KUNTHAVAI NAACHIYAAR GOVT ARTS COLLEGE FOR WOMEN, THANJAVUR

DEPARTMENT OF PHYSICS

II M.SC PHYSICS

SPECTROSCOPY

CODE – 18KP3P09

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UNIT – I

MICROWAVE AND INFRA-RED SPECTROSCOPY

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INTRODUCTION

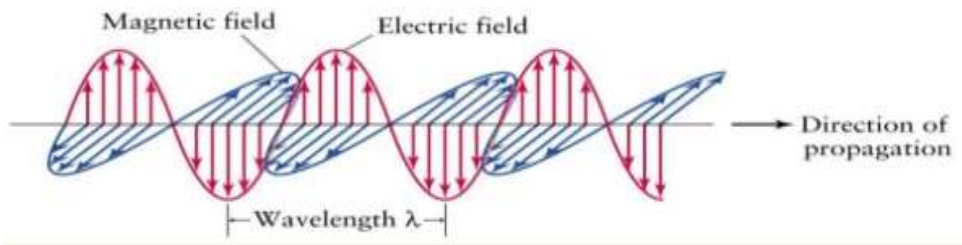
DEFINITION- Spectroscopy is the study of "interaction of electromagnetic radiation with matter.

E.M wave/radiation is a form of energy which is found around us. It has electric and magnetic properties.

E.M. Radiation is a form of energy emitted and absorbed by charged particles which exhibits wave-like behavior as it travels through space.

It propagates as wave motion with velocity of c=3x10^8m/s.

Electric and magnetic fields oscillates perpendicular to the direction propagation of wave as shown below.



Frequency (ν) - number of waves produced per second OR number of waves passes a point per second (unit-Hertz (Hz).
Wavelength (λ)- distance between two successive waves (unit-meter(m)
Amplitude (A)- maximum displacement of the medium from the equilibrium (rest)position. *Or m*aximum distance a wave extends beyond its middle position (unit-meter (m).
Speed (c)- wavelength x frequency**.** **c= λ ν**

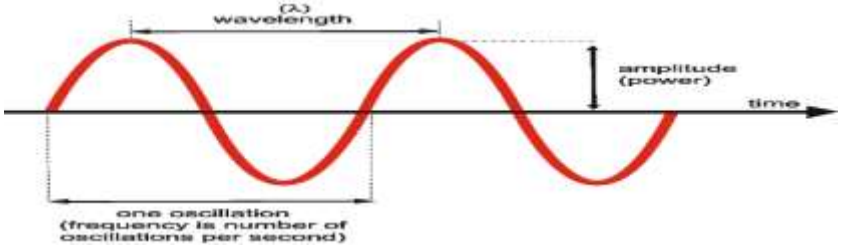
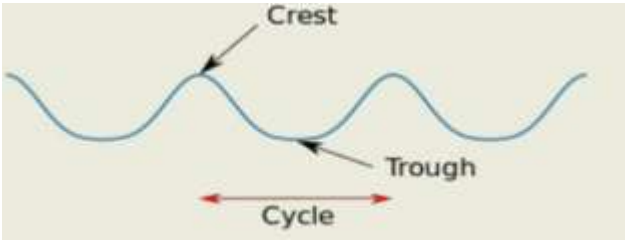


Fig. Wavelength, frequency and amplitude of an E.M.R

Crest – A crest is the point on a wave with the maximum value or upward displacement within a cycle.

Trough - A trough is the opposite of a crest, so the minimum or lowest point in a cycle.



E.M.Waves and energy

Different EM waves carry different amounts of energy. The amount of energy carried by em waves depends on the wavelength or frequency. Thus,

- Shorter wavelength/higher frequency = higher energy.
- longer wavelength/shorter frequency lower energy.

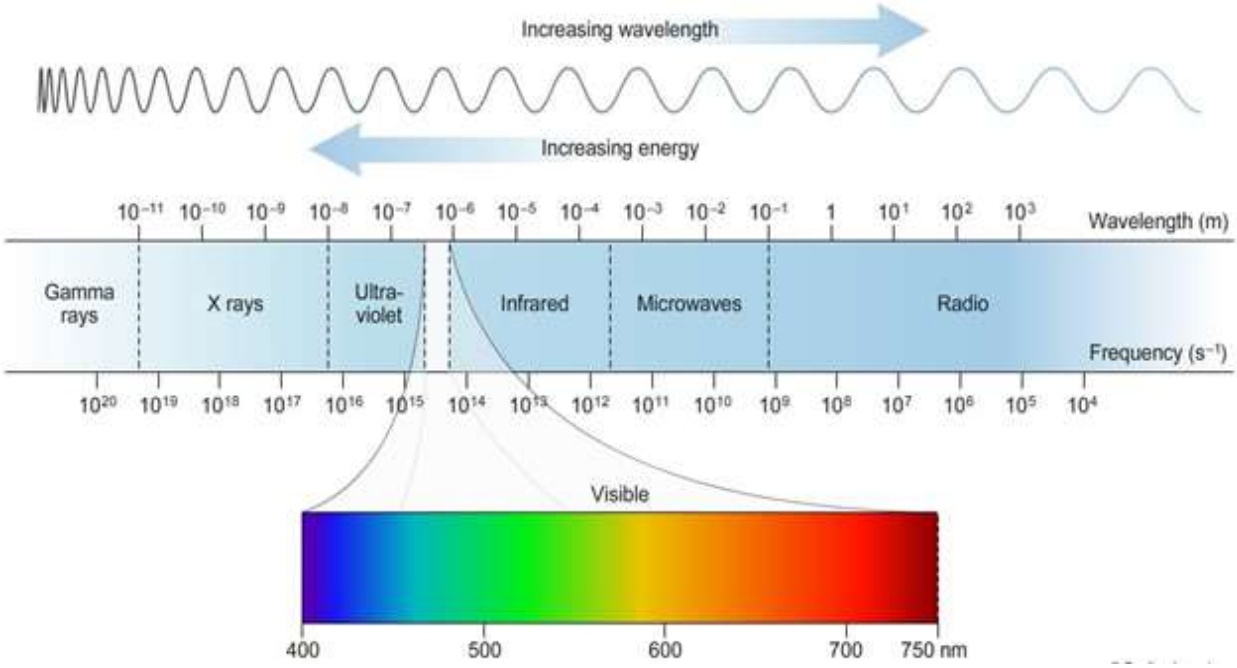


Fig. Electromagnetic spectrum

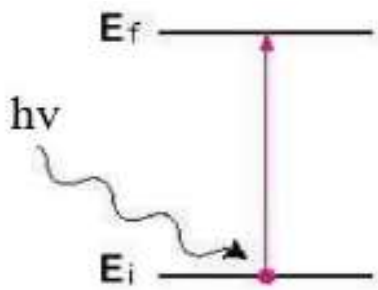
EM spectrum ranges from shorter wavelength (gamma) to longer wavelengths (radio). Visible range – 400 to 750 nm.
#shorter wavelength– blue end.
#longer wavelength – red end.

Applications of Spectroscopy

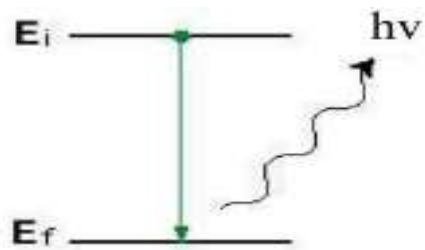
- determine the 3-dimensional structure of molecules.
- determine the molecular weight of the compound
- determine the presence of functional groups and also the position of functional groups.
- determine and identify different elements or chemical compounds.

What happens when radiation interacts with matter?

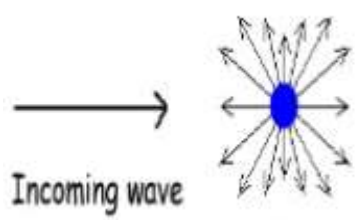
1. Absorption



2. Emission



3. Scattering



Types of Spectroscopy

- **Absorption Spectroscopy**
  - ✓ Here em radiation is absorbed by an atom or molecule.
  - ✓ So there is transition from lower energy state to higher energy state or excited state.
  - ✓ Absorption take place only when the in incident radiation energy matches with the energy difference in two levels.

Electromagnetic Radiation	Spectroscopy type
X-ray	X-ray absorption spectroscopy
UV-Visible	UV-Vis absorption spectroscopy
IR	Infrared absorption spectroscopy
Microwave	Microwave absorption spectroscopy
Radiowave	Electro spin resonance spectroscopy (ESR) Nuclear magnetic resonance spectroscopy(NMR)

- Emission Spectroscopy
  - ✓ Atoms or molecules that are excited to higher energy levels decay to lower energy levels by emitting radiation.
  - ✓ The substance first absorbs energy and then emits this energy as radiation.

- Scattering Spectroscopy
  - ✓ The scattering of em radiation by the atoms and molecules present in the sample.
  - ✓ The scattered light is an invaluable tool for molecular fingerprinting.

MICROWAVE SPECTROSCOPY

- Microwave radiation excites the rotational levels of molecules.
- It accomplishes this through the interaction of the electric dipole moment of the molecules with the radiation.

Characteristics of Microwaves

Wavelength – 1 cm to 100 μm

Wavenumber – 1 to 100 cm^{-1}

Frequency – 3×10^{10} to 3×10^{12} Hz

Energy – 10 to 1000 Joules / mole

MICROWAVE ACTIVE MOLECULES

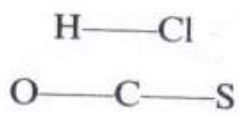
Molecules with permanent dipoles are **microwave** active (the **molecule** must be polar), e.g. heteronuclear diatomics - HCl, CO, NO, etc.

Homonuclear molecules are **microwave** inactive (e.g. O_2, N_2, etc.)

Rotation of Molecules

The rotation of a three dimensional body can be explained based on the rotational components about three mutually perpendicular directions through the centre of gravity. That is the principal axes of rotation. Thus a body has 3 principal moments of inertia, one about each axis I_A, I_B and I_C. Molecules are classified into groups based on these three MoI.

1. *Linear molecules.* These, as the name implies, are molecules in which all the atoms are arranged in a straight line, such as hydrogen chloride HCl, or carbon oxysulphide OCS, illustrated below. The three directions of rotation may be taken as (*a*) about the bond axis, (*b*) end-over-end

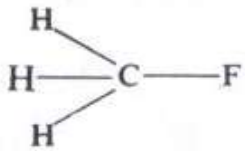


rotation in the plane of the paper, and (*c*) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (*b*) and (*c*) are the same (i.e., $I_B = I_C$) while that of (*a*) is very small. As an approximation we may say that $I_A = 0$

Thus for linear molecules we have:

$$I_B = I_C \qquad I_A = 0$$

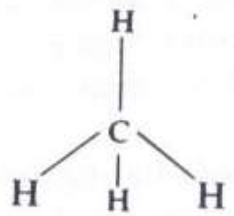
2. *Symmetric tops.* Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below. As in the case of linear molecules, the end-over-end rotation in,



and out of, the plane of the paper are still identical and we have $I_B = I_C$.

$$\text{Symmetric tops:} \quad I_B = I_C \neq I_A \qquad I_A \neq 0$$

3. *Spherical tops.* When a molecule has all three moments of inertia identical, it is called a spherical top. A simple example is the tetrahedral molecule methane CH_4. We have then:



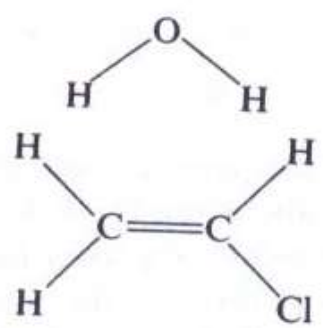
Spherical tops: $I_A = I_B = I_C$

Since they can have no dipole moment owing to their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable.

4. *Asymmetric tops.* These molecules, to which the majority of substances belong, have all three moments of inertia different:

$$I_A \neq I_B \neq I_C$$

Simple examples are water H_2O, and vinyl chloride $CH_2{=}CHCl$.



DIATOMIC MOLECULES

THE RIGID DIATOMIC MOLECULE

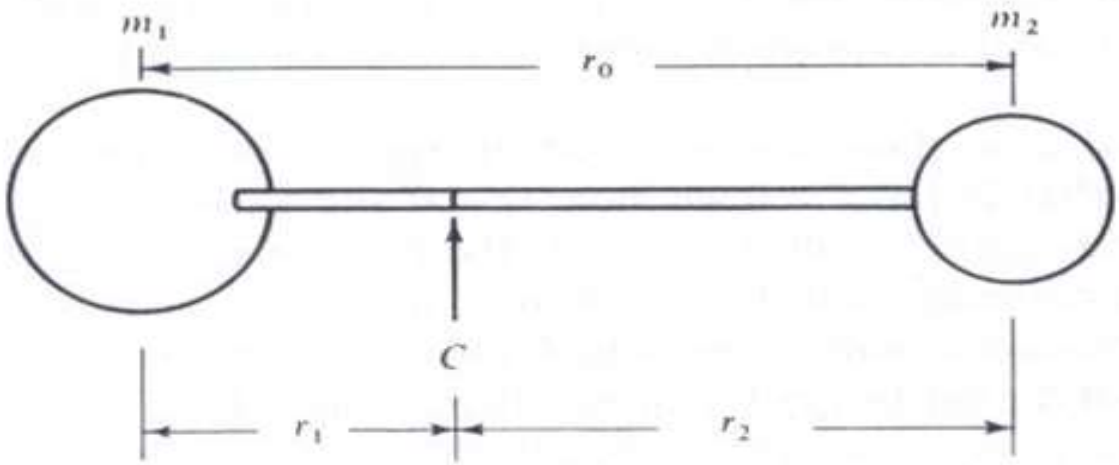
Diatomic molecules are molecules composed of only two atoms, of the same or different chemical elements.

Consider a diatomic molecule consists of two masses bound together.

The distance between the masses, or the bond length, (l) can be considered fixed because the level of vibration in the bond is small compared to the bond length.

Masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2 \qquad (1)$$



The molecule rotates end-over-end about a point C, the centre of gravity: this is defined by the moment, or balancing, equation:

$$m_1 r_1 = m_2 r_2 \qquad (2)$$

The moment of inertia about C is defined by:

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

From equation (2)

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

$$= r_1 r_2 (m_1 + m_2) \qquad (3)$$

From Equation (1) and (2)

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

therefore,

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

Substitute (4) in (3)

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \qquad (5)$$

Where

$$\mu = m_1 m_2/(m_1 + m_2)$$

Is called as reduced mass of the system. Equation (5) defines the moment of inertia interms 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:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules} \qquad \text{where } J = 0, 1, 2, \ldots \qquad (6)$$

In this expression h is Planck's constant, and 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*: its restriction to integral values arises directly out of the solution to the Schrödinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule.

Equation (6) expressed the allowed energies in joules. But the energies are expressed in terms of frequency or wavenumber.

frequency, $\nu = \Delta E/h$ Hz, or wavenumber, $\bar{\nu} = \Delta E/hc$ cm^{-1}

Therefore energies expressed in these units is given by

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \quad (7)$$

$$(J = 0, 1, 2, \ldots)$$

where c, the velocity of light, is here expressed in cm s^{-1}, since the unit of wavenumber is reciprocal *centimetres.*

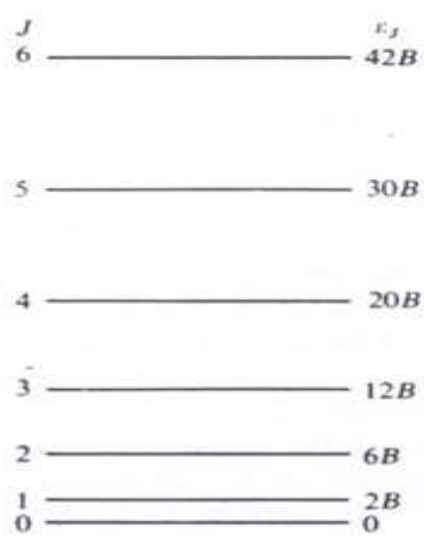
Equation (7) is abbreviated to

$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} \quad (8)$$

where B, the *rotational constant*, is given by

$$B = \frac{h}{8\pi^2 I_B c} \text{ cm}^{-1} \quad (9)$$

From equation (8) the allowed energy levels for a rigid diatomic molecules are represented diagrammatically



Plainly for $J = 0$ we have $\varepsilon_J = 0$ and we would say that the molecule is not rotating at all. For $J = 1$, the rotational energy is $\varepsilon_1 = 2B$ and a rotating molecule then has its lowest angular momentum.

We now need to consider *differences* between the levels in order to discuss the spectrum. If we imagine the molecule to be in the $J = 0$ state (the *ground rotational state*, in which no rotation occurs), we can let incident radiation be absorbed to raise it to the $J = 1$ state. Plainly the energy absorbed will be:

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \quad \text{cm}^{-1}$$

and, therefore,

$$\bar{\nu}_{J=0\to J=1} = 2B \quad \text{cm}^{-1} \qquad (10)$$

In other words, an absorption line will appear at $2B$ cm^{-1}. If now the molecule is raised from the $J = 1$ to the $J = 2$ level by the absorption of more energy, we see immediately:

$$\bar{\nu}_{J=1\to J=2} = \varepsilon_{J=2} - \varepsilon_{J=1}$$

$$= 6B - 2B = 4B \quad \text{cm}^{-1} \qquad (11)$$

In general, to raise the molecule from the state J to state $J + 1$, we would have:

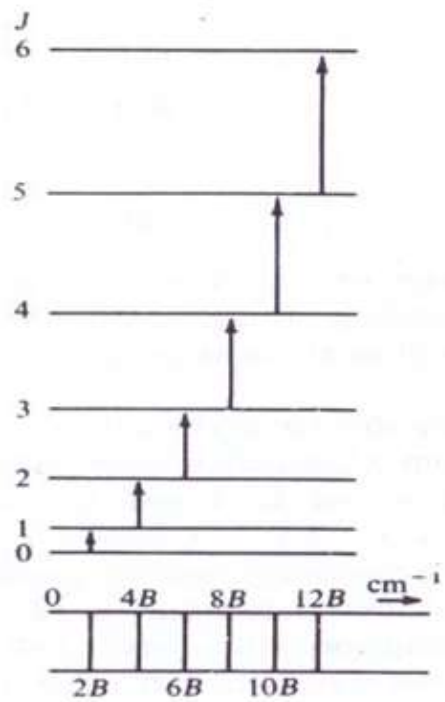
$$\bar{\nu}_{J\to J+1} = B(J+1)(J+2) - BJ(J+1)$$

$$= B[J^2 + 3J + 2 - (J^2 + J)]$$

or

$$\bar{\nu}_{J\to J+1} = 2B(J+1) \text{ cm}^{-1} \qquad (12)$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B$, $4B$, $6B$, ..., cm^{-1}



Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

<u>Selection Rule</u>

"The possible transition from one level to another level" is selection rule. All the other transitions are spectroscopically forbidden.

Selection rule $\Delta J = \pm 1$

Non-rigid Rotator- When the molecule rotates the atoms are subject to centrifugal forces which stretch the bonds - this is the non-rigid rotor

- **Rotation of atoms affects the rigid nature (length) of the chemical bonds and it increases the moment of inertia of a given molecule.**
- More faster the rotation of a diatomic molecule, the greater the centrifugal force tending to move the atoms apart. This results increase in the bond length ⇒ MoI also increases. **Increase in MoI reduces energy separation.**

Spectrum of a 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:

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

or

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

where B, the *rotational constant*, is given by

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

and D is the *centrifugal distortion constant* given by,

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \quad \text{cm}^{-1} \quad \rightarrow 3$$

which is a positive quantity.

Equation 2 applies for a simple harmonic force field only. If the force field is anharmonic the expression becomes

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \cdots \text{cm}^{-1} \quad \rightarrow 4$$

Where H, K are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by equation 2.

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

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} \quad \rightarrow 5$$

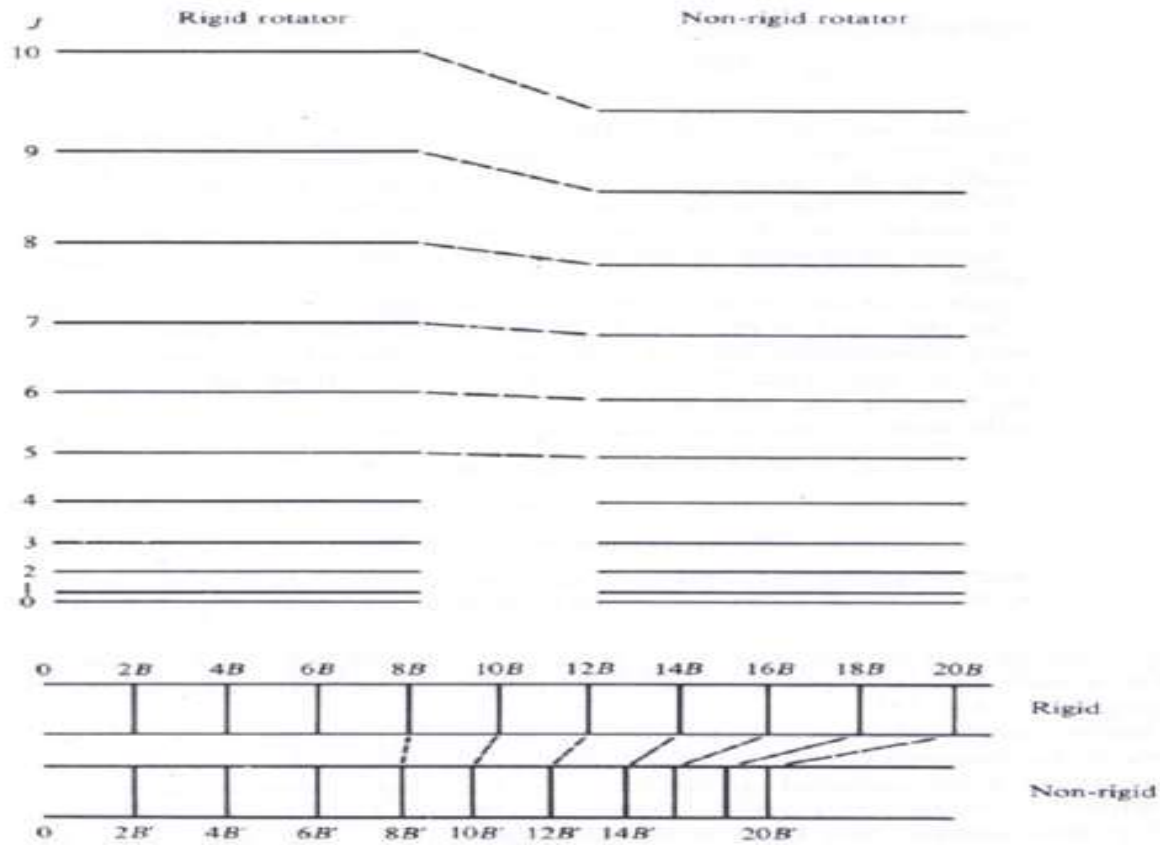
where $\bar{\omega}$ is the vibrational frequency of the bond, and k has been expressed by the equation (k-force constant)

$$k = 4\pi^2\bar{\omega}^2 c^2 \mu$$

The value of B is of the order of 10 cm^{-1}
The value of D is of the order of $10^{-3} cm^{-1}$
i.e., D is very small compared with B

For small J , $DJ^2(J+1)^2$ is negligible , For J≫ 10 it may become appreciable.

The rotational energy levels are lowered when passing from the rigid to the non-rigid diatomic molecule.



Selection Rule

$$\Delta J = \pm 1$$

analytical expression for the transitions:

$$\begin{aligned}\varepsilon_{J+1} - \varepsilon_J = \bar{\nu}_J &= B[(J+1)(J+2) - J(J+1)] \\ &\quad - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1}\end{aligned}$$

where $\bar{\nu}_J$ represents equally the upward transition from J to $J+1$,

Thus spectral lines are not equidistant. But their separation decreases slightly with increasing J. The knowledge of D gives two useful information

1. To determine the J value of lines in an observed spectrum.
2. To determine the vibrational frequency of a diatomic molecule.

POLYATOMIC MOLECULES –Linear Molecules

Examples – carbon oxysulphide OCS and chloroacetylene HC≡CCl

Since $I_B = I_C$ *and* $I_A = 0$ for diatomic molecules the energy levels are identical with the following equation.

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + \cdots \text{ cm}^{-1}$$

Whole discussion on diatomic molecules applies for all linear molecules. Three points underlined are

1. The MoI of the end-over-end rotation of the polyatomic linear molecule is greater that diatomic and the B value will be smaller and the spectral lines more closely spaced. B values for diatomic is 10/cm and for triatomic is 1/cm and for larger molecules smaller still.
2. Molecule must possess a dipole moment if it exhibits a rotational spectrum. Thus OCS is microwave active while OCO is microwave inactive. Isotopic substitution does not lead to a dipole moment since bond lengths and atomic charges are unaltered.
3. A non cyclic polyatomic molecule contains N atoms has N-1 bond length to be determined. However only one bond length can be determined from the spectrum.

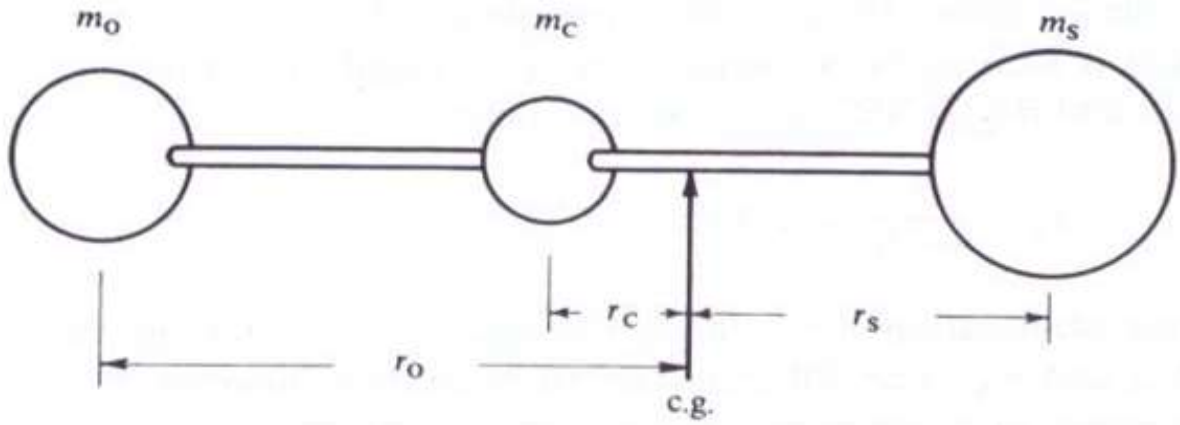
Below table shows Microwave spectrum of carbon oxysulphide

$J \rightarrow J+1$	$\bar{\nu}_{obs.}$ (cm^{-1})	$\Delta\bar{\nu}$	B (cm^{-1})
$0 \rightarrow 1$	...		
		$2 \times 0{\cdot}4055$	0·2027
$1 \rightarrow 2$	0·8109		
		0·4054	0·2027
$2 \rightarrow 3$	1·2163		
		0·4054	0·2027
$3 \rightarrow 4$	1·6217		
		0·4054	0·2027
$4 \rightarrow 5$	2·0271		

Over the four lines observed there is seen to be no appreciable centrifugal distortion, and taking the value of B as 0.2027 cm^{-1} we calculate

$$I_B = \frac{h}{8\pi^2 Bc} = 137{\cdot}95 \times 10^{-47} \text{ kg m}^2$$

Consider the rotation of OCS molecule as shown in figure.



r_O, r_C, and r_S represent the distances of the atoms from the centre of gravity. Consideration of moments gives:

$$m_O r_O + m_C r_C = m_S r_S \quad \text{(1)}$$

The moment of inertia is:

$$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2 \quad \text{(2)}$$

and we have the further equations:

$$r_O = r_{CO} + r_C \qquad r_S = r_{CS} - r_C \quad \text{(3)}$$

where r_{CO} and r_{CS} are the bond lengths of the molecule.

Substitute 3 in 1

$$(m_C + m_O + m_S) r_C = m_S r_{CS} - m_O r_{CO}$$

or

$$M r_C = m_S r_{CS} - m_O r_{CO} \quad \text{(4)}$$

M for the total mass of the molecule.

Substitute 3 in 2

$$I = m_O(r_{CO} + r_C)^2 + m_C r_C^2 + m_S(r_{CS} - r_C)^2$$
$$= Mr_C^2 + 2r_C(m_O r_{CO} - m_S r_{CS}) + m_O r_{CO}^2 + m_S r_{CS}^2$$

Substitute for r_c from 4

$$I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})^2}{M} \quad \rightarrow 5$$

Considering now the isotopic molecule, ^{18}OCS, we may write m'_O for m_O throughout

$$I' = m'_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m'_O r_{CO} - m_S r_{CS})^2}{M'} \quad \rightarrow 6$$

and we can now solve for r_{CO} and r_{CS}, provided we have extracted a value for I' from the microwave spectrum of the isotopic molecule. Note that we do *not* need to write r'_{CO}, since we assume that the bond length is unaltered by isotopic substitution.

SYMMETRIC TOP MOLECULE

Although the rotational energy levels of this type of molecule are more complicated than those of linear molecules, we shall see that, because of their symmetry, their pure rotational spectra are still relatively simple. Choosing methyl fluoride again as our example we remember that

$$I_B = I_C \neq I_A \qquad I_A \neq 0$$

There are now two directions of rotation in which the molecule might absorb or emit energy—that about the main symmetry axis (the C—F bond in this case) and that perpendicular to this axis.

Here two quantum numbers are needed to describe the degree of rotation

one for I_A and one for I_B or I_C.

Here J represents total angular momentum and K represent angular momentum about the top axis i.e., C-F bond in this case.

for a total angular momentum J, we see that K can take values:

$$K = J, J - 1, J - 2, \ldots, 0, \ldots, -(J - 1), -J \quad \rightarrow 1$$

which is a total of $2J + 1$ values altogether.

Schrödinger equation may be solved to give the allowed energy levels for rotation as:

$$\varepsilon_{J,K} = E_{J,K}/hc = BJ(J+1) + (A-B)K^2 \quad \text{cm}^{-1} \longrightarrow 2$$

$$B = \frac{h}{8\pi^2 I_B c} \quad \text{and} \quad A = \frac{h}{8\pi^2 I_A c}$$

The selection rules for this molecule may be shown to be:

$$\Delta J = \pm 1 \text{ (as before)} \quad \text{and} \quad \Delta K = 0 \longrightarrow 3$$

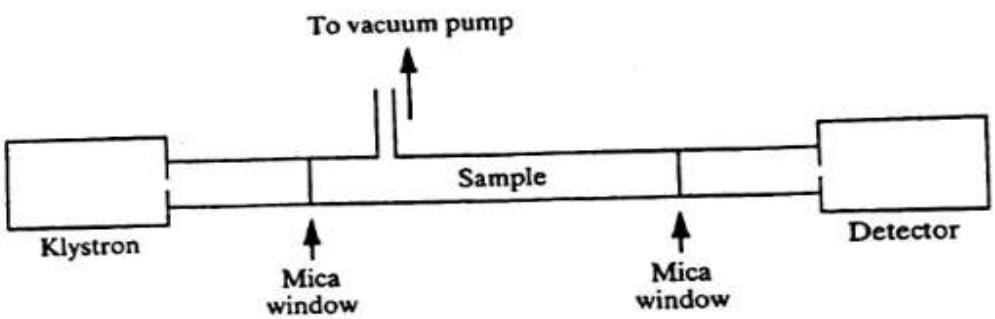
This is applied to equation 2

$$\varepsilon_{J+1,K} - \varepsilon_{J,K} = \bar{\nu}_{J,K} = B(J+1)(J+2) + (A-B)K^2 - [BJ(J+1) + (A-B)K^2]$$

$$= 2B(J+1) \text{ cm}^{-1} \longrightarrow 4$$

Thus the spectrum is independent of K, and hence rotational changes about the symmetry axis do not give rise to a rotational spectrum. The reason for this is quite evident—rotation about the symmetry axis does not change the dipole moment perpendicular to the axis (which always remains zero), and hence the rotation cannot interact with radiation.

MICROWAVE SPECTOMETER Techniques and Instrumentation



1. *The source and monochromator.* The usual source in this region is the klystron valve which, since it 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 slight disadvantage 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.

2. *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.
3. *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 thin mica windows in a piece of evacuated waveguide.
4. *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.

INFRARED Spectroscopy

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms.

IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule. Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.

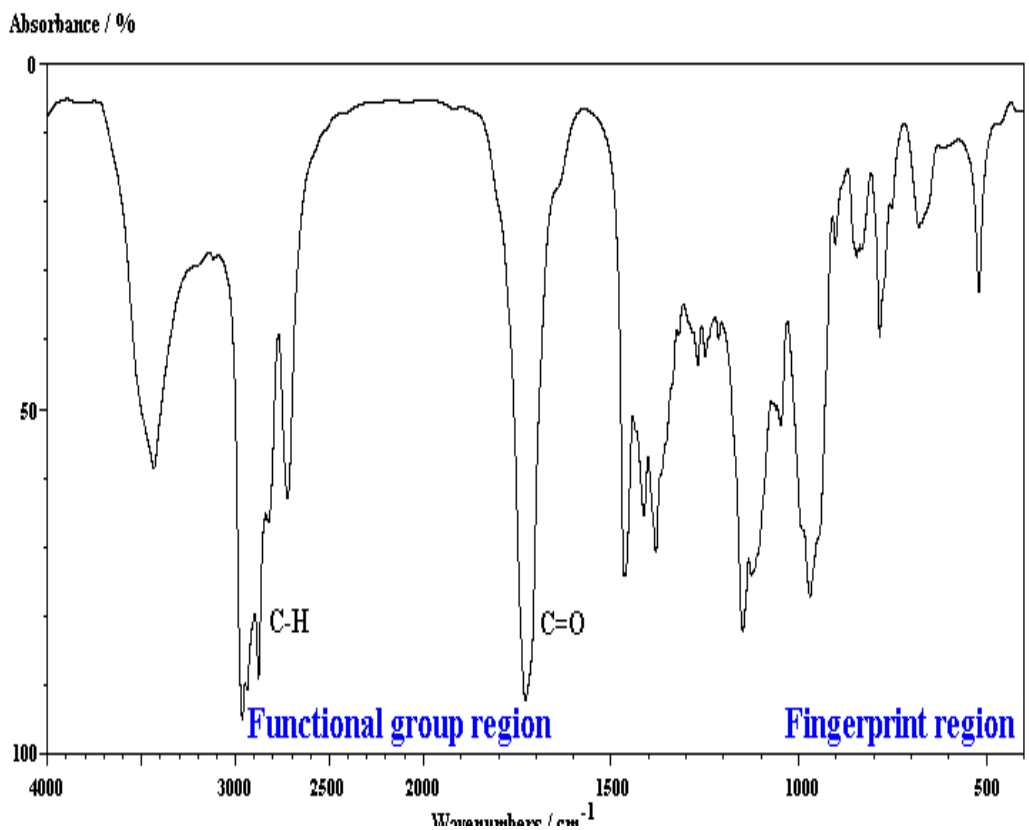
Infra red (IR) spectroscopy deals with the interaction between a molecule and radiation from the IR region of the EM spectrum (IR region = 4000 - 400 cm^{-1}). The cm^{-1} unit is the wave number scale and is given by 1 / (wavelength in cm). IR radiation causes the excitation of the vibrations of covalent bonds within that molecule. These vibrations include the stretching and bending modes.

Regions of the Infrared spectrum

IR spectrum is split into two approximate regions:

Most of the bands that indicate what functional group is present are found in the region from 4000 cm^{-1} to 1300 cm^{-1}. Their bands can be identified and used to determine the functional group of an unknown compound.

Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from 1300 cm^{-1} to 400 cm^{-1}. These bands are only used to compare the spectra of one compound to another.



Diatomic Vibrating Rotator

Consider a typical diatomic molecule that execute rotations and vibrations independently. The combined rotational-vibrational energy is given by

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

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

---------- 1

Where the rotational energy level is given by the equation

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \cdots \text{ cm}^{-1}$$

----------2

Vibrational energy level is represented by the equation

$$\varepsilon_v = (v + \tfrac{1}{2})\bar{\omega}_e - (v + \tfrac{1}{2})^2\bar{\omega}_e x_e \quad \text{cm}^{-1} \qquad (v = 0, 1, 2, \ldots)$$

----------3

where $\bar{\omega}_e$ is an oscillation frequency (expressed in wavenumbers) and x_e is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive

Substitute equation 2 and 3 in equation 1

$$\begin{aligned}\varepsilon_{J,v} &= \varepsilon_J + \varepsilon_v \\ &= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \ldots \\ &\quad + (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1}\end{aligned}$$

---------- 4

ignore the small centrifugal distortion constants D, H,

$$\varepsilon_{\text{total}} = \varepsilon_{J,v} = BJ(J+1) + (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e$$

---------- 5

It may be shown that the selection rules for the combined motions are the same as those for each separately; therefore we have:

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

---------- 6

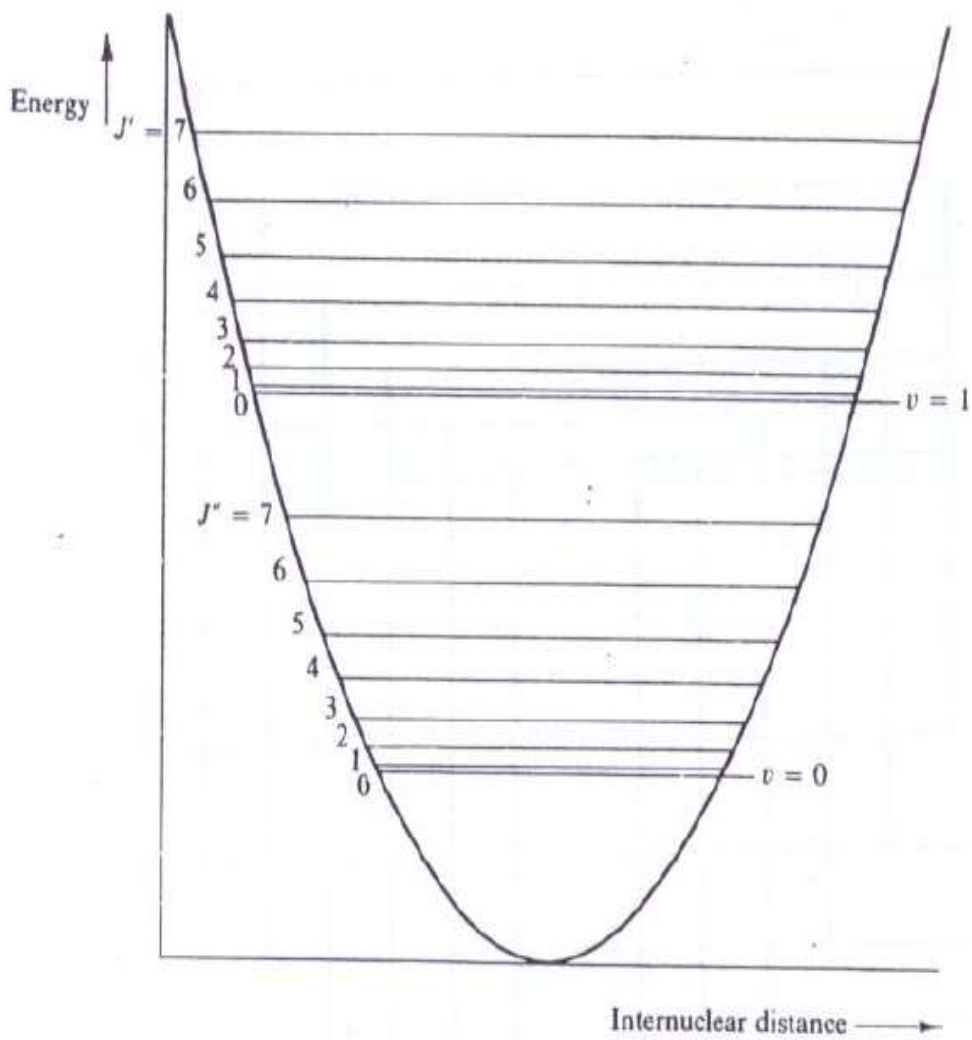


Fig: The rotational energy levels for two different vibrational states of a diatomic molecule.

The rotational quantum number in the state v=0 is designated as J'' and in the state v=1 as J'

The analytical expression for the spectrum may be obtained by applying the selection rulesEqn 6 to the energy levels eqn 5. Considering the transition *v*=0 to *v*=1

$$\begin{aligned}\Delta\varepsilon_{J,v} &= \varepsilon_{J',v=1} - \varepsilon_{J'',v=0}\\ &= BJ'(J'+1) + 1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e - \{BJ''(J''+1) + \tfrac{1}{2}\bar{\omega}_e - \tfrac{1}{4}x_e\bar{\omega}_e\}\\ &= \bar{\omega}_o + B(J'-J'')(J'+J''+1) \quad \text{cm}^{-1}\end{aligned}$$

where, for brevity, we write $\bar{\omega}_o$ for $\bar{\omega}_e(1-2x_e)$.

1. $\Delta J = +1$, i.e., $J' = J''+1$ or $J'-J'' = +1$; hence

$$\Delta\varepsilon_{J,v} = \bar{\omega}_o + 2B(J''+1)\ \text{cm}^{-1} \qquad J'' = 0, 1, 2, \ldots$$

2. $\Delta J = -1$, i.e., $J'' = J'+1$ or $J'-J'' = -1$; and

$$\Delta\varepsilon_{J,v} = \bar{\omega}_o - 2B(J'+1)\ \text{cm}^{-1} \qquad J' = 0, 1, 2, \ldots$$

---------- 7 a and 7 b

These two expressions may conveniently be combined into:

$$\Delta\varepsilon_{J,v} = \bar{\nu}_{\text{spect.}} = \bar{\omega}_o + 2Bm \quad \text{cm}^{-1} \qquad m = \pm 1, \pm 2, \ldots$$

---------- 7 c

Where m, replacing J'' +1 in eqn, 7a and J'+1 in eqn in 7b has positive values for $\Delta J = +1$ and is negative if $\Delta J = +1$

The frequency $\bar{\omega}_o$ is usually called the *band origin* or *band centre*.

Eqn 7c represents the combined vibration-rotation spectrum.

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

Lines arising from $\Delta J =$	-2	-1	0	$+1$	$+2$	
called:	O	P	Q	R	S	branch

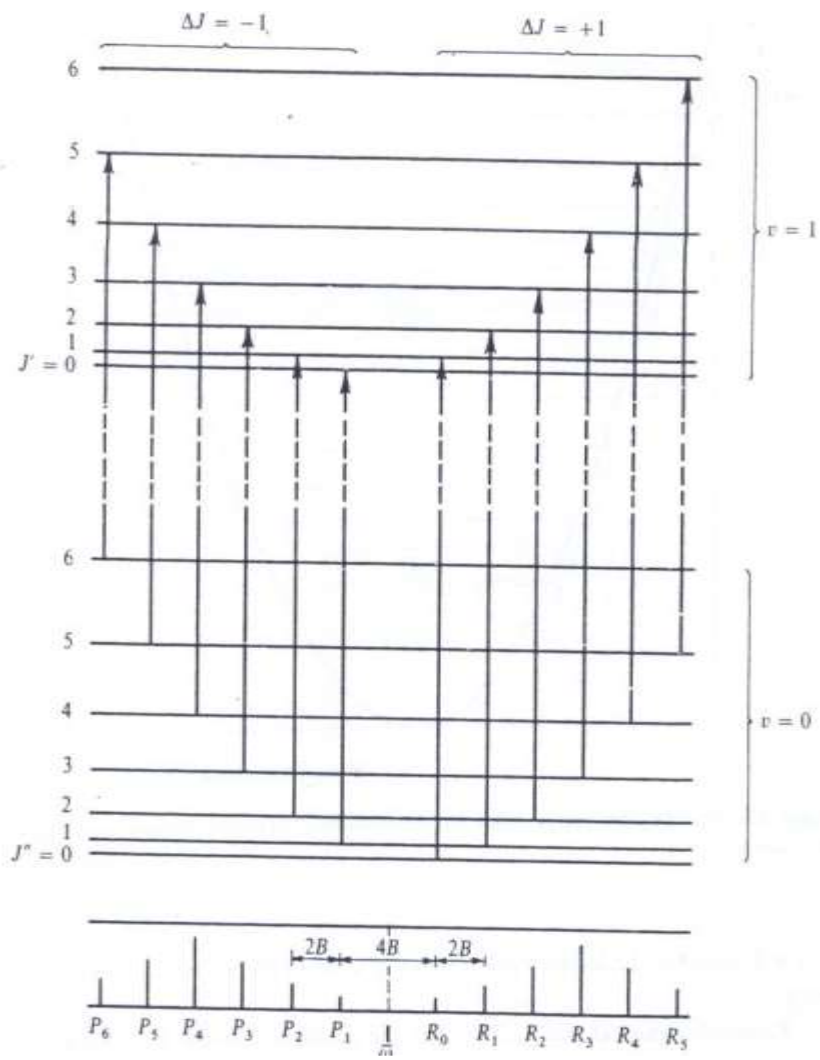
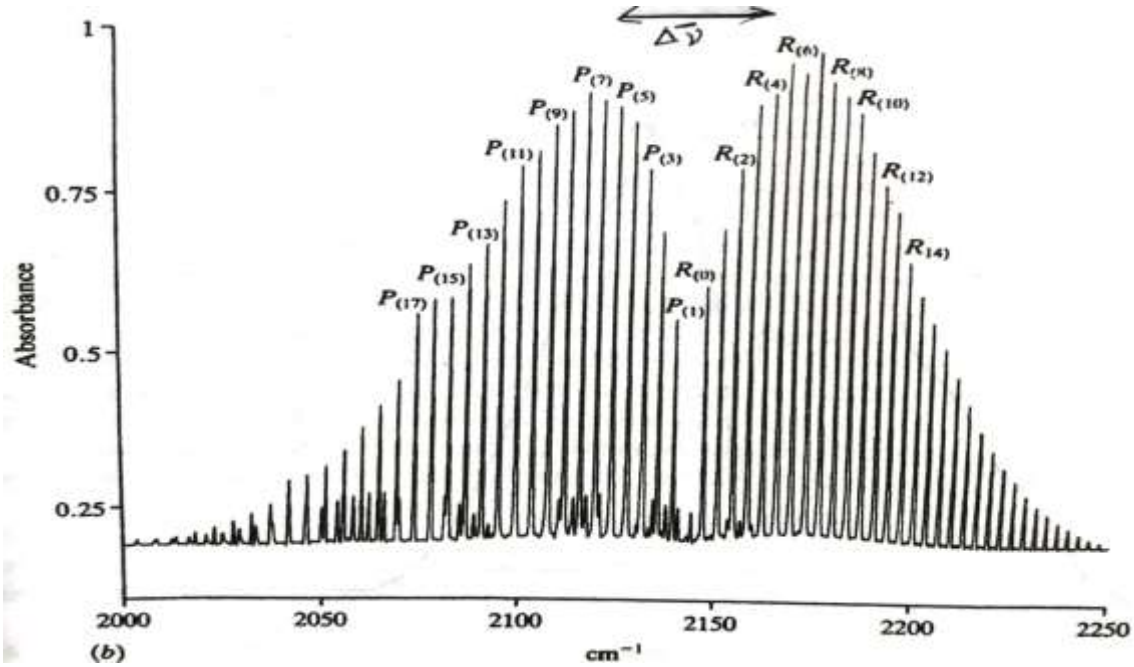


Fig: Transitions between rotational-vibrational energy levels of a diatomic molecule.

The Vibration-Rotation Spectrum of Carbon Monoxide

The fundamental vibration-rotation band of carbon monoxide under high resolution, with some lines in the P and R branches numbered according to their J" values is shown below.



The below table gives the observed wave numbers of the first five lines in each branch. It is observed that there is slight decrease in separation between the rotational lines as the wave number increases. From the table it is seen that the band centre is at about 2143 cm^{-1} while the average line separation near the centre is 3.83 cm^{-1}. This immediately gives

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

Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$	Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$
$P_{(1)}$	2139·43		$R_{(0)}$	2147·08	
		3·88			3·78
$P_{(2)}$	2135·55		$R_{(1)}$	2150·86	
		3·92			3·73
$P_{(3)}$	2131·63		$R_{(2)}$	2154·59	
		3·95			3·72
$P_{(4)}$	2127·68		$R_{(3)}$	2158·31	
		3·98			3·66
$P_{(5)}$	2123·70		$R_{(4)}$	2161·97	

The maximum intensity of transition, occurs at a J value of

$$J = \sqrt{kT/2Bhc} - \frac{1}{2} \qquad -----1$$

We know that m = J+1 ----------2

$\Delta\in = \bar{\nu} = \overline{\omega_o} + 2B\text{m}$ ---------- 3

Substitute equation 1 in 2

$$\text{m} = \sqrt{kT/2Bhc} - \tfrac{1}{2} + 1 \quad = \quad \sqrt{kT/2Bhc} + \tfrac{1}{2} \qquad ----4$$

Put equation 4 in 3

$$\Delta\in = \bar{\nu} = \overline{\omega_o} \pm 2B\,(\sqrt{kT/2Bhc} + \frac{1}{2})$$

+ represents R branch and – represents P branch.

$$\Delta\bar{\nu} = \left\{\overline{\omega_o} \pm 2B\left(\sqrt{kT/2Bhc} + \frac{1}{2}\right)\right\} - \left\{\overline{\omega_o} \pm 2B\left(\sqrt{kT/2Bhc} + \frac{1}{2}\right)\right\}$$

$$\Delta\bar{\nu} = 4B\left(\sqrt{kT/2Bhc} + \frac{1}{2}\right)$$

$$\Delta\bar{\nu} = \sqrt{16\,B^2 kT/2Bhc} + 2B = \sqrt{8B\,kT/hc} + 2\text{B}$$

$$\Delta\bar{\nu} \approx \sqrt{8B\,kT/hc} \qquad (\Delta\bar{\nu})^2 \approx 8B\,kT/hc$$

$$\boldsymbol{B = \frac{(\Delta\bar{\nu})^2\,hc}{8kT}}$$

Where c is expressed in cms^{-1}. In the case of carbon monoxide the separation is about 55 cm^{-1}, while the temperature at which the spectrum was obtained was about 300K. From the table we see that the band origin, at the midpoint of $P_{(1)}$ and $R_{(0)}$ is at 2143.26 cm^{-1}. This, then, is the fundamental vibration frequency of carbon monoxide, if anharmonocity is ignored. The latter can be taken into account, however, since the first over tone is found to have its origin at 4260.04 cm^{-1}. Then

$$\bar{\omega}_e(1 - 2x_e) = \bar{\omega}_o = 2143{\cdot}26$$
$$2\bar{\omega}_e(1 - 3x_e) = 4260{\cdot}04$$

from which $\omega_e = 2169{\cdot}74\ \text{cm}^{-1}$, $x_e = 0{\cdot}0061$.

Influence of rotation on the spectrum of polyatomic molecules
LINEAR MOLECULES

Parallel vibrations The selection rule for these is identical with that for diatomic molecules, i.e.,

$\Delta J = \pm 1 \qquad \Delta v = \pm 1$ for simple harmonic motion

---------- 1

$\Delta J = \pm 1 \qquad \Delta v = \pm 1, \pm 2, \pm 3, \ldots$ for anharmonic motion

---------- 2

(This is, in fact, as expected, since a diatomic molecule is linear and can undergo only parallel vibrations.) The spectra will thus be similar in appearance, consisting of P and R branches with lines about equally spaced on each side, no line occurring at the band centre. Now, however, the moment of inertia may be considerably larger, the B value correspondingly smaller, and the P or R line spacing will be less.

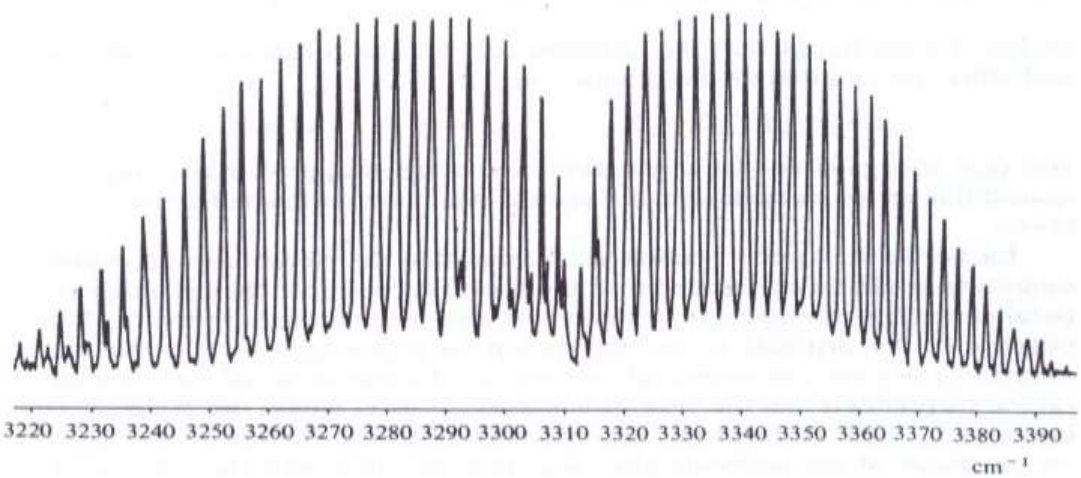


FIG: SPECTRUM OF HCN MOLECULE

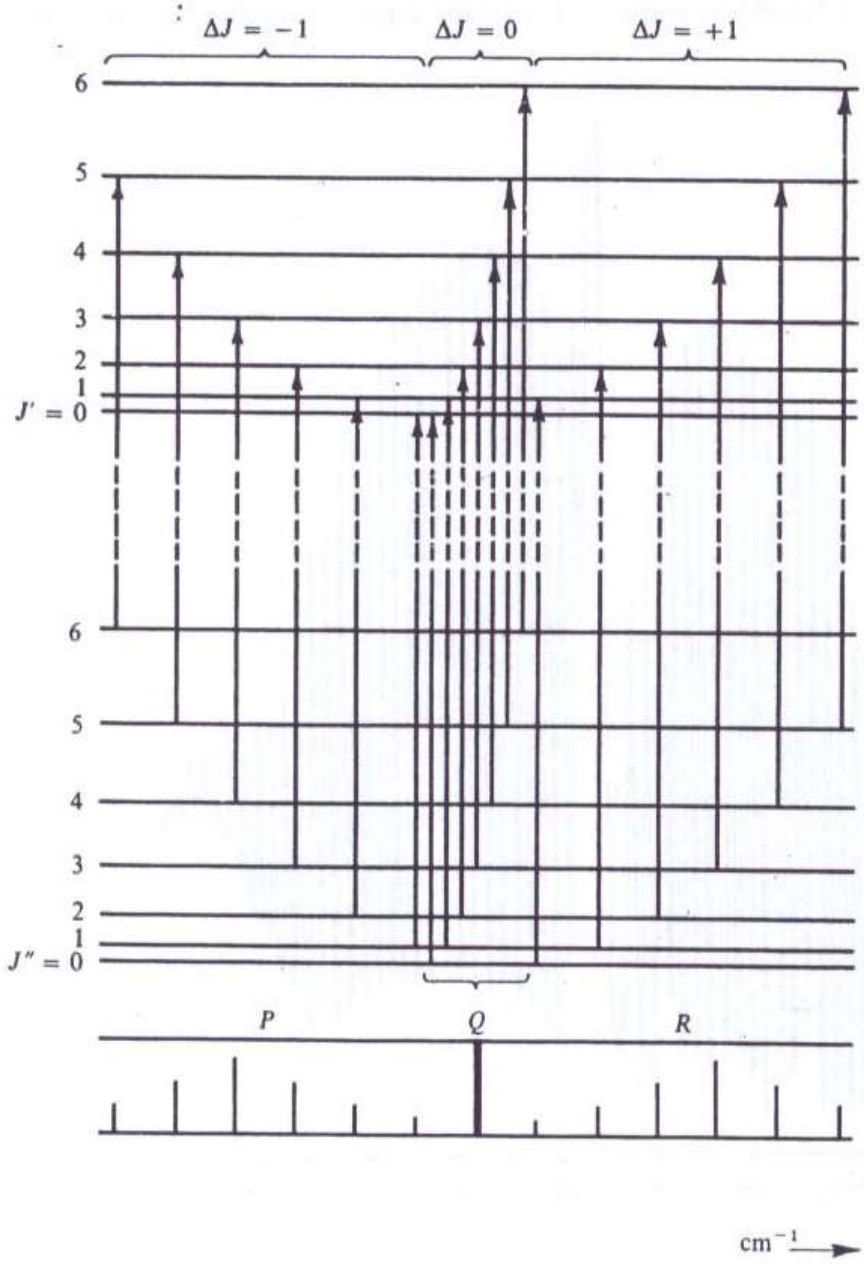
Figure shows part of the spectrum of HCN, a linear molecule whose structure is H—C≡N. The band concerned is the symmetric stretching frequency at about 3310 cm^{-1}, and the spacing is observed to be about 2·8–3·0 cm^{-1} near the band centre.

For still larger molecules the value of B may be so small that separate lines can no longer be resolved in the P and R branches.

Perpendicular vibrations For these the selection rule is found to be:

$$\Delta v = \pm 1 \qquad \Delta J = 0, \pm 1 \qquad \text{for simple harmonic motion}$$

which implies that now, for the first time, a vibrational change can take place with *no simultaneous rotational transition.*



The rotational energy levels for two vibrational states showing the effect on the spectrum of transitions for which $\Delta J = 0$.

Symmetric Top Molecules

Following the Born-Oppenheimer approximation, the vibrational-rotational energy levels for symmetric top molecules is the sum of the vibrational levels and rotational levels. The vibrational level is

$$\varepsilon_{\text{vib.}} = (v + \tfrac{1}{2})\bar{\omega}_e - (v + \tfrac{1}{2})^2 x_e \bar{\omega}_e \quad \text{cm}^{-1} \qquad [v = 0, 1, 2, 3, \ldots]$$

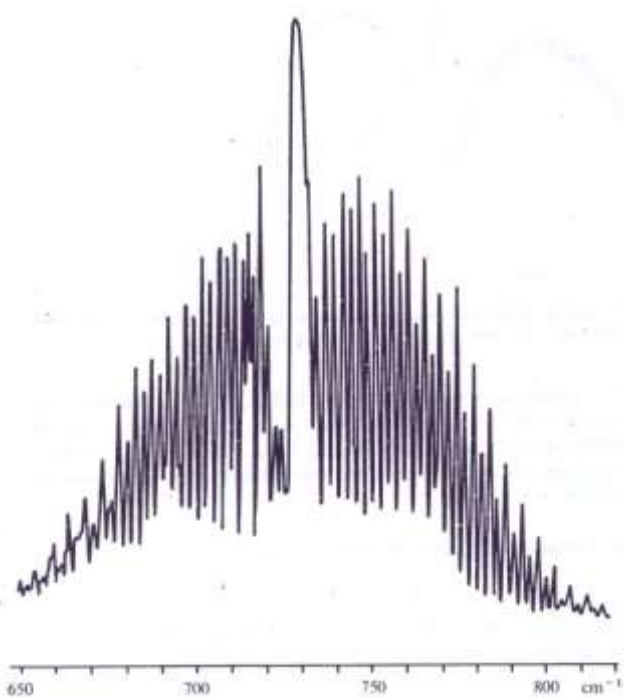
The rotational level is

$$\varepsilon_{\text{rot.}} = BJ(J+1) + (A - B)K^2 \quad \text{cm}^{-1} \qquad [J = 0, 1, 2, \ldots; \; K = J, (J-1), (J-2), \ldots, -J]$$

thus

$$\varepsilon_{J,v} = \varepsilon_{\text{vib.}} + \varepsilon_{\text{rot.}} = (v + \tfrac{1}{2})\bar{\omega}_e - (v + \tfrac{1}{2})^2 x_e \bar{\omega}_e + BJ(J+1) + (A - B)K^2 \quad \text{cm}^{-1}$$

Centrifugal distortion is negligible.



The spectrum of a bending mode of acetylene, HC≡CH, showing the strong, weak, strong, weak, … intensity alternation in the rotational fine structure due to the nuclear spin of the hydrogen atoms.

Again it is necessary to divide the vibrations into those which change the dipole (1) parallel and (2) perpendicular to the main symmetry axis—which is nearly always the axis about which the 'top' rotates. The rotational selection rules differ for the two types.

Parallel vibrations Here the selection rule is:

$$\Delta v = \pm 1 \qquad \Delta J = 0, \pm 1 \qquad \Delta K = 0$$

Here ΔK=0. Terms in K will be identical in the upper and lower state and so the spectral frequencies will be independent of K. The spectrum will contain P, Q and R branches with a P, R line spacing of 2B and a strong central Q branch.

Such a spectrum, a parallel band of methyl iodide CH_3I is shown is spectrum.

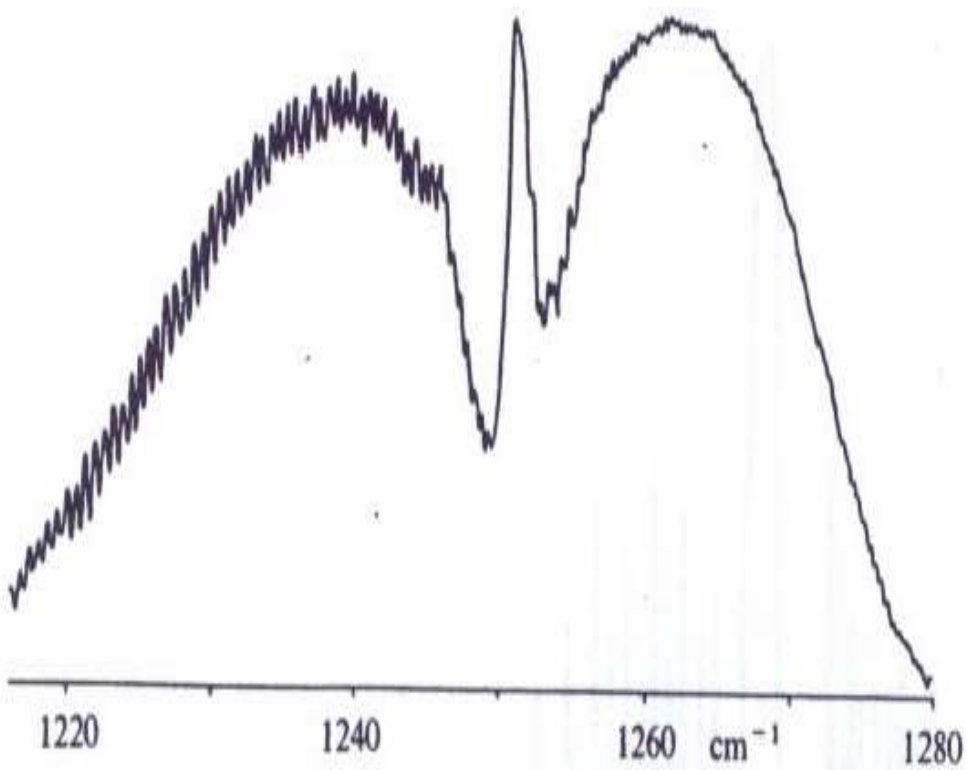


Fig – The parallel stretching vibration, centered at 1251 cm^{-1}, of the symmetric top molecule methyl iodide

Perpendicular vibrations For these the selection rule is:

$$\Delta v = \pm 1 \qquad \Delta J = 0, \pm 1 \qquad \Delta K = \pm 1$$

(1) $\Delta J = +1$, $\Delta K = \pm 1$ (R branch lines):

$$\Delta\varepsilon = \bar{\nu}_{\text{spect.}} = \bar{\omega}_o + 2B(J+1) + (A-B)(1 \pm 2K) \quad \text{cm}^{-1}$$

(2) $\Delta J = -1$, $\Delta K = \pm 1$ (P branch lines):

$$\bar{\nu}_{\text{spect.}} = \bar{\omega}_o - 2B(J+1) + (A-B)(1 \pm 2K) \quad \text{cm}^{-1}$$

(3) $\Delta J = 0$, $\Delta K = \pm 1$ (Q branch lines):

$$\bar{\nu}_{\text{spect.}} = \bar{\omega}_o + (A-B)(1 \pm 2K) \quad \text{cm}^{-1}$$

We see, then, that this type of vibration gives rise to many sets of P and R branch lines since for each J value there are many allowed values of K ($K = J, J-1, \ldots, -J$). The wings of the spectrum will thus be quite complicated and will not normally be resolvable into separate lines. The Q branch is also complex, since it too will consist of a series of lines on both sides of $\bar{\omega}_o$ separated by $2(A-B)$.

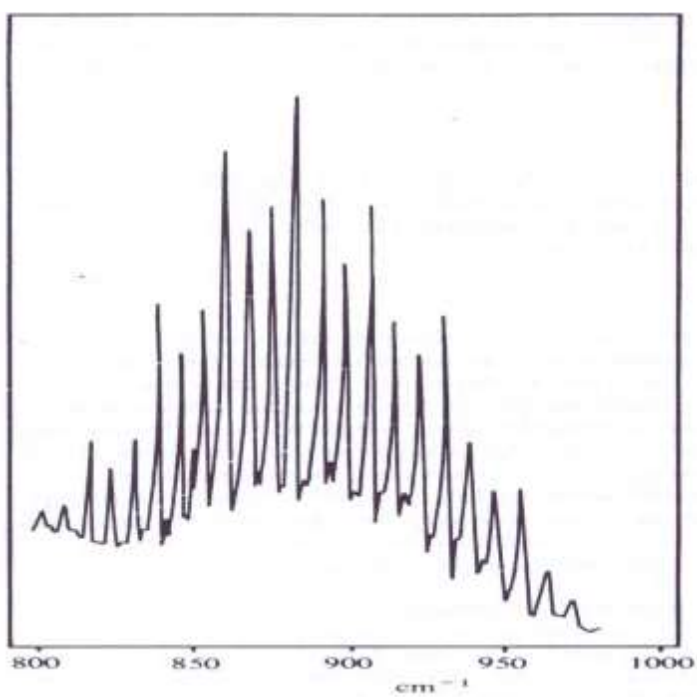


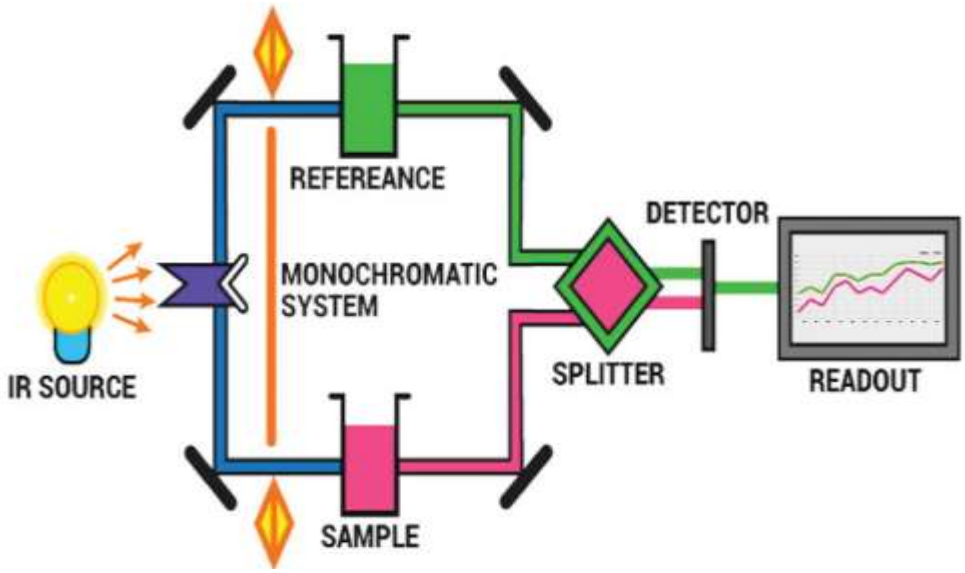
Fig- A perpendicular stretching vibration of methyl iodide swing the typical Q branch sequence.

Infrared Spectrometer

- Infrared (IR) spectroscopy or vibrational spectroscopy is an analytical technique that takes advantage of the vibrational transitions of a molecule.
- It is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them.
- The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum.

The main parts of IR spectrometer are as follows:

1. Radiation source
2. Sample cells and sampling of substances
3. Monochromators
4. Detectors
5. Recorder



Source

IR instruments require a source of radiant energy which emit IR radiation which must be steady, intense enough for detection and extend over the desired wavelength.

Various sources of IR radiations are as follows.

1. Nernst glower
2. Incandescent lamp
3. Mercury arc
4. Tungsten lamp
5. Nichrome Wire

Samples

IR spectroscopy has been used for the characterization of solid, liquid or gas samples.

i. Solid – Various techniques are used for preparing solid samples such as pressed pellet technique, solid run in solution, solid films, mull technique etc.

ii. Liquid – Samples can be held using a liquid sample cell made of alkali halides. Aqueous solvents cannot be used as they will dissolve alkali halides. Only organic solvents like chloroform can be used.

iii. Gas– Sampling of gas is similar to the sampling of liquids.

Monochromators

- Various types of monochromators are prism, gratings and filters.
- Prisms are made of Potassium bromide, Sodium chloride or Caesium iodide.
- Filters are made up of Lithium Fluoride and Diffraction gratings are made up of alkali halides

Detectors

- Detectors are used to measure the intensity of unabsorbed infrared radiation.
- Detectors like thermocouples, Bolometers, thermisters, Golay cell, and pyro-electric detectors are used.

Recorders

- Recorders are used to record the IR spectrum.

The fundamental measurement obtained in infrared spectroscopy is an infrared spectrum, which is a plot of measured infrared intensity versus wavelength (or frequency) of light.

<u>Applications of Infrared Spectroscopy</u>

- Protein characterization
- Nanoscale semiconductor analysis and
- Space exploration.
- Analysis of gaseous, liquid or solid samples
- Identification of compounds
- Quantitative analysis.
- Information regarding functional groups of molecules and constitution of molecules can be deduced from IR spectrum.
- To know about interaction among molecules.

UNIT – II RAMAN SPECTROSCOPY

Raman Effect

In 1928, Sir C.V. Raman discovered that when a beam of monochromatic light was allowed to pass through a substance in the solid, liquid or gaseous state, the scattered light contains some additional frequencies over and above that of incident frequency. This is known as Raman effect. Raman scattering is defined as the scattering of photons by the excited molecules that are at higher energy levels. The photons are in-elastically scattered, which means that the kinetic energy of an incident particle is either lost or increased and is composed of stokes and anti-stokes portions.

Principle of Raman Spectroscopy

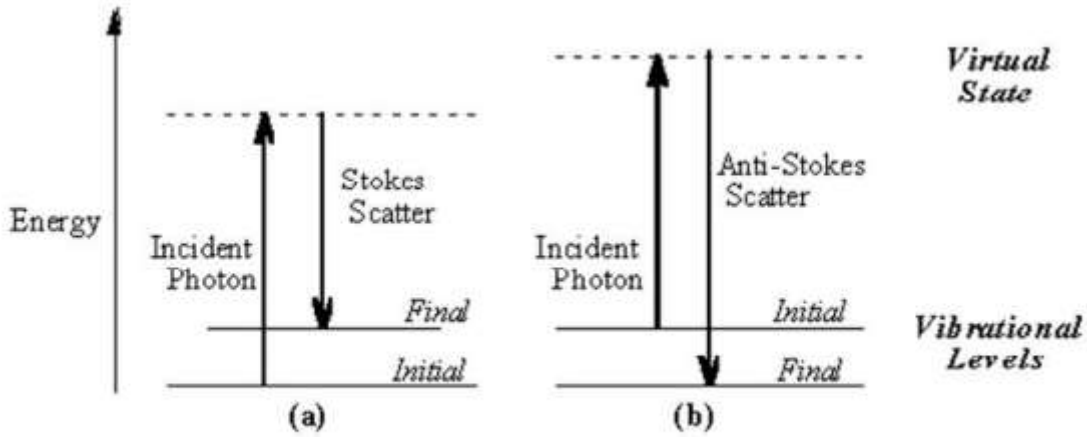
The principle behind Raman spectroscopy is that the monochromatic radiation is passed through the sample such that the radiation may get reflected, absorbed, or scattered. The scattered photons have a frequency which is different from the incident photon as the vibration and rotational property varies. Raman spectroscopy occurs as a result of a molecular vibration causing a "change in polarizability" of the molecule. A simple case of a Raman Active molecule would be a species such as CS_2.

The difference between the incident photon and the scattered photon is known as the **Raman shift**. When the energy associated with the scattered photons is less than the energy of an incident photon, the scattering is known as **Stokes scattering.** When the energy of the scattered photons is more than the incident photon, the scattering is known as **anti-Stokes scattering.** **T**he lines whose wavelengths have been modified in Raman effect are called Raman lines. The lines having wavelengths greater than that of the incident wavelength are called Stoke's lines and those having shorter wavelengths are called Anti-Stokes's lines.

If ν_i is the frequency of incident radiation and ν_s is the scattered radiation then the Raman shift $\Delta\nu$ is defined by

$$\Delta\nu = \nu_i - \nu_s$$

For Stoke's line Δν is positive and for Anti-Stoke's lines Δν is negative.



(a) Stokes Raman scattering **(b) Anti-Stokes Raman scattering**

The Raman shift does not depend upon the frequency of the incident light but it is regarded as a characteristic of the substance causing Raman effect. Raman scattering produces scattered photons with a different frequency which is dependent on the source as well as on the vibrational and rotational properties of the scattered molecules. Raman spectroscopy is based on Raman scattering which is used to study the materials by chemists and physicists. In olden days, to record spectra, a mercury lamp and photographic plates were used whereas in modern days lasers are used.

Raman Spectra - To analyse the Raman effect, the wavelength of the scattered photon is converted to wavenumber. These wavenumbers are plotted on the x-y plane. The wavenumbers are taken along the x-axis and the Raman intensity is taken on the y-axis. The difference between the wavenumbers and the intensity is known as the Raman spectrum.

Difference between Raman Spectra and Infrared Spectra

Raman Spectra	**Infrared Spectra**
Raman Spectra is due to scattering of light by the vibrating molecule	Infrared Spectra is due to absorption of light by vibrating molecules.
Due to polarizability of molecules	Due to presence of permanent dipoles.

Quantum theory of Raman Effect

Raman effect is much more complex than ordinary infrared absorption and full quantum theory is still being worked out. Classical theory is able to explain the existence of Raman effect whereas quantum theory is needed to predict selection rules and intensities correctly.

According to this theory, the Raman effect may be regarded as the out come of the collision between the light photons and molecules of the substance.

Let,

m be the mass of the molecule,

V_1 be the velocity of the molecule before collision and V_2 after collision,

E_1 be the energy of the molecule before collision and E_2 after collision,

ν is the frequency of photon before collision and ν' after collision and

$h\nu$ is the energy of incident photon .

This molecule will undergo change in its energy after collision. Then the new energy state of the molecule after the collision will be described on the basis of law of conservation of energy

$$E_1 + \frac{1}{2} mV_1^2 + h\nu = E_2 + \frac{1}{2} mV_2^2 + h\nu'$$

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

$$E_1 + h\nu = E_2 + h\nu'$$

$$\nu' = \nu + \{(E_1 - E_2) / h\}$$

$$\nu' = \nu + \Delta\nu$$

1) If $E_1 = E_2$, the frequency difference (Raman shift), $\Delta\nu = 0$. It means that $\nu' = \nu$ and this refers to the unmodified line, where the molecule simply deflect the photon without receiving the energy from it. This collision is elastic and analogous to Rayleigh scattering.
2) If $E_1 > E_2$ then $\nu' > \nu$ which refers to the anti stokes lines. It means that the molecule was previously in the excited state and it handed over some

of its intrinsic energy to the incident photon. Thus, the scattered photon has greater energy.

3) If $E_1 < E_2$ then $\nu' < \nu$ which refers to the stokes lines. The molecule has absorbed some energy from the photon and consequently the scattered photon will have lowest energy.

As the change in the intrinsic energy of the molecule is governed by the quantum rules, it can be written as

$$E_1 - E_2 = nh\nu_c$$

Where n = 1,2,3 ……. Etc and ν_c is the characteristic frequency of the molecule. Therefore, the characteristic frequency is expressed by the relation.

$$\nu' - \nu = \pm \nu_c \approx (\Delta\nu)$$

From the above equation it follows that the frequency difference (ν' - ν) between the incident and scattered photon in the Raman effect corresponds to the characteristic frequency of the molecule. The Raman lines are equidistant from the unmodified parent line on the either side, at distances equal to the characteristic frequency of the molecule.

Pure Rotational Raman Spectra

Pure rotational Raman spectra arise from transitions of the molecule from one rotational energy state to the other of the same vibrational state. They appear on both sides of Rayleigh line. The selection rule for rotation Raman transitions is different from that for purely rotational (far infra-red) changes.

The energy of the rigid rotator is given by

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

The selection rule for rotational Raman spectrum is as follows,

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

When, ΔJ= 0, the scattered Raman radiation will be of the same frequency as that of incident light (Rayleigh's scattering).

The transition,

ΔJ= + 2; gives Stoke's lines (longer wavelength) whereas,

ΔJ = -2; gives the antistoke's lines (shorter wavelength).

When ΔJ = +2, the values of rotational Raman shifts (stoke's lines) will be given by

$$\Delta\bar{v} = \frac{h^2}{8\pi^2 I_c} [(J+2)(J+3) - (J+1)]$$

$$\Delta\bar{v} = 2B(2J+3)$$

Where,

$$B = \frac{h2}{8\,\pi^2 I_c}$$

Ic = moment of inertia of the molecule

When ,

ΔJ = -2, the values of rotational Raman shifts (antistoke's lines) will be given by

$$\Delta\bar{v} = -2B(2J+3)$$

On combining the equation of stokes and anti-stokes lines, the Raman shift can be put in the form

$$\Delta\bar{v} = \pm 2B(2J+3); \text{ where } J = 0,1,2,3, \ldots \ldots \ldots$$

Therefore, the corresponding Raman shift in terms of wave number Δv (cm^{-1}) is given by

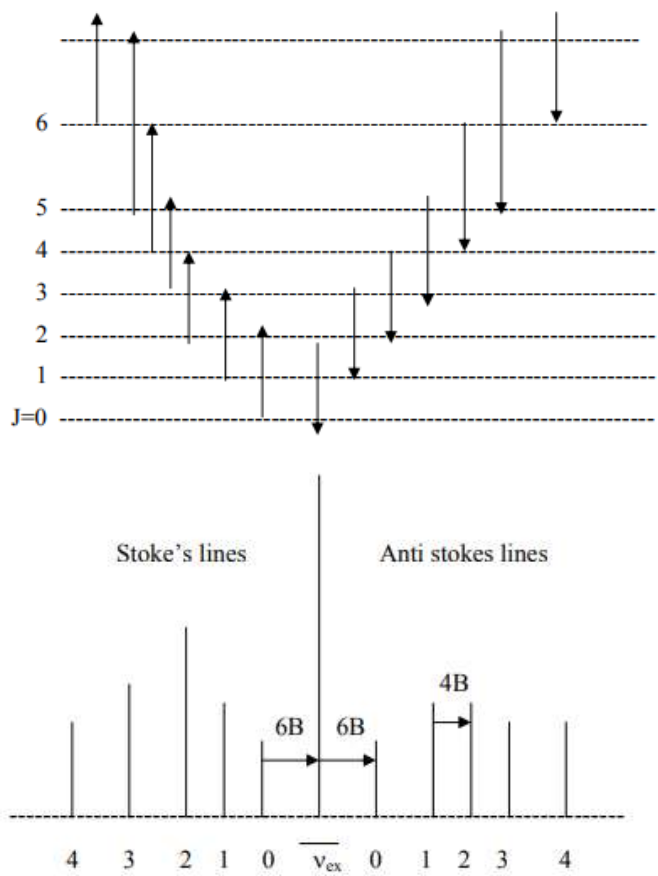
$$\Delta v = \bar{v}_s - \bar{v}_{ex}$$

Where,

$\bar{v}_{ex}$ = Wave number of exciting radiation

$\bar{v}_s$ = Wave number of scattered radiation

The transition and the Raman spectrum are shown the below figure.



The frequency separation of successive lines is 4B cm^{-1} and the separation of the first line from the exciting line will be 6B cm^{-1}.

Vibrational Raman Spectra

The vibrational Raman Spectrum arises due to transition of molecule from one vibrational energy state to the other of the same electronic state. For every vibrational mode we can write an expression of the form

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

$$where \ \ v = 0,1,2, \ldots..$$

$\bar{\omega}_e$ is the equilibrium vibrational frequency expressed in wave numbers and x_e is the anharmonicity constant. This expression is general whatever the shape of the molecule or the nature of the vibration. The selection rule is

$$\Delta v = 0, \pm 1, \pm 2, \ldots\ldots -----2$$

Apply the selection rules to the energy level expression and the obtain the transition energies

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

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{v=1} - \varepsilon_{v=0} \\ &= (1 + \tfrac{1}{2})\bar{\omega}_e - x_e(1 + \tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\} \\ &= \bar{\omega}_e(1 - 2x_e) \quad \text{cm}^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta\varepsilon &= (2 + \tfrac{1}{2})\bar{\omega}_e - x_e(2 + \tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\,\bar{\omega}_e\} \\ &= 2\bar{\omega}_e(1 - 3x_e) \quad \text{cm}^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta\varepsilon &= (3 + \tfrac{1}{2})\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\,\bar{\omega}_e\} \\ &= 3\bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1}\end{aligned}$$

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 the *first and second overtones* respectively. Thus we have ,

$$\left.\begin{aligned} v = 0 \rightarrow v = 1 &: \Delta\varepsilon_{\text{fundamental}} = \bar{\omega}_e(1 - 2x_e) \quad \text{cm}^{-1} \\ v = 0 \rightarrow v = 2 &: \Delta\varepsilon_{\text{overtone}} = 2\bar{\omega}_e(1 - 3x_e) \quad \text{cm}^{-1} \\ v = 1 \rightarrow v = 2 &: \Delta\varepsilon_{\text{hot}} = \bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1} \end{aligned}\right\} \quad 3$$

Since the Raman scattered light is, in any case, of low intensity we can ignore completely all the weaker effects such as overtones and 'hot' bands, and restrict our discussion merely to the fundamentals.

We would expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibration. In other words we can write:

$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_{\text{fundamental}} \quad \text{cm}^{-1} \qquad \text{---------- } 4$$

where the minus sign represents the Stokes' lines (i.e., for which the molecule has gained energy at the expense of the radiation) and the plus sign refers to the anti-Stokes' lines.

The vibrational Raman spectrum of a molecule is, then, basically simple. It will show a series of reasonably intense lines to the low-frequency side of the exciting line with a much weaker, mirror-image series on the high-frequency side. The separation of each line from the centre of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule.

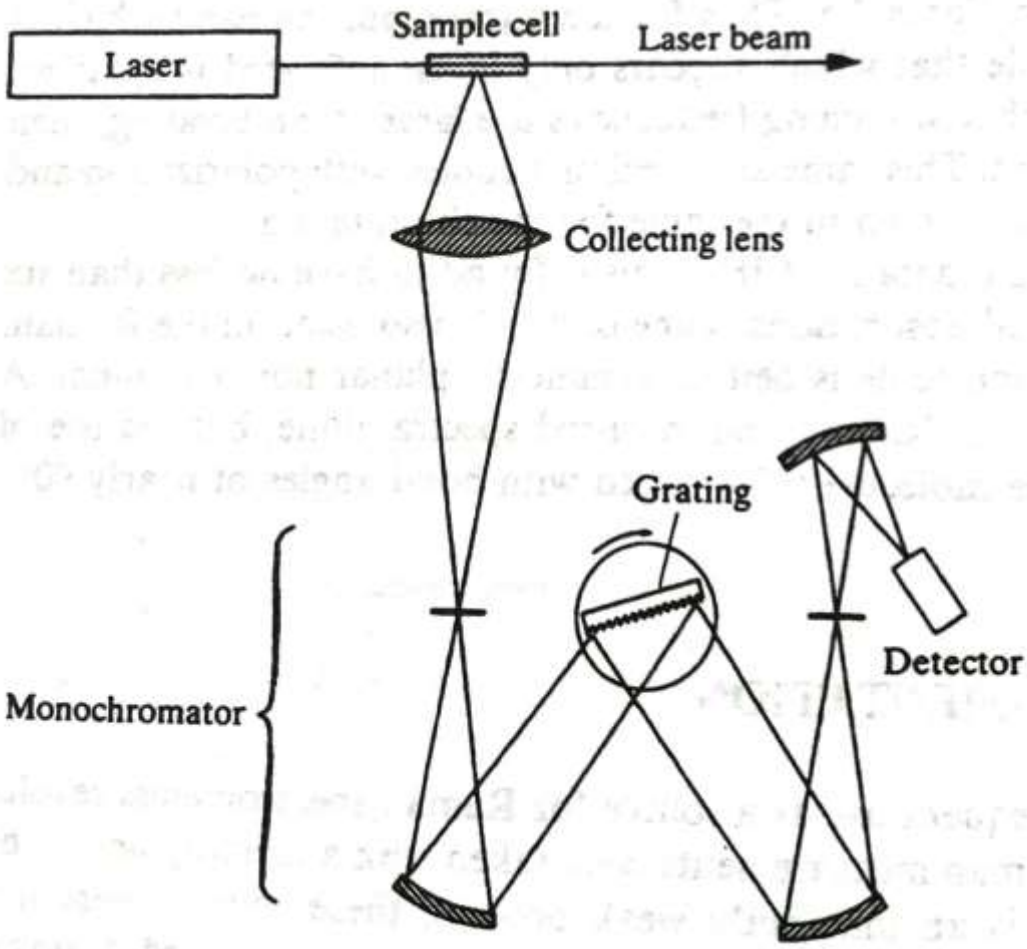
Raman Spectrometer

Raman Spectrophotometers all have the same basic components – Source, Sample and Detector.

- A LASER source is needed to excite the target species. The laser beam is passed through a cell, usually glass or quartz tube filled with the sample. The laser beam is plane polarized by keeping a polarizing filter between the sample and the collecting lens. Although the incident radiation can vary, a great deal of success was reported with a hollow cathode ion LASER that produces light at 224 and 248 nm.
- The sample holder used depends upon the intensity of source and the nature and the availability of the samples. The study of Raman spectra of gases requires

sample holders which are generally bigger in size than those for liquids. Solids are dissolved before subjecting to Raman spectrograph. Any solvent which suitable for the ultraviolet spectra can be used for the study of Raman spectra. Water is regarded as a good solvent for the study of inorganic compounds in Raman Spectroscopy.

- A filter collects the Raman scattered light (Stokes) and filters out the Raleigh and Anti Stokes light.
- A diffraction grating bends the Raman shifted light according to wavelength.
- A detector records the signal and passes the signal to a computer for decoding. The detector is the spectrometer. Here, important performance factors are small form factor, high resolution, low power consumption, and low noise. An appropriate detector is very important and must be utilized depending on which excitation laser is being used. For visible excitation, a standard CCD is selected; for UV excitation, a photomultiplier tube (PMT) or CCD is typically chosen; and for NIR excitation, an indium gallium arsenide (InGaAs) array is normally employed.



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