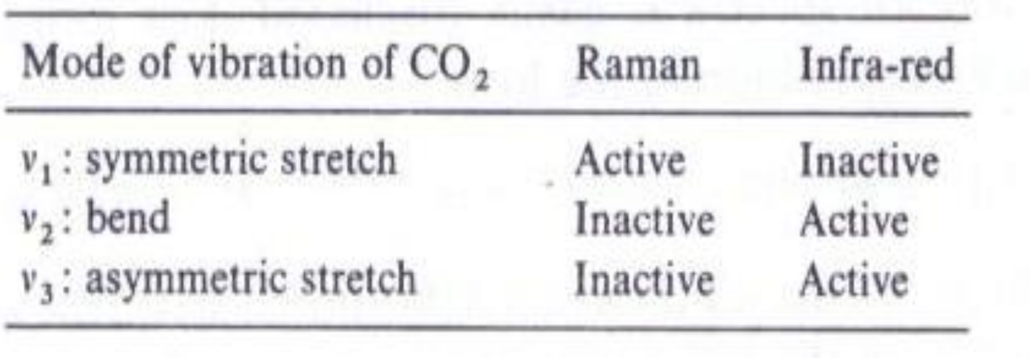
(*c*) ν_3, asymmetric stretching mode

Figure 3.6 Modes of vibration of CO_2

3.7 Mutual exclusion principle:

If a molecule has a centre of symmetry then Raman active vibrations are infra-red inactive and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and IR active.

Table.3.1 Modes of vibration



Mode of vibration of CO_2	Raman	Infra-red
ν_1 : symmetric stretch	Active	Inactive
ν_2 : bend	Inactive	Active
ν_3 : asymmetric stretch	Inactive	Active

The converse of this rule is also true. The observance of Raman and IR spectra showing no common lines implies that the molecules has a centre of symmetry; but here caution is necessary since, a vibration may be Raman active but too weak to be observed.

However, if some vibrations are observed to give coincident Raman and IR absorption it is certain that the molecule has no centre of symmetry. Thus extremely valuable structural information is obtainable by comparison of the Raman and IR spectra of substance.

3.8 Determination of N_2O structure:

N_2O (Nitrous oxide) $N \equiv N^{+} - O^{-}$

No. of atoms : 3

Total No.freedoms : 3 x 3 = 9

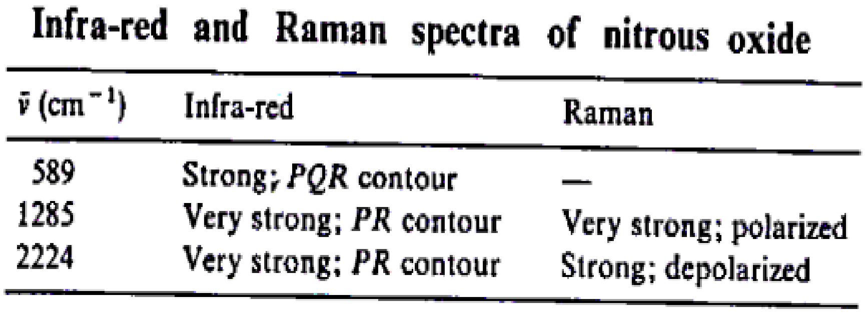
Structure : Linear

Vibrational deg. of freedom : 3 x 3 – 5 = 42 modes degenerate

- N_2O is isoelectronic with CO_2. It is linear but not symmetrical. It as three intense IR absorptions at (bending) 598, (symmetric)1285 , and (assymmetric) 2224 cm^{-1} .

- Two of these (symmetric)1285 , and (asymmetric) 2224 cm-1 appear in Raman spectrum; the (bending) 598 is not observed due to weak intensity. Thus according to rule of mutual exclusion, the molecule has no center of symmetry, i.e., it does not have the symmetric structure N – O – N because two bands are common to its IR and Raman spectra. Hence N2O has a unsymmetrical structure N – N – O, confirmed by its rotational spectrum.
- IR lines with PR structure: linear molecule
- No center of symmetry: N-N-O

Table 3.2



Infra-red and Raman spectra of nitrous oxide

$\bar{\nu}$ (cm^{-1})	Infra-red	Raman
589	Strong; *PQR* contour	—
1285	Very strong; *PR* contour	Very strong; polarized
2224	Very strong; *PR* contour	Strong; depolarized

3.9 Instrumentation Technique and Block diagram:

- **Source of excitation (laser)**

A laser is used as a light source in Raman spectroscopy. The bandwidth of the utilized laser source determines the radiation’s spectrum. In general, a shorter wavelength produces more Raman scattering. Because Raman scattering intensity varies as the fourth power of frequency, argon, and krypton ion sources emitting in the blue and green regions of the spectrum have an advantage over other sources.

- **Sample**

Laser is irradiated on the sample present in the sample chamber. After interacting with the laser beam it gives elastic and inelastic scattering before passing through the filter.

Liquid Samples:

A significant advantage of Raman spectroscopy sample handling over infrared is that water is a poor Raman scattered but a powerful absorber of infrared radiation. As a result, aqueous solutions can be examined using Raman spectroscopy but not infrared.

This benefit is especially essential for biological and inorganic systems, as well as studies dealing with water pollution issues.

Solid samples

Solid-state Raman spectra are frequently obtained by filling a tiny cavity with the sample after it has been ground to a fine powder. Polymers are typically evaluated immediately without sample preprocessing.

Gas samples

Gas is often contained in glass tubes that are 1-2 cm in diameter and around Imm thick. Small capillary tubes can also be used to seal gases.

- **Filter**

In Raman spectroscopy, a filter is employed to separate Raman scattered light from rayleigh scattered light. This is done in order to obtain high-quality Raman spectra. Notch, long pass, and volume halogen filters are examples of filters.

- **The detector**

The detector aids in the detection of the scattered light signal. LCD array detectors are commonly employed in current Raman spectrometers. They are designed to detect signals of various wavelengths, as well as very weak signals.

- **Computer**

A computer with relevant software aids in the creation of a final Raman spectroscopy graph/ spectrum.

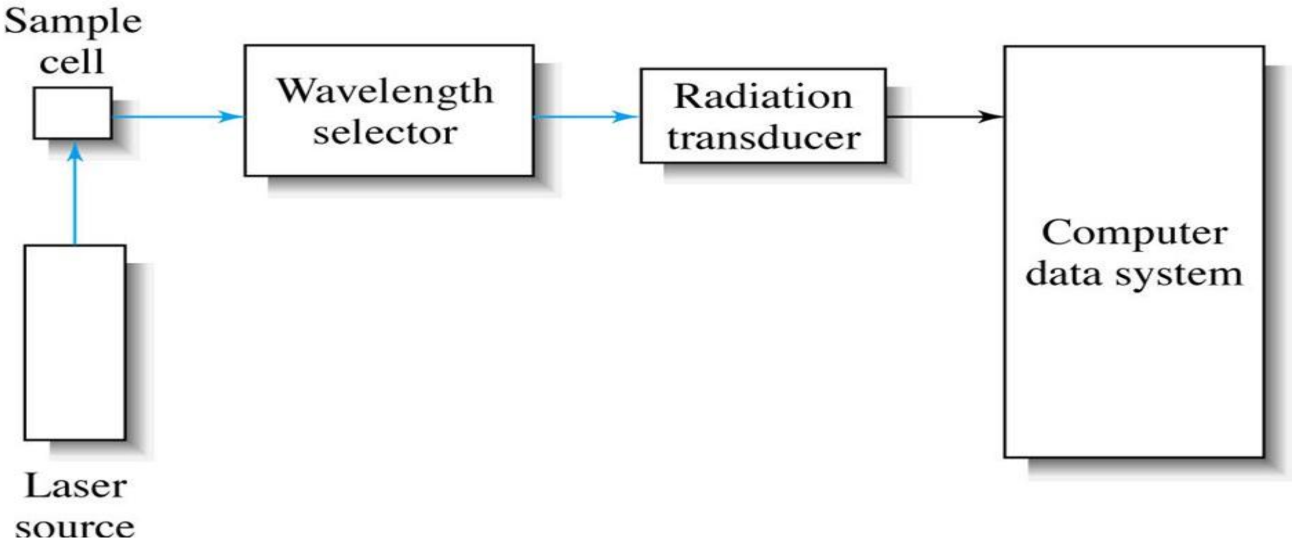
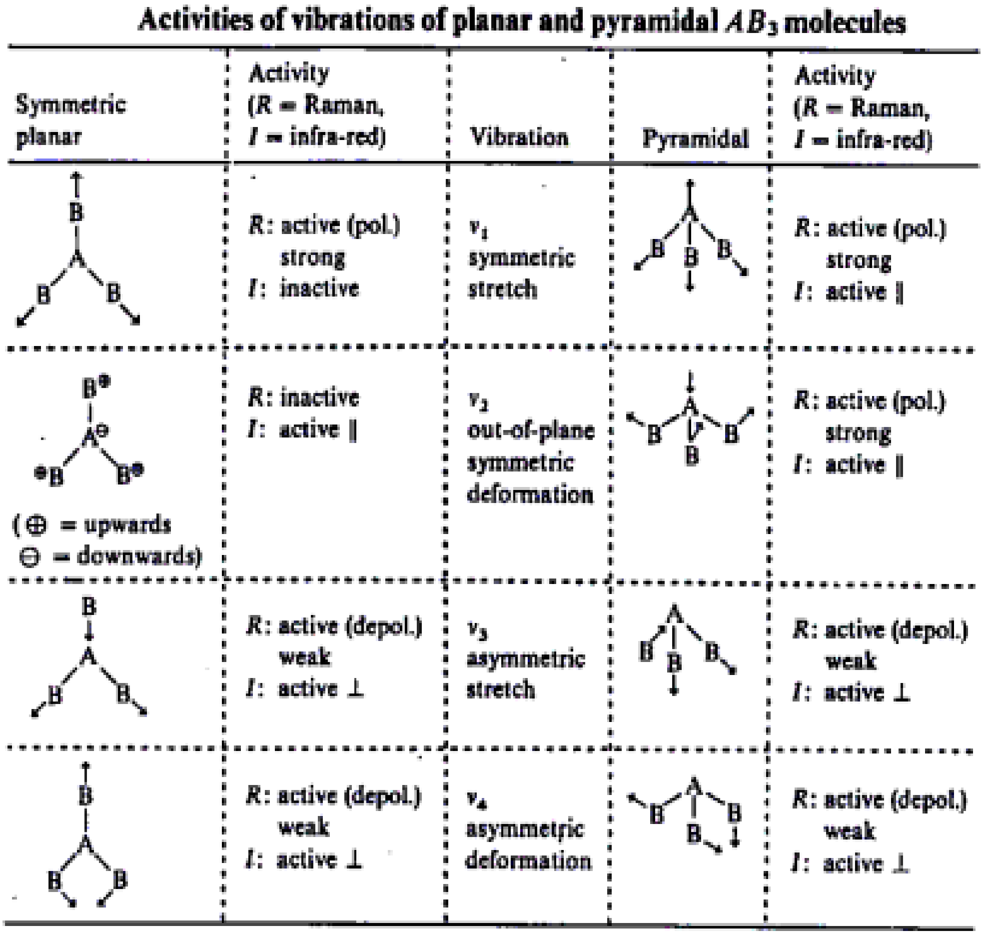


Figure 3.7 Block diagram - Raman spectroscopy

3.9 Structure determination of planar and non-planar molecules using IR and Raman techniques:

Table 3.3



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.) strong 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 ⊥

Planar AB_3: 1 vibration Raman active only (ν_1)
1 infra-red active only (ν_2)
2 vibrations both Raman and infra-red active (ν_3, ν_4).
Pyramidal AB_3: All four vibrations both Raman and infra-red active.
Non-symmetric AB_3: Possibly more than four different fundamental frequencies.

3.10 FT Raman spectroscopy:

The instrumentation set-up meant for FT Raman techniques and conventional (or traditional) Raman spectroscopy is diverse.

The conventional laser Raman technique has been available for quite some time and has also advanced significantly.

However, FT Raman instruments have been introduced in scientific community only lately and the first FT Raman instrument was demonstrated in the year 1986. It is possible that advancements in FT instrumentation will be developed in coming years.

Compared to traditional Raman spectroscopic technique, FT Raman instruments are built around an interferometer while conventional uses dispersive monochromators of different kinds. Interferometer bedded instruments have several benefits over dispersive spectrometers which uses gratings. Precisely, Jacquinot and Felgett are the two advantages of FT.

The second approach is termed as “multiplex” advantage works on the principle that in which all light wavelength are detected concurrently.

This is explained as the main reason due to which the spectrum is recorded in less time in FT Raman spectrometer compared to a a grating instrument.

Also accuracy of the wave numbers can be achieved in FT instrument spectra. This has become conspicuous when Raman spectra are used to enhance the signal-to-noise ratio.

Besides interferometer, Fourier Transform Raman spectrometer needs a laser source for excitation of sample, more than one filters for efficiently blocking the scattering of rayleigh, a exceedingly precise detector, and also an interferogram.

Now days, improved filters and detectors have also been developed. It was also observed that gold-coated optical components provide better clarity. Figure 3.8 is the diagrammatic representation of FT Raman instrument.

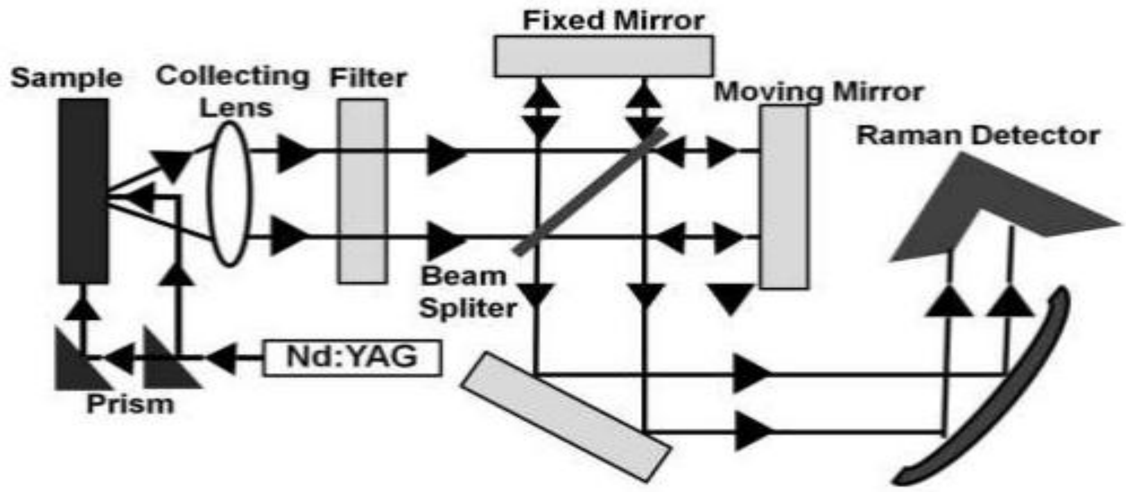


Figure 3.8. FT Raman

Two types of Raman spectrophotometers are recognized: dispersive and non-dispersive. Raman spectrophotometer which is dispersive is equipped with prism/grating while non-dispersive one is fitted with interferometer like Michelson interferometer used in Fourier Transform Raman spectrophotometer.

In early days Mercury lamp was used as a source in Raman spectrophotometers. Laser sources came into play in late 1960’s and mercury lamp completely replaced.

The most important advantage of using laser is; it provides radiations which are very stable and also of high intensity.

Broad variety of lasers sources for example Argon laser (488 & 514.5 nm), Helium–Neon (632.8 nm), Krypton ion laser (530.9 & 647.1 nm), Near Infrared (IR) diode lasers (785 & 830 nm), Neodymium–Yttrium Aluminum Garnet (Nd: YAG) can be used as source in Raman spectrophotometers.

Commercial available Fourier Transform spectrophotometers were first introduced in 1980’s to enhance the capability of detectors and to overcome the detection limitations of charge-coupled devices and other various kind of detectors that works in the near-IR range on use of 1064 nm laser source.

FT-Raman spectrophotometer fitted with Michelson interferometer and continuous wave laser like Nd–YAG which produce the radiation of 1064 nm. Germanium (Ge) and In GaAs detectors are operate at cryogenic temperatures in order to reduce noise effect and thus enhance the signal-to-noise ratio.

Cryogenic temperature is a temperature at which molecular motion ceased completely as theoretically possible. At cryogenic temperature, materials are in static and highly ordered state as much as possible.

UNIT IV

RESONANCE SPECTROSCOPY

Nuclear and Electron spin-Interaction with magnetic field - Population of Energy levels - Larmor precession- Relaxation times - Double resonance- Chemical shift and its measurement - NMR of Hydrogen nuclei - Indirect Spin - Spin Interaction – interpretation of simple organic molecules – Instrumentation techniques of NMR spectroscopy – NMR in Chemical industries- MRI Scan Electron Spin Resonance: Basic principle –Total Hamiltonian (Direct Dipole- Dipole interaction and Fermi Contact Interaction) – Hyperfine Structure (Hydrogen atom) – ESR Spectra of Free radicals –g-factors – Instrumentation - Medical applications of ESR

4.1 Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy takes advantage of the magnetic properties of certain nuclei and records the absorption of energy between quantized nuclear energy levels.

In an NMR experiment, the spectrometer is tuned to the frequency of a particular nucleus and the spectrum reveals all such nuclei in the molecule being investigated. It is thus a very powerful technique, the closest analogy being a powerful microscope that allows the chemist to "see" the structure of molecules in solution

4.2 Nuclear and Electron spin-Interaction with magnetic field:

When an electron having magnetic moment μ is placed in a magnetic field B, the interaction energy,

$$E = -\mu . B = -\ \mu\, B \cos\theta \qquad \text{-----}(1)$$

Where θ is the angle between μ and B. If the system has only spin magnetic moment μ , then it is given by

$$\mu = -g\mu_B\, S = g\mu_B\, m_S$$

-----(2)

The Eq. (2) becomes,

$$E = -g\mu_B\, B\, m_s$$

For electron, $m_s = \pm\frac{1}{2}$ and we get two levels with energies

$$E_{-1/2} = -\frac{1}{2} g\mu_B\, B, \quad E_{1/2} = \frac{1}{2} g\mu_B\, B$$

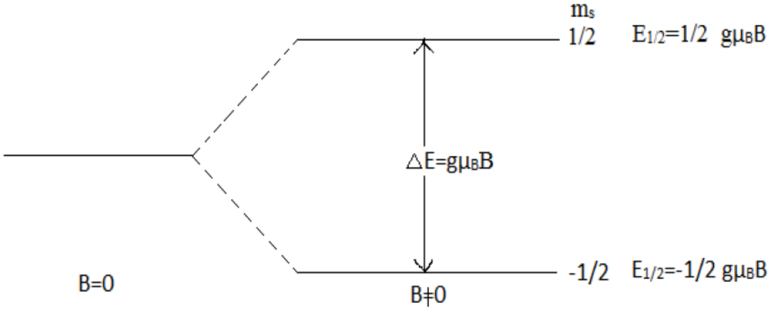


Figure 4.1 **Nuclear and Electron spin-Interaction with magnetic field**

If electromagnetic radiation of frequency γ satisfying the relation.

$$h\gamma = E_{1/2} - E_{-1/2} = g\mu_B\, B,$$ **---- (3)**

is present, transition between these Zeeman levels occur which is studied by ESR. Eq.(5.30) gives the resonance condition for ESR observation. For free electron, g = 2.0023. In a field of 0.34T, from Eq. (3).

$$\gamma = \frac{2.0023(9.274\text{x}10^{-24}\, JT^{-1})0.34T}{6.626\text{x}10^{-34}\, J.Sec}$$

$$= 9528\, MH_Z$$

This frequency falls in the microwave region. Hence microwave source and techniques have to be applied for the observation of ESR.

4.3 Nuclear Spin And Larmor Precession:

The total angular momentum of a nucleus is represented by a symbol I and it is commonly known as nuclear spin. Nuclear magnetic moment is associated with nuclear spin I, which interacts with the external magnetic field.

The origin of nuclear magnetic moment is related to magnetic field associated with nucleons constituting the nucleus. As nucleus contains charge particles, the spin of charge particles gives rise to a magnetic field. This magnetic field is analogous to the magnetic field produced by an electric current when passed through a coil of wire.

This nuclear magnetic field is measured in terms of a resulting nuclear magnetic dipole μ which is characteristic of the nuclei and which is oriented along the axis of spin.

When such a nucleus is placed in an external magnetic field, it tends to get oriented such that the direction of magnetic dipole i.e. spin axis is parallel to the external magnetic field. The potential energy of the nuclei is dependent on the orientation of the dipole with respect to the applied field. The potential energy of such nuclei is given by the following equation:

$$E = -\mu_H H_o$$

where μ_H is the component of magnetic moment in the direction of the field and Ho is the strength of the external magnetic field measured in gauss. For a nuclei with spin quantum number I and magnetic quantum number m is given by:

$$E = -\frac{m\mu}{I}\beta H_o$$

where m has values +I, +(I-1),……, -I, β is a constant known as nuclear magneton ($\beta = 5.049 \times 10^{-24}$ erg/gauss), μ is the magnetic moment of the particle expressed in the units of nuclear magnetons (for proton m is 2.7927 nuclear magneton and for electron it is 1836 nuclear magneton). As for proton I = 1/2 has two values of magnetic quantum number +1/2 and -1/2. These two values represent two spin states of proton and the energies corresponding to these two spin states is given by:

$$m = +\frac{1}{2} \qquad E_1 = -\frac{\frac{1}{2}\mu}{\frac{1}{2}}\beta H_o = -\mu\beta H_o$$

$$m = -\frac{1}{2} \qquad E_1 = -\frac{\frac{1}{2}\mu}{-\frac{1}{2}}\beta H_o = +\mu\beta H_o$$

These two nuclear spin states are the possible orientation of the spin axis with respect to direction of applied magnetic field. The orientation m = + 1 / 2 is aligned to the external magnetic field and similarly the orientation m = − 1/ 2 is opposed with respect to the external field. The aligned state i.e. m = + 1 /2 has lower energy while the opposed state m = − 1/ 2 has higher energy. The energy difference between these two spin states for hydrogen nucleus is given by:

$$\Delta E = 2\,\mu\,\beta\,H_o$$

In general for any nucleus with I spin quantum number the energy difference between spin states is given by the following expression:

$$\Delta E = \frac{\mu\beta H_o}{I}$$

For excitation from lower to higher spin states if hν energy is absorbed then ΔE = hν, so above equation becomes:

$$h\nu = \frac{\mu\beta H_o}{I}$$

In general in NMR studies $H_o = 10^4$ gauss, then the frequency of radiation required for this transition is obtained by putting μβ = 2.79 × 5.05 × 10−24 magnetons, h = 6.626 × $10–^{27}$erg-sec and I = 1/2. On putting these values in equation the values of frequency (ν) is calculated to

$$\nu = 4 \times 10^7 \text{ Hz}$$

This frequency value is in the region of radio waves of the electromagnetic spectrum. Thus radio wave radiations are required to cause transitions between spin levels, so that the spin with aligned orientation changes to spin with opposed orientation.

Consider a nucleus for which I = 1/2, so it has two spin states represented as m = +1/2 and -1/2 (see section 2.5). From quantum mechanics, the energy of these two spin states is given by:

$$E_\alpha = +\frac{1}{2}\,v$$

$$E_\beta = -\frac{1}{2}\,v$$

where ν is Larmor frequency of nuclear magnetic moment vector of the nucleus. In general the energy is given by:

$$E_m = mv$$

The Larmor frequency depends on the gyromagnetic ratio γ, chemical shift δ and strength of the applied magnetic field.

Now the most important point is this precessional frequency or Larmor frequency depends upon the magnetic field experienced by the proton.

In a NMR experiment, different protons in a compound experienced different magnetic field depending upon the electronic surrounding. As the surrounding electrons, by virtue of their motion in orbitals (in presence of external magnetic field) produce a induce magnetic field that may be diamagnetic or paramagnetic (i.e. shielding and deshielding).

This induced magnetic field may increases or decreases the actual magnetic field on protons. In this way the magnetic field experienced by protons in a compound is varied and depends on electronic surrounding.

That is why the precession and Larmor frequency of chemically equivalent protons is same and similarly the Larmor frequency of non-equivalent protons is different.

In order to absorb radio waves, the frequency of radio wave must matches with the processional (or Larmor) frequency (ν).

In other words, the frequency of radio wave (ν) must be equal to the processional frequency for absorption of radiowave by a proton i.e. to attain NMR signal.

So from the above discussion it can be concluded that the nuclear spin quantum number (I) and nuclear magnetic moment forms the basis of NMR spectroscopy.

The various nuclear spin states arise due to spin quantum number and the transition between these states results in NMR signal.

The concept of NMR signal is related to resonance between radiowaves and precessing nuclear magnetic moment vector. When this resonance takes place radiowaves are absorbed and NMR signal in attained.

4.4 Chemical And Magnetic Equivalence:

All the protons having identical chemical (electronic) environment within molecule are chemically equivalent. In a given external magnetic field, protons when same precessional frequency of their nuclear magnetic moment vector are said to be magnetically equivalent, such nuclei absorbs same radiowave frequency and thus gives same signal. In general protons that are chemically equivalent are also magnetically equivalent. This generalisation helps to know the similar type of protons from a signal observed in the NMR spectrum

Consider the example of propane

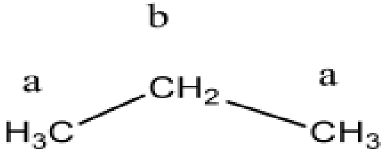


Figure 4.2 Propane

There are two types of protons as shown in the structure marked as ‘a’ and ‘b’, the chemical environment of six protons of ‘a’ type are equivalent, similarly the chemical environment of two ‘b’ type protons are equivalent. In the NMR spectrum of propane we get two peaks, in the ratio of 3:1 for these protons. The two signal confirms that propane has two different protons magnetically, which corresponds to chemically distinct type ‘a’ and ‘b’ protons.

The ratio 3:1 gives empirical numbers between chemically (magnetically) distinct protons. In propane it confirms 6:2 ratio (from empirical 3:1) for six ‘a’ and two ‘b’ type protons.

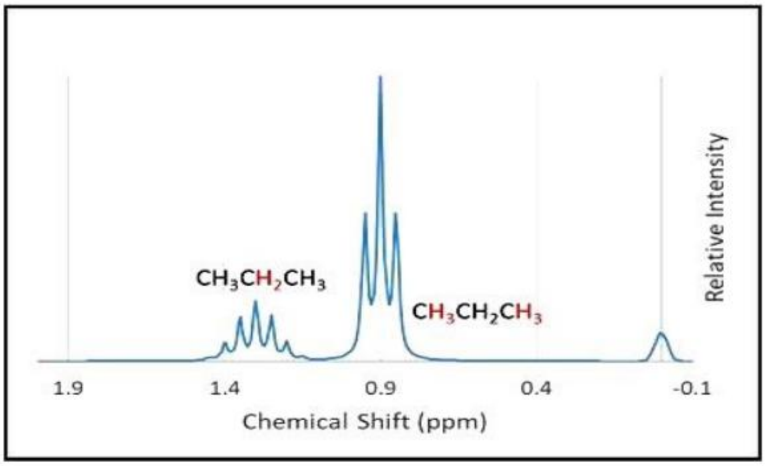


Figure 4.3 NMR spectrum

4.5 Chemical Shift:

The different types of protons will have different electronic environment and they absorb radio waves at different frequency in presence of applied magnetic field. It is the electronic environment which determines where the proton shows absorption in the spectrum. When a proton is placed in a magnetic field then surrounding electrons circulate and thus produce a secondary (induced) magnetic field. The electrons move about the proton generates a magnetic field in such a way that it opposes the external field, then the proton is said to be shielded.

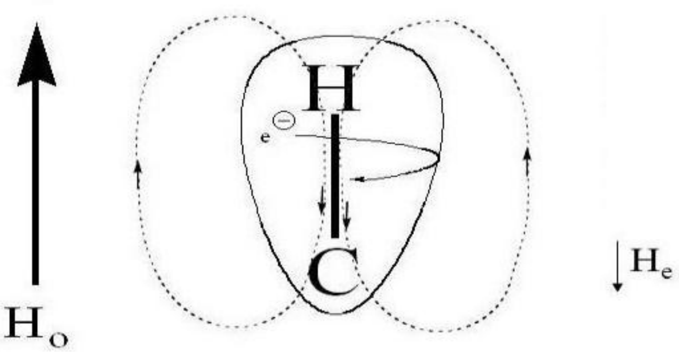


Figure 4.4

The circulation of electrons, if the induced magnetic field produced opposes the external field, then this circulation of electrons is called local diamagnetic current and the shielding caused is called diamagnetic shielding or diamagnetic anisotropy. The higher the electron density around the nucleus, greater is the diamagnetic shielding. Thus the nucleus process at lower frequency, also the radiofrequency radiation absorbed will be of lower frequency.

If the induced field (Hi) reinforces the applied field, then the proton experience greater strength and proton is said to be deshielded.

We will consider the different cases of shielding and deshielding in next unit. The protons in a molecule are in slightly different chemical environment thus the difference in radiofrequency is very small, that can be measured in hertz.

It is important to remember that the applied magnetic field has the strength corresponding 60 MHz (in case of proton absorption). For example- The difference in resonance frequency of protons in chloromethane and fluoromethane is only 72 Hz, when the field applied is 1.41T (and the radiofrequency used is 60MHz).

Thus there is a large difference between radiofrequencies of the instrument and difference in signal for various protons. In NMR a reference compound is placed in the solution of substance and the resonance frequency of each proton in the sample is measure relative to the resonance frequency of the protons of reference substance.

The standard reference substance used is Tetramethylsilane, $(CH3)_4Si$ (TMS).

This compound was chosen because the protons of its methyl group are more shielded and give a signal at one end of the range.

The shift from TMS for a given proton depends upon the strength of applied magnetic field. The following are the advantages of TMS as reference in NMR-

- Due to low electronegativity of silicon, the shielding of equivalent proton in TMS is greater than most of the organic compounds, and therefore the signal of protons of TMS is well highly upfield shifted and generally well separated from signal proton attached with carbon in NMR spectrum.
- TMS is inert and it does not react with most of the organic compounds.
- It is volatile and easily miscible with most of the organic compounds.

The separation between a signal of a specific proton (of the compound under study) and the signal of proton of TMS is known as chemical shift, which is a measure of variation in electronic environment of the concerned proton. The chemical shift is defined by:

$$\delta = \frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}} \times 10^6 \text{ ppm}$$

This parameter is independent of applied field strength and is obtained in ppm. The chemical shift in δ units express the amount by which a proton resonance is shifted from TMS signal. The chemical shift also expressed in terms τ (tau), which is related with δ as

$$\tau = 10 - \delta$$

The chemical shift values helps to establish the electronic environment of the proton, and thereby helps in ascertaining the possible groups surround the specific proton. The increase in electron density around the proton, enhances the induced secondary field which opposes the applied field. Thus greater external field will be needed to cause the proton absorption. The concept of shielding is represented in terms of shielding parameter (α), the field H felt by the proton is given by

$$H = (1 - \alpha)\, H_0$$

where, H_0 is the applied magnetic field. Thus the net magnetic field felt by proton is different from applied field. Also greater the value of α, greater is the applied field needed by proton to undergo resonance with radio wave.

$$v = \frac{\gamma\, H}{2\,\pi}$$

$$\mathrm{v} = \frac{\gamma\, H_0\, (1 - \alpha)}{2\,\pi}$$

In terms of chemical shift, shielding means increase in τ value or decrease in δ value. The presence of electronegative atom or group results in decrease in electron density around the proton that is deshielding takes place and absorption is shifted downfield. This means decrease in τ value takes place.

4.6 Chemical Shift Range

The chemical shift value for magnetically active nuclei depends upon the extent of effect of secondary electronic field. That is why the chemical shift (δ) range for proton is about 0 to 12 ppm, while in case C-13, it is about 0-220 ppm. The reason of greater chemical shift in C-13, is the circulating electron are more close to carbon, than hydrogen atom in hydrocarbon chain. In proton-NMR (PMR), the different protons in functional groups shows peaks in specific chemical shift δ values, depending upon the number and closeness of electronegative atom(s). The possible chemical shift range of some common functional groups is shown in Figure. 4.5.

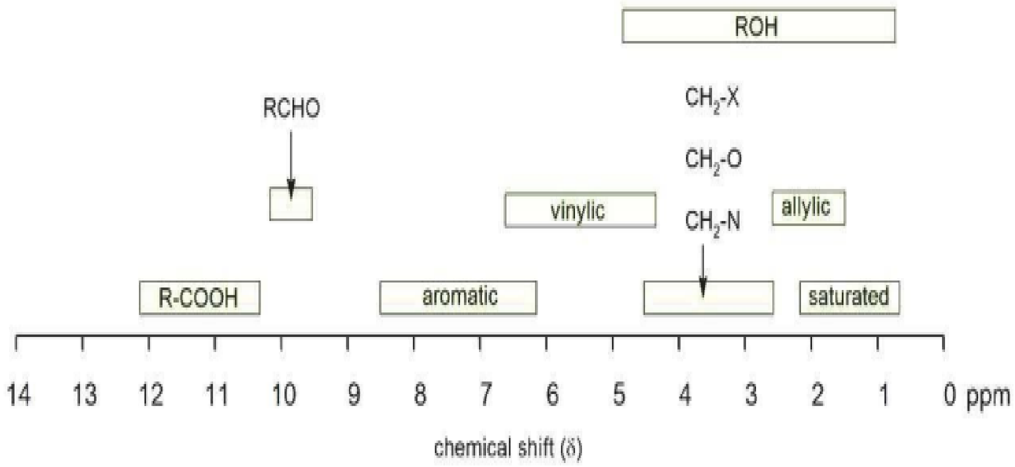


Figure 4.5 Chemical Shift Range

4.7 SPIN–SPIN COUPLING, SPLITTING OF A SIGNAL AND COUPLING CONSTANT:

The spin–spin splitting is explained by ‘n + 1’ rule, each type of proton are affected by number of equivalent proton ‘n’ on the atom adjacent to the carbon atom with which hydrogen under observation is attached. Thus its resonance peak split into ‘n + 1’ components. In order to understand the spin-spin coupling, consider the following examples:

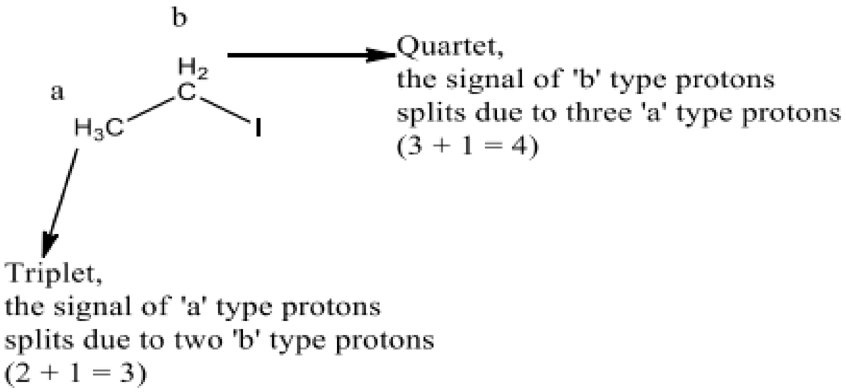


Figure 4.6 Spin–spin splitting

In the above example the set of protons ‘a’ have equivalent electronic atmosphere, so gives one signal. But due to interaction of neighbouring nuclear spins of two ‘b’ type protons, the one signal of ‘a’ type protons splits. The splitting is according ‘n+1’, where n is the number of neighbouring protons. So in this case the one signal splits into triplet, as n=2 (two ‘b’ type protons), so ‘n+1’ gives 2+1 = 3. Similarly the ‘quartet’ for ‘b’ type protons can be explained.

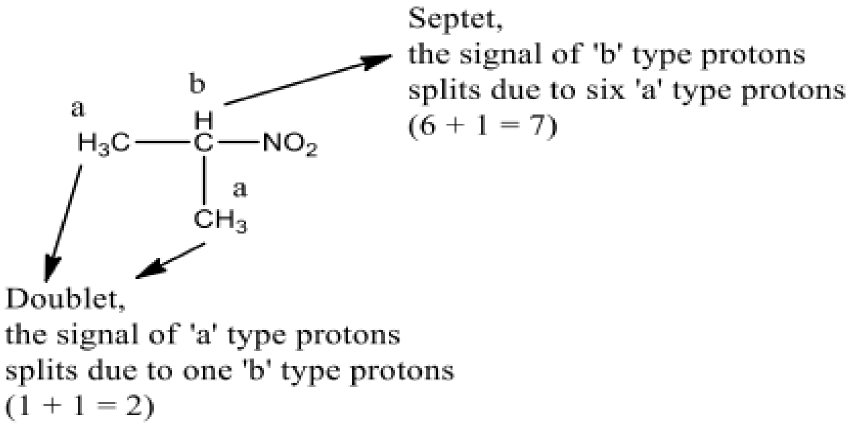


Figure 4.7 Spin–spin splitting

4.8 Spin – Spin Coupling

The spin–spin splitting arises because protons on adjacent carbon atom can sense the spin direction of each other. The chemical shift of proton is influenced by the direction of spin of neighbouring protons. This interaction is magnetic in nature and is termed as spin – spin coupling.

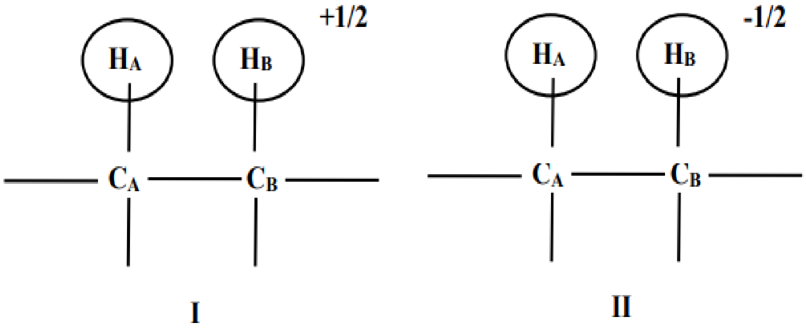


Figure 4.8 Spin – Spin Coupling

Consider two cases I & II, the hydrogen on the carbon A (presented as CA) can sense the spin direction of the hydrogen on carbon B (presented as CB).

In some molecules HB has spin +1/2 (I) and in some molecules HB has spin -1/2 (II). The chemical shift of proton A is influenced by the direction of spin of HB. Proton A is said to be coupled with proton B and its magnetic environment is affected by spin of proton B.

Thus proton A absorb at a slightly different chemical shift in case I and II. As there is a equal probability of case I and II, the two absorptions have nearly equal intensity.

The resonance of proton A is said to be split by proton B and the phenomenon is known as spin-spin coupling.

4.9 Instrumentation Techniques of NMR Spectroscopy

The instrument contains a radio frequency transmitter to transmit the radio frequency. The sample under study is placed in a spinning tube, which is placed between two magnet poles.

Two sweep coils are placed between the spinning tube and the magnets. The sweep coils are fitted with a sweep generator.

The radio frequency transmitter transmits radio frequency which passes through the sample under observation and is then received in radio frequency receiver and amplifier.

Finally, it is recorded in the control console and recorder. The block diagram of NMR spectrometer is shown in figure.

The basic requirements of a typical NMR spectrometer are:

i. **Electromagne**t: A powerful electromagnet provides a homogeneous and stable magnetic field.It should be constant over the area of the sample and during the period of the experiment.

ii. **Sweep Generator** : It supplies variable current to a secondary magnet. As a result the total applied magnetic field can be varied over a small range.

iii. **Sample Tube**: A sample tube is usually made of glass. It is the tube which contains the sample under investigation. The sample tube is rotated by an air-driven turbine which provides homogeneous magnetic field to the sample under investigation.

iv. **Radio-frequency Transmitter**: A radio frequency transmitter transmits desired energy to the sample.

v. **Radio-frequency Receiver & Amplifier**: A radio frequency receiver receives the signals coming from the sample. It also amplifies the signal.

vi. **Control Console and Recorder**: It is a read out system. It records the signal coming from the receiver. It also increases the sensitivity and resolution. It plots the output results in the form of spectrum.

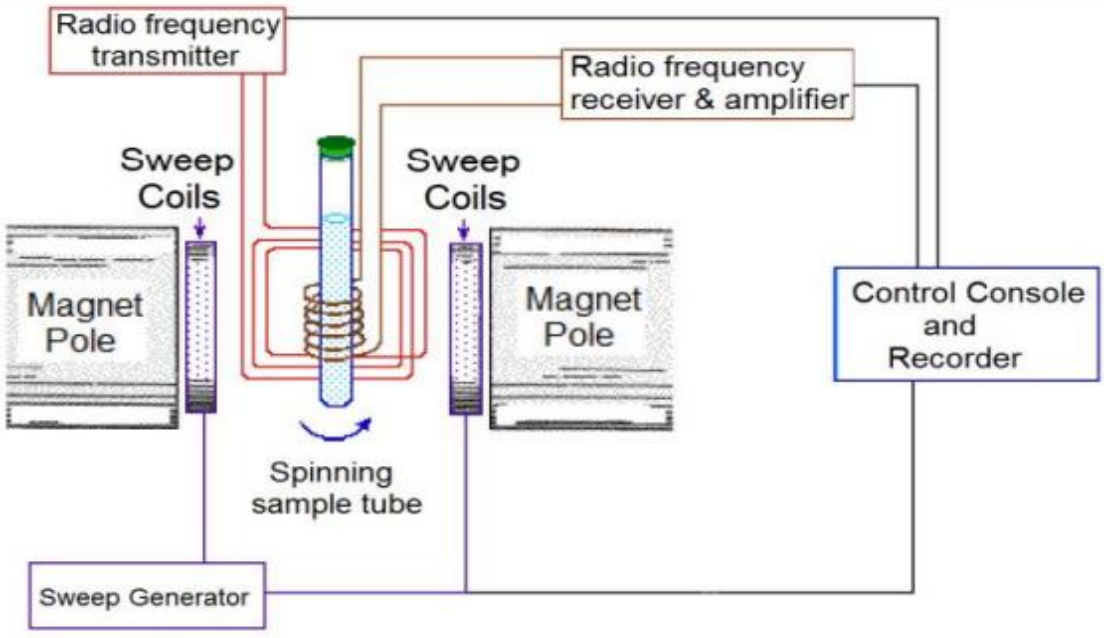


Figure 4.9 Block diagram of NMR spectrometer

4.10 NMR in Chemical industries:

1. IDENTIFICATION OF SUBSTANCES.

Lie IR spectrum, NMR spectrum can also be used as a fingerprint of the substances. If the PMR spectrum of a given sample is exactly the same as that of a known compound, the given compound must be identical with the known compound.

2.DERTERMINATION OF MOLECULAR STRUCTURE.

NMR spectra are often very complex. But this complexity is not a disadvantage but is often useful in determining the molecular structure since it makes the spectra characterteristic.

3.Identification Of Reaction Products.

Where ever in reaction, two or more products are theortically possible. NMR spectroscopy has been used to identify the actual product .

4.Distinction Between Geometrical Isomers .

NMR spectroscopy can be used to distinguish between cis and trans isomers the distinction is based up on the magnitude of coupling constant.

5.Distinction Between Inter And Intramolecular Hydrogen Bonding .

During H bonding transfer of electrons occurs from the hydrogen atom to the neighboring electronegative atoms . As a result hydrogen bonded hydrogen gets deshielded.

Electron Spin Resonance:

4.11 Basic principle:

Electron paramagnetic Resonance (EPR), often called Electron Spin Resonance (ESR) was discovered by Soviet physicist , Zavoisky in 1945.

Figure 4.10 Electron Spin Resonance (ESR)

ESR is a branch of absorption spectroscopy in which electromagnetic radiation having frequency in the microwave region is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spin i.e. electronic spin $S < 0$. The magnetic energy splitting is done by applying a strong static magnetic field, which is exposed to an orthogonal low amplitude high frequency field.

The free electron behaves as a spinning, negatively charged particle with a resulting magnetic moment. By virtue of its charge and spin an electron acts as a bar magnet and can thus interact with an external magnetic field.

4.12 Types of Substances with Unpaired Electrons :

a) Stable Paramagnetic Substances : These include stable substances which can be studied very easily eg. NO, O_2 and NO_2 and transition metal ions and rare earth elements.

b) Unstable Paramagnetic Substances : These can be produced either as the intermediate in chemical reaction or by irradiation of stable molecules with a beam of nuclear particles or with U.V. or X-ray radiation i.e. the free radicals or radicals ions.

4.13 Theory Of ESR:

i) Electron Behaviour :

In ESR, the energy levels are produced by the interaction of the magnetic moment of an unpaired electron in a molecule ion with an applied magnetic field.

The ESR spectrum results in due to the transitions between three energy levels by absorbing radiation microwave frequency.

The magnetism of an electron can be expressed by saying that an electron with a magnetic moment μ which is proportional to e/m, where e and m having their usual meanings has a spin, $S = 1/2$. This particle like proton has 2 magnetic energy levels. The lower level corresponds to $m = -\frac{1}{2}$ and higher to $m = +\frac{1}{2}$.

The magnetic moment thus given by:

$$\mu = - g \beta s \qquad \text{------(1)}$$

g = spectroscopic splitting factor or g – factor or gyromagnetic ratio.

g = ~ 2 or 2.0023193

β = Bohr magneton

$$\text{i.e} = \frac{e\,h}{4\,\pi\,n_e} = 9.2740 \times 10^{-24} \quad \frac{J}{T}$$

e & m_e being electronic charge and mass,

h = Planck's constant When electrons placed in magnetic field they will have their energies changed by certain number of ergs.

$$\begin{aligned} E &= \mu\,H \\ &= -g\,\beta_s\,H \\ &= \pm\,\frac{1}{2}\,(\,g\,\beta\,H) \qquad \text{-----(2)} \end{aligned}$$

Where H = field strength of external magnetic field.

S.I. units = Tesla (T) But in EPR gauss (1G = 0.0001T)

Thus the difference in energy ΔE between the two levels is given by

$$\begin{aligned} \Delta E &= g\beta H \\ &= h\,\upsilon \qquad \text{.... (3)} \end{aligned}$$

The overall magnetic momentum, μ_{eff} can be expressed via overall angular momentum. J & g values :

$$\mu_{eff} = \; g\,\beta\,[\,J\,(\,J+1)\,]^{1/2} \qquad \text{-----(4)}$$

In ESR spectroscopy unlike others, there is splitting of the energy levels and hence the frequency capable of causing transitions between these levels is a function of magnetic field strength H.

For the unpaired electrons there are thus 2 energy levels.

The population difference between the two energy levels of a sample having unpaired electrons in the thermodynamic equation in magnetic field is given by Boltzman law :

$$\frac{n_1}{n_2} = \exp\left(\frac{\Delta\,E}{k\,T}\right) \; = \; \exp(-\,\frac{g\,\beta\,H}{k\,T}) \qquad \text{-----(5)}$$

n_1 and n_2 = population in upper and lower level respectively.

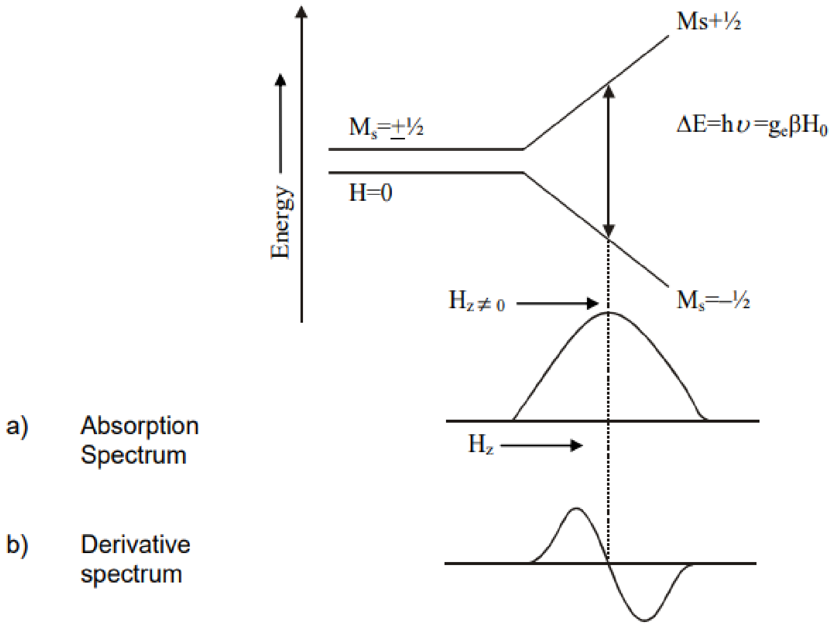
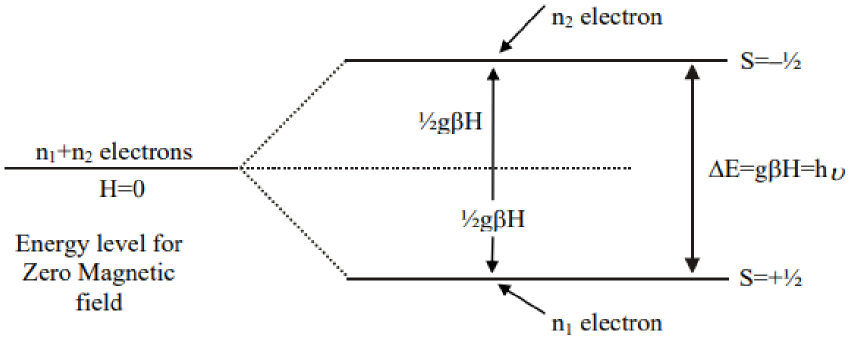


Figure 4.11

ENERGY LEVEL DIAGRAM SHOWING ESR SPECTRUM



ENERGY LEVELS FOR MAGNETIC FIELD H

Figure 4.12

Energy levels in ESR spectroscopy When radiation is supplied to the sample of frequency 2 in such a manner that energy between the electron states (i.e. $h \upsilon = \Delta E = g\beta H$), then resonance occur.

ii) THE G-FACTOR:

The g-actor is one of the important quantities determined from the ESR spectra of odd-electron systems.

The value for g for an unpaired electron in gaseous atom or ion, for which Russel-Saunders coupling is applicable is given by the expression.

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

For a free electron (S=½, L=0, J=½) value of g=2.0 is easily calculated from the above equation. Thus the actual value is 0.0023 due to relativistic correction. From the relation

$$\upsilon = g\beta H_o/h,$$

we see that $G = h\,\upsilon\,/\beta H_o$.

Thus, the g-factor is essentially a measure of the ratio between frequency and magnetic field, for the free electron g has a value 2.0023.

The organic radicals such as methyl radical, have the g-value very close to the free electron g-value molecule containing the unpaired electron with respect to the magnetic field.

In a solution or in the gas phase, g is averaged over all orientations because of the free motion of the molecules, but in a crystal movement is restricted.

If the paramagnetic radicals or ion is located in a perfectly cubic crystal site (eg. Octahedral or tetrahedral site), the g-value is independent of the orientation of the crystal and is said to be isotropic.

In a crystal site of lower symmetry the g-value depends upon the orientation of the crystal is said to be anisotropic.

The g_z value is equivalent to $g \parallel$, the g value obtained when z axis is parallel with the external magnetic field.

The g value along x and y axes are g_x and g_y, which in a tetragonal site are equal and referred to as $g\perp$, the g-value thus obtained with the external magnetic field perpendicular to the z-axis.

If θ is angle between magnetic field and z axis, the experimental g value is given by the following equation for a system with axial symmetry.

$$g^2 = g_{||}^2 \cos^2\theta + g\perp^2 \sin^2\theta$$

iii) HYPERFINE SPLITTING:

The detection of electron spin resonance signal proves the presence of unpaired electrons in the sample.

The intensity of the absorption line is proportional to the number of unpaired electrons. The ESR spectroscopy has been widely used in studying various photochemical, electro-chemical reaction proceeding via free radical mechanism because of the presence of hyperfine structure which is the result of the interaction between the unpaired electrons and magnetic nuclei in the paramagnetic species. It further gives two important informations:

1) It tells about the environment of the molecule and distribution of the electron density within the molecule.

2) It allows identification of paramagnetic substance in number of cases. The resonance frequency of an electron actually depends upon the magnetic field at the electron and electron infact is affected by the applied field, Ho and any local field due to magnetic fields of nuclei, H_{local}.

Thus the equations :

$$\Delta E = g\beta H = h\upsilon \qquad \text{becomes}$$

$$h\upsilon = g.\,\beta\,(H_O + H_{local})$$

The effect of magnetic moments of nuclei on ESR spectrum is known as hyperfine interaction and is responsible for splitting of ESR line, giving rise to hyperfine structure.

When an unpaired electron comes in the vicinity of a nuclear with a spin I, an interaction takes place which causes the absorption signal to be split into 2I+1 components, where I is the spin quantum number of the nucleus.

The cause of splitting in an isotropic system is the nuclear spin electron spin coupling arising mainly from the Fermi contact term.

This effect is simply illustrated by considering as an example of hydrogen atom (I=½ for the proton).

The proton thus has a magnetic moment and the electron will be affected by the magnetic field of the nucleus (a proton) as well as that of the applied magnetic field.

The energy of the electron will be modified by the orientation of the magnetic moment of the proton which can also be parallel or antiparallel to the magnetic field. The relative orientation of the nuclear magnetic moment and the electron magnetic moment causes a splitting of original 2 level to 4 level.

4.14 The Selection Rule For The Hyperfine Transition :

$$\Delta m_s = +1, \Delta m_I = 0$$

This selection rule may be interpreted by saying that the nuclear motion is much slower than the electronic motion so that during the time electron changes its spin orientation, the nucleus, being heavier has no time to reorient its spin so that $\Delta m_I = 0$ The EPR spectrum of a Hydrogen atom in a solid matrix consists of 2 peaks of equal intensity centered at g=2.0023.

The two-energy levels of a free electron in a magnetic field are shown in the Figure with $m_s = -\frac{1}{2}$ aligned with the field and $m_s = +\frac{1}{2}$ aligned opposed to the field. (The spectrum of a free electron would consist of a single peak corresponding to a transition between these levels).

For each value of electron spin angular momentum quantum number m_s, the nuclear spin angular momentum quantum number m_I, can have values of +½, giving rise to four different energy levels.

4.15 Instrumentation:

It consists of the following

Klystrons (source):

The source of the radiation ν is a klystron tube operating in the X-band (3 cm) region at about 9 G. The klystron can be turnover the range of about ± 0.5 gauss by a control which varies the dimensions of a resonant cavity inside the tube. The output frequency is also a function of a resonator and reflector voltages fed to the klystron by a power supply. It is generally stabilized against temperature fluctuations by immersion in an oil bath or by a feed-back Automatic Frequency Control (AFC) circuit. The power output of klystrons used in ESR spectrometer is generally about 300 milliwatts.

Wave Guide:

A microwave radiation is conveyed to the sample and crystal by a wave guide, a hallow rectangular brass tube 0.9 inch x 0.4 inch.

Attenuators:

The power propagated down the wave guide can be continuously decreased by interseting a variable attenuator consisting of a piece of resistive material into the wave guide. By the use of this attenuators, the power at the sample may be varied from the full power of the klystron to one attenuated by a factor of 100 or more.

Cavities:

The sample is contained in a resonant cavity in which a standing wave is setup. The cavity is analogous to a tuned circuit (e.g. a parallel L-C combination) used at low frequencies. The sensitivity of a spectrometer is directly proportional to the value of Q. Two frequently used cavities are the rectangular TE102 cavity and the cylindrical TE011 cavity. Since the component of interest is the magnetic field; which interacts with the sample to cause spin resonance, the sample is placed where the intensity of the magnetic field is at its highest. The electric field, however, also interacts with the sample and if the sample has a high dielectric constant (i.e. lossy) the Q of the cavity may be drastically decreased.

Crystal detectors:

The detector of the microwave radiations is usually a silicon crystal detector (which converts AC radiation to DC). An appreciable amount of noise is generated in a crystal detector; the magnitude of this noise is decreases with increasing frequency of the output signals. Therefore, the signal is usually modulated at a high frequency (6 k to 100 k) to decrease this source of noise.

Magic T's Bridge:

Microwave bridges (which are analogous to impedance bridges in conventional circuits) can be of the "magic-T" variety.

Power entering arm A will divide between arms B and C if the impedances of B and C are the same, so that no power will enter in arm D. Under these conditions the bridge is said to be balanced. If the impedance of arm B changes, say because a resonant cavity coupled to the end arm B changes its Q because of the occurance of ESR absorption by a sample in it. The bridge becomes unbalanced and some microwave power enters into arm D containing the crystal detectors. In this way the ESR absorption occurs as an increase of a small signal rather than as a decrease in a large one.

Magnets:

An electromagnet capable of producing field of at least 5000 gauss is required for ESR. The homogeneity of the field for solution studies should be about 50 milligauss over the ESR sample region. The ESR spectrum is recorded by slowly varying the magnetic field through the resonance conditions by sweeping the current supplied to the magnet by the power supply. This sweep is generally accomplished with a variable speed motor drive. Both the magnet and power supply may required water cooling.

Modulation Coils:

The modulation of the signal at a frequency constant with good signal to noise (S/N) ratios in the crystal detector is accomplished by a small alternating variation of the magnetic field. The variation is produced by supplying an a.c. signal to modulation coils oriented with respect to the sample in the same direction as the magnetic field. For low frequency modulations (400 cycle per second or less) the coils can be mounted outside the cavity and even on the magnet pole pieces. High modulated frequencies (1 KV or more) cannot penetrate metal effectively and either the modulation coils must be mounted inside the resonant cavity or cavities constructed of a non-metallic materials (e.g. quartz with a thin silvered plating) must be employed.

Display devices:

A cathode ray oscilloscope is used to adjust the spectrometer and sometimes to observe the signal.

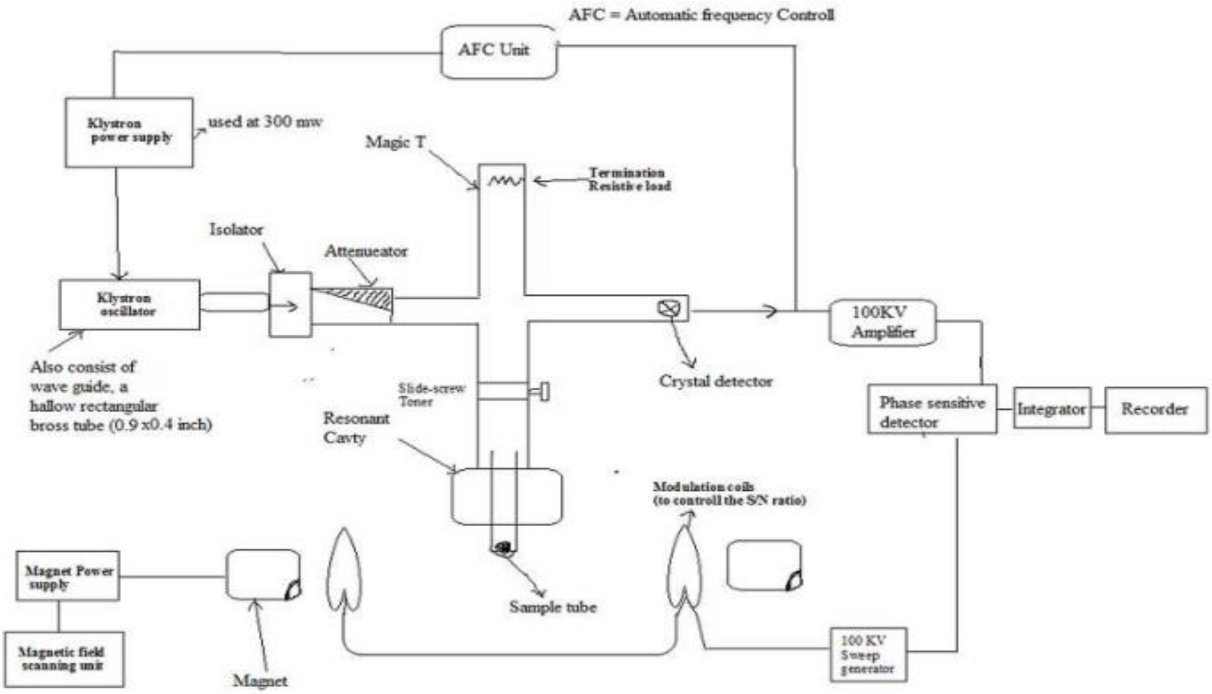


Figure 4.13 ESR

UNIT V

UV SPECTROSCOPY

Origin of UV spectra - Laws of absorption – Lambert Bouguer law – Lambert Beer law - molar absorptivity – transmittance and absorbance - Color in organic compounds- Absorption by organic Molecule -Chromophores -Effect of conjugation on chromophores - Choice of Solvent and Solvent effect - Absorption by inorganic systems - Instrumentation - double beam UV Spectro photometer -Simple applications

5.1 ELECTROMAGNETIC RADIATIONS

Visible light is a form of energy which can be described by two complementary theories i,e. Corpuscular theory and wave theory . Neither of these theories can explain all the properties of light, some properties of light such as photochemical effect ,black body radiations can be explained only by the corpuscular theory ,while the other properties of light such as diffraction ,interference etc can be explained only by the wave theory .

5.2 Electromagnetic wave theory

Wave theory was put forward by James Maxwell in 1864 .According to this theory

1. Energy is emitted from any source continuously in form of wave s or radiations and the energy thus emitted is called radiant energy. The most common example of radiant energy is heat, light X-rays etc.

2. Each radiation consists of mutually perpendicular oscillating electric and magnetic fields both of which are perpendicular to the direction of propagation of the radiation .

3. All radiations have wave character and travel with the velocity of light i,e. $3x10^{10}$

5.3 ELECTROMAGNETIC SPECTRUM

The field of spectroscopy deals with the study of absorption or emission of electromagnetic radiations .We are familiar with the number of different types of electromagnetic radiations such as cosmic rays, X-rays, Ultra violet light , visible light ,infra red radiations ,radio waves radar waves etc. All the electromagnetic radiations travel with the same velocity i,e.3x10^{10} cm/sec but differ from one another in the wave length of their waves .The arrangement of all types of electromagnetic radiations in the order of their increasing wavelength or decreasing frequency is called the electro magnetic spectrum.

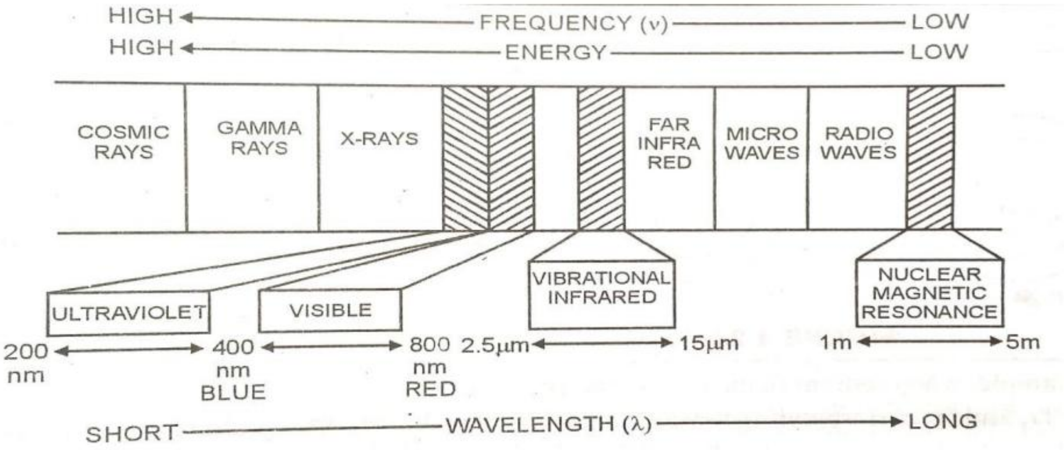


Figure 5.1 Electro magnetic spectrum

Spectroscopy is the study of the interaction between matter and electromagnetic radiation— radiant energy that displays the properties of both particles and waves. Several different spectrophotometric techniques are used to identify compounds.

Each employs a different type of electromagnetic radiation. We will start here by looking at ultraviolet and visible (UV/Vis) spectroscopy UV/Vis spectroscopy provides information about compounds with conjugated double bonds. Ultraviolet light and visible light have just the right energy to cause an electronic transition—the promotion of an electron from one orbital to another of higher energy. Depending on the energy needed for the electronic transition, a molecule will absorb either ultraviolet or visible light.

If it absorbs ultraviolet light, a UV spectrum is obtained; if it absorbs visible light, a visible spectrum is obtained. Ultraviolet light is electromagnetic radiation with wavelengths ranging from 180 to 400 nm (nanometers); visible light has wavelengths ranging from 400 to 780 nm. (One nanometer is or 10 Å.) Wavelength is inversely related to the energy: The shorter the wavelength, the greater is the energy. Ultraviolet light, therefore, has greater energy than visible light.

$$E = hc / \lambda$$

h =Planck's constant
c= velocity of light

The normal electronic configuration of a molecule is known as its ground state—all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an excited state.

Thus, an electronic transition is the promotion of an electron to a higher energy MO. The relative energies of the bonding, nonbonding, and antibonding molecular orbitals are shown.. Ultraviolet and visible light have sufficient energy to cause only the two electronic transitions shown in Figure 5.1.

The electronic transition with the lowest energy is the promotion of a nonbonding (lone-pair) electron (n) into a antibonding molecular orbital. This is called an (stated as ―n to star‖) transition.

The higher energy electronic transition is the promotion of an electron from a bonding molecular orbital into a antibonding molecular orbital, known as a (stated as ― to star‖) transition. This means that only organic compounds with electrons can produce UV Vis spectra.

5.4 PRINCIPLES OF UV SPECTROSCOPY

Whenever UV radiation is passed through the solution of an organic compound, it is either absorbed or transmitted depending up on the wavelength and its molecular structure of the organic compound.

As a result of the absorption of the energy an electron gets excited from the electronic state to some higher electronic state.

During this absorption process, some of the molecules of the organic compound will collide with the photons of the radiant energy.

Although a large number of such photon molecule collisions are possible , but only those will result in absorption of energy in which the energy of the photon exactly matches the difference in energies of the electron in the ground and the excited electronic states of the molecule

If E_0 and E_1 are the energies of the ground and the first ex between these states , then cited electronic states of the molecule respectively and ΔE is the difference in energy

$$\Delta E = (E_1 - E_0)$$

$$= hv$$

$$= h\,c/\lambda$$

5.5 The Beer–Lambert Law

Wilhelm Beer and Johann Lambert independently proposed that at a given wavelength, the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a solution of the sample.

In other words, absorbance depends on both the concentration of the sample and the length of the light path through the sample. The relationship among absorbance, concentration, and length of the light path is known as the Beer–Lambert law and is given by

$$A = \epsilon c l$$

Where A = absorbance of the sample

$\log_{I0}/I_{\ I0}$ = intensity of the radiation entering the sample

I = intensity of the radiation emerging from the sample

c = concentration of the sample, in moles/liter

l = length of the light path through the sample, in centimeters

ϵ = molar absorptivity (liter mol^{-1} cm^{-1})

5.6 Molar absorptivity

The molar absorptivity (formerly called the extinction coefficient) of a compound constant that is characteristic of the compound at a particular wavelength. It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00 cm path length.

The molar absorptivity of acetone, for example, is 9000 at 195 nm and 13.6 at 274 nm. The solvent in which the sample is dissolved when the spectrum is taken is reported because molar absorptivity is not exactly the same in all solvent So the UV spectrum of acetone in hexane would be reported as 195 nm (hexane); 274 nm (hexane).

Because absorbance is proportional to concentration, the concentration of a solution can be determined if the absorbance and molar absorptivity at a particular wavelength are known.

$$\epsilon = A/c\ l$$

5.7 Presentation Of Spectra

The ultraviolet–visible spectrum is generally recorded as a plot of absorbance versus wavelength. It is customary to then replot the data with either e or log e plotted on the ordinate and wavelength plotted on the abscissa. Figure5.2., the spectrum of benzoic acid, is typical of the manner in which spectra are displayed. However, very few electronic spectra are reproduced in the scientific literature; most are described by indications of the wavelength maxima and absorptivities of the principal absorption peaks.

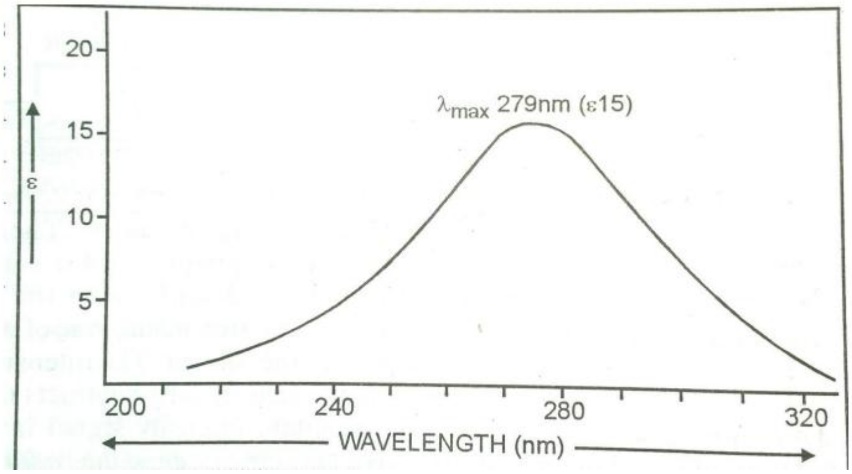


Figure 5.2 Ultraviolet–visible spectrum

5.8 SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important. The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined.

Usually solvents that do not contain conjugated systems are most suitable for this purpose, although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation. Table 5.1 lists some common ultraviolet spectroscopy solvents and their cutoff points or minimum regions of transparency.

Of the solvents listed in Table 5.1 , water, 95% ethanol, and hexane are most commonly used. Each is transparent in the regions of the ultraviolet spectrum in which interesting absorption peaks from sample molecules are likely to occur.

A second criterion for a good solvent is its effect on the fine structure of an absorption band. Figure 5.3. illustrates the effects of polar and non polar solvents on an absorption band. A non polar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed.

In a polar solvent, the hydrogen bonding forms a solute–solvent complex, and the fine structure may disappear

Table 5.1 Some Common Ultraviolet Spectroscopy Solvents And Their Minimum Regions Of Transparency

S.No	Solvents	Minimum Regions Of Transparency nm
1.	Acetonitrile	190
2.	Chloroform	240
3.	Cyclohexane	195
4.	1,4-Dioxane	215
5.	95% Ethanol	205
6.	n-Hexane	201
7.	Methanol	205
8.	Isooctane	195
9.	Water	190
10.	Trimethyl phosphate	210

5.9 Types of Electronic transitions

The absorption of electronic transition by organic compounds in the UV and Visible region occurs due to extinction of electrons from bonding or non-bonding molecular orbitals (ground state) to the antibonding moleculer orbitals (excited state) which are usually vacant in the ground state of the molecule. The electronic transitions that occur in UV and visible region are of following types:

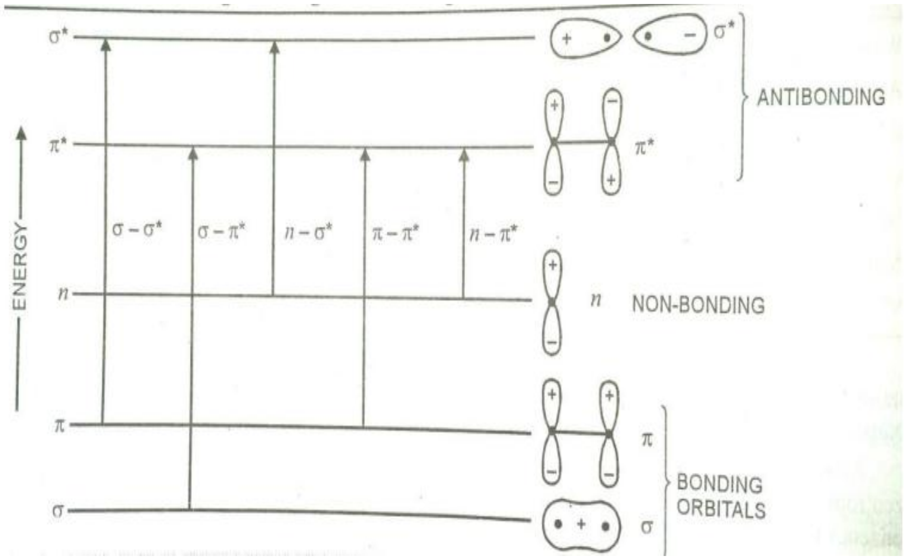
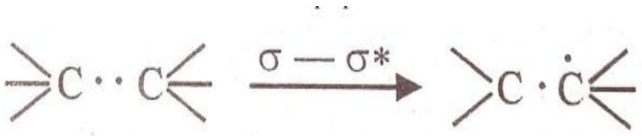


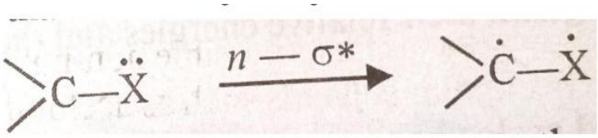
Figure 5.3 Fine Structure Of An Absorption Band

(ii) Transitions.(σ ---σ*)

Transitions in which an electron is excited from sigma bonding MO to sigma star antibonding MO are called σ---σ* transitions. These transitions are shown by only those compounds which all the electrons are involved in σ—bond formation i.e, in saturated hydrocarbons. These require very high energy. Therefore, these transitions occur at short wavelengths or high frequency and are usually found in vacumm or far ultraviolet region. For example, methane absorbs at 125nm and propane at 135nm.

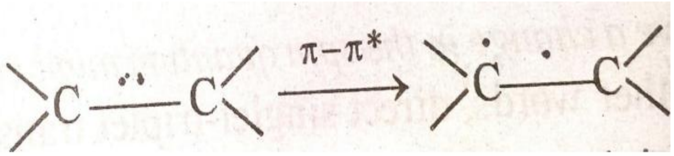


(ii) n—σ* Transitions in which a non—bonding electron is excited to σ* antibonding MO are called n—σ* transitions. These transitions occur in those compounds which contain heteroatoms such as oxygen, nitrogen , sulphur, halogens etc. For example alcohol, ethers, alkyl halides, amines, aldehydes and ketones show this type of transition. These transitions require lower energy than σ—σ* transitions and hence occur at longer wavelengths than σ—σ* transitions



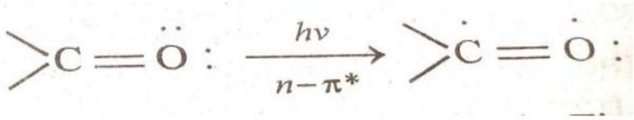
In fact the energy required for these transitions depends up on the electronegativity of the heteroatom. Lower the electronegativity , higher the wavelength of absorption. For example metyhyl alcohol absorbs at λmax 258.

(iii)π--- π *Transitions .transitions in which a π-electron is excited to a antibonding orbital π *MO are called π--- π *



This type of transition occurs in saturated compounds containing double bonds and also in aromatic compounds .These transitions generally require a large amount of energy and hence occur at short wavelength .For example organic compounds containing isolated unsaturated centre,t he absorption due to π--- π *transition occurs well outside the range of ordinary spectro photometers. In saturated aldehydes and ketones the π--- π * transition produces a n absorption band of high intensity at about 285nm.

(iv) n---- π * transitions. transitions in which an electron is excited from the non bonding atomic orbital to the π *MO are called n---- π * t6ransitions.



All organic compounds containing a double between carbon and some hetero atom such as c=0,c=s,n=o etc this type of transition.

5.10 The Effect Of Conjugation

One of the best ways to bring about a bathochromic shift is to increase the extent of conjugation in a double-bonded system. In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together. As a result, the energy required to produce a transition from an occupied electronic energy level to an unoccupied level decreases, and the wavelength of the light absorbed becomes longer. Figure illustrates the bathochromic shift that is observed in a series of conjugated polyenes as the length of the conjugated chain is increased

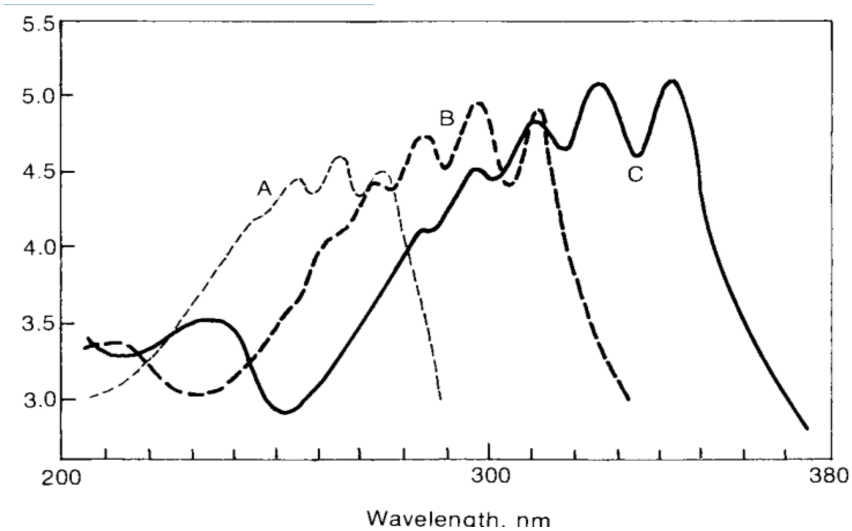


Figure 5. 4. Bathochromic Shift

5.11 The Effect Of Conjugation On Alkenes

The bathochromic shift that results from an increase in the length of a conjugated system implies that an increase in conjugation decreases the energy required for electronic excitation. This is true and can be explained most easily by the use of molecular orbital theory.

According to molecular orbital (MO) theory, the atomic p orbitals on each of the carbon atoms combine to make p molecular orbitals. For instance, in the case of ethylene (ethane), we have two atomic p orbitals, f_1 and f_2.

From these two p orbitals we form two p molecular orbitals, y_1 and y_2*, by taking linear combinations. The bonding orbital y1 results from the addition of the wave functions of the two p orbitals, and the antibonding orbital y2* results from the subtraction of these two wave functions. The new bonding orbital, a has an energy lower than that of either of the original p orbitals; likewise, the antibonding orbital has an elevated energy.

5.12 Chromophoric group

The term chromophoric was originally applied to a system which imparts colour to a compound (Greek, chromophorus=color carrier). For example, nitro group is a chromophre since it imparts yellow colour to a compound.

Similarly, aryl conguted azo group (Ar---N=N-- --Ar) is a chromophore since it imparts colour to the azo dyes. But now the term chromophore is used in a much broader sense.

Thus, a chromophore is now defined as any functional group that absorbs electromagnetic radiations irrespective of the fact whether it imparts colour to the compound or not.

For example, a coarbonyl group is a chromophore since it absorbs in the UV region at about 279 nm with a molar extinction coefficient of about15. Chromophores such as >C=C< and –C=C—which contains π- electrons and hence undergo π-π* transitions. Chromophores such as >C=O,--N=N--, --NO2 etc., which contain both π- and n- electrons and hence undergo π- π* and n- π* transitions.

5.13 Instrumentation :

A spectrophotometer is an instrument which uses monochromatic light. It measures the absorbance of various solutions at different wavelengths. This instrument scans the entire UV-visible regions. In a double beam spectrophotometer, radiation from hydrogen lamp or tungsten lamp enters the monochromator, which produces very narrow band widths. The beam is then passed through a reference cell and the sample cell by means of rotating mirrors. The photomultiplier tube is used as a detector which receives alternate pulses of radiation from the reference and sample beam.

Sources:

Commonly used sources of UV radiation are the hydrogen lamp and the deuterium lamp. Tungsten filament lamp is used for the visible range. Filters and Monochromators: Tinted glass filters are used to produce monochromatic radiations. Filters resolve polychromatic light into a relatively wide bandwidth to produce monochromatic radiations. Monochromator is a device which resolves polychromatic radiation into its individual wavelength and isolates them into very narrow bands.

Prism:

A prism disperses polychromatic light from a source into its constituent wavelengths. Cornu quartz and littro prisms are used. Glass prisms are used for visible range while silica, fused silica or quartz prisms are used for the UV range.

Sample Holder (Cells / Cuvette) :

The sample container should be transparent to the UV-visible radiation. Cuvettes are made ordinary glass or quartz. Fused silica cells are used for the UV range. The path length of these cuvettes is usually 1 cm.

Solvents:

A solvent is selected in such a way that it does not absorb in the UV-visible range. The solvents that are frequently used are water, methanol, ethanol, hexane, chloroform etc. Detectors: The commonly used detectors are photocells, phototubes and photomultiplier tubes.

Amplification and Read out:

The transmitted radiation is converted into electrical signal and the electrical signals are interpreted using ammeters, amplifiers and potentiometers.

5.14 Double beam UV Spectro photometer

Double beam spectrophotometer is an analytical instrument in which the light beam coming from the light source splits into two fractions.

One fraction acts as the reference (the reference beam) while the other fraction passes through the sample (sample beam). As a result, the reference beam does not pass through the sample.

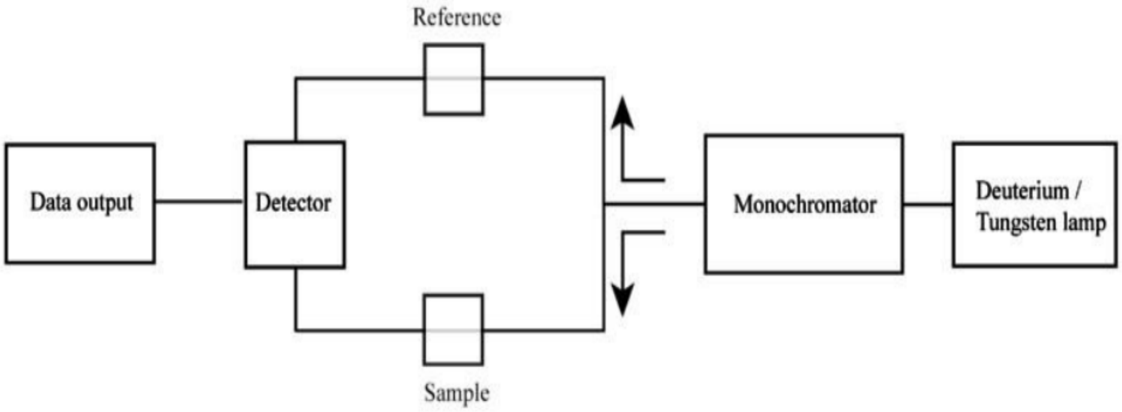


Figure 5.9 Double beam UV Spectro photometer

The sample beam can measure the absorbance of the sample. The reference beam can measure the absorption (the sample beam can be compared with the reference beam).

Therefore, the absorption is the ratio between the sample beam (after passing through the sample) and a reference beam. A spectrophotometer has a monochromator that isolates the desired wavelengths from a light beam.

The reference beam and sample beam recombine before moving to the monochromator. Consequently, this avoids or compensates the electronic and mechanical effects on both sample and reference beams, equally.

5.15 Applications:

1. Detection of Impurities

It is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. Also by measuring the absorbance at specific wavelength, the impurities can be detected.

2. Structure elucidation of organic compounds

It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of unsaturation, the presence of hetero atoms.

3. UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation.

4. UV absorption spectroscopy can characterize those types of compounds which absorbs UV radiation thus used in qualitative determination of compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

5. This technique is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.

6. Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

7. Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

8. Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

9. UV spectrophotometer may be used as a detector for HPLC.