Rotational spectra of Polyatomic molecules.

Linear and diatomic molecules.

At equilibrium configuration $I_a = 0$

$$I_b = I_c = I$$

$$\epsilon_J = BJ(J+1) \text{ cm}^{-1} \quad \text{when } J = 0,1,2,\ldots$$

Frequency of Spectral line : If a rotational transition occurs from an upper level with quantum number J' to lower level of quantum number J'' then frequency of spectral line expressed in wave numbers is given by

$$\bar{\nu} = B\left[J'(J'+1) - J''(J''+1)\right]$$

Spherical top molecule

~~$I_a = I_b = I_c$~~

The moment of inertia of the spherical top molecule is independent of the orientation of the rotational axis in the molecule

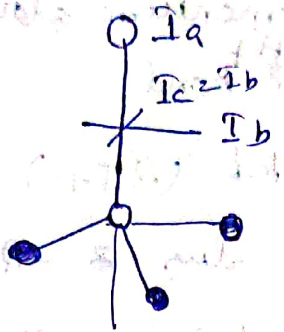
$$I_a = I_b = I_c = I$$

Thus there is only one value of the moment of inertia in a spherical top molecule and energy levels are given by

$$\epsilon_J = BJ(J+1)$$

Thus the energy level pattern is identical with that of a linear molecule. Since a spherical top molecule is by symmetry, nonpolar, its rotation produces no change in moment and no dipole transitions occur.

Symmetric top molecules : Ascldors



$I_a \neq 0$, $I_b = I_c$

Any molecule with a three fold rotation axis must be a symmetric axis and the I_a axis coincides with the symmetry axis. The I_b axes would lie in a plane perpendicular to the top axis ex - CH_3Cl ; NH_3

Energy levels and Selection rules

The rotational energy, in general is written as

$$E_r = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

P_a; P_b; P_c are the angular momentum about the axes

Prolate type : $I_b = I_c$

$$\therefore E_r = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_b}$$

The total angular momentum $P = \sqrt{J(J+1)}\ \frac{h}{2\pi}$ $J = 0, 1, 2 \ldots$

The rotational energy in such type of molecules depends upon two quantum number J and k

In the linear molecule J represents the end over end rotation of a molecule

J – total angular momentum

k – angular momentum about the symmetry axis C – ~~Cl~~ ~~H~~ F bend

The value of J > k , k can take (2J+1) values

for J = 2, k can take values ~~3~~ -2, -1, 0, 1, 2

In the case of symmetric top the schrodinger equation may be solved to give the allowed energy levels for rotation as (rigid)

$$\boxed{\varepsilon_{J,k} = BJ(J+1) + k^2(A-B)\ \text{cm}^{-1}}$$

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

Then all states $k > 0$ are doubly degeneracy

The selection rules for this molecule may be written as

$$\Delta J = \pm 1 \text{ and } \Delta k = 0$$

The frequency of transition between level J+1 and J

$$\varepsilon_{J+1,k} - \varepsilon_{J,k} = \bar{\nu}_{J,k}$$

$$= [B(J+1)(J+2) + (A-B)k^2]$$

$$- [BJ(J+1) + (A-B)k^2]$$

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

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 is rotation about the symmetry axis does not change the dipole moment perpendicular to the axis (which always zero) and hence the rotation cannot interact with radiation

{In the case of a rigid symmetric top the bonds are not supposed to stretch}

When centrifugal stretching is taken into account

$$\varepsilon_{J,K} = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 \text{ cm}^{-1}$$

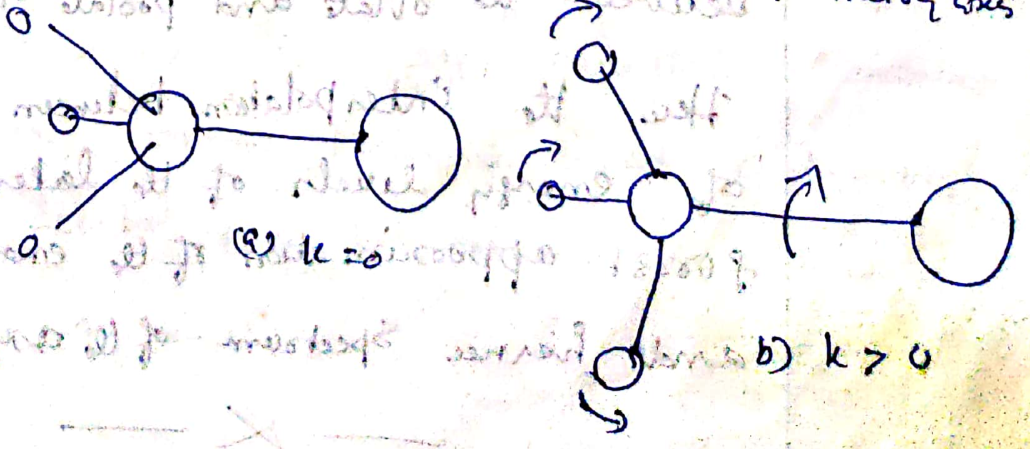
D, D_{JK} and D_K are small correction terms for non rigidity. The selection rules are unchanged i.e $\Delta J = \pm 1$ and $\Delta K = 0$ as before

$$\bar{\nu}_{JK} = \varepsilon_{J+1,K} - \varepsilon_{J,K}$$

$$= 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK}(J+1)K^2 \text{ cm}^{-1}$$

The spectrum will be basically that of a linear molecule with an additional term depending on K^2.

It is easy to see why this spectrum now depends on the axial rotation (i.e, depends on K), although such rotation produces no dipole change. Fig (CH_3F) in a $= K = 0$, no axial rotation and (b), $K > 0$, the molecule rotating about the symmetry axis



(a) $K = 0$

b) $K > 0$

We see from the fig (2) the axial rotation widens the HCH angle and stretches the C–H bonds. The distorted molecule has a different moment of inertia for end-over-end rotation from (a).

~~$\bar{\nu}_{JK} = 2(J+1)\left[B - 2D_J(J+1)^2 - D_{JK}K^2\right]$~~ cm

Asymmetric top molecule

~~Spherical tops show no microwave spectrum~~

The asymmetric top molecule have all all the three moment of inertia different i.e $I_a \neq I_b \neq I_c$.

The analysis of these molecules is quite complex and there is no simple expression for the energy term.

In this case the best method so far has been considered is treating the asymmetric top as falling somewhere between the oblate and prolate symmetric top. Here the interpolation between the two sets of energy levels of the latter leads to a first approximation of the energy levels - and hence spectrum - of the asymmetric molecules.

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Instrumentation for Microwave Spectroscopy

A microwave spectrometer consists of the following essential components:

1) The source and Monochromator

Reflex klystron value is the main source of radiations in microwave region. As the klystron value emits radiation of a very narrow frequency range (called monochromatic), its acts as its own monochromator. Furthermore the frequency of the emitted radiation depends on the voltage that is applied to the klystron value. As the voltage is varied over a given range, the emitted radiation can thus be made to sweep through a region of the microwave range.

One slight disadvantage of the klystron value is that it radiates out very small energy which is of the order of 30 milliwatts. However, since the energy radiated is concentrated into very narrow frequency band, a sharply tuned detector may be activated to produce a strong signal.

The radiation emitted by klystron canot be handled with mirrors and lenses, but can be most advantageously transmitted through hollow metallic conductors of such geometry that the electric and magnetic fields can be utilised to the greatest extent. These are known as wave guides. These are hollow tubes of copper or silver of rectangular cross section inside which the radiation is confined. In order to maintain the direction of beam as well as its focusing the wave guides may be bent or tapered. The waveguides are generally evacuated because if air is present in them, considerable absorption of the radiation will occur. The wave guides used in microwave spectrometer is now commonly used in chemical research facilities.

3. Sample and Sample space : The sample is placed in a piece of evaculated wave guide which is closed at both ends by thin mica windows. Round holes are made in the tube for evacuation purposes and for introduction of the gas under test.

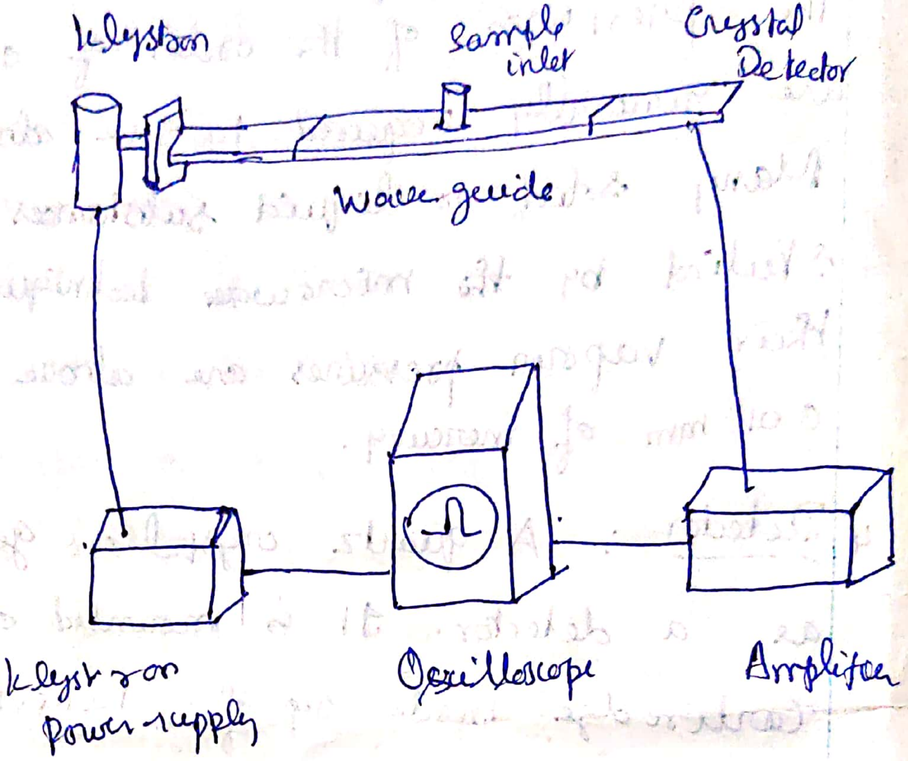
The pressure of the gas is adjusted to make the absorption line sharp.

The sample must be in the gaseous state for studying in the microwave region. The pressures of the order of 0.01 mm mercury are generally required to give absorption spectrum. Many solid or liquid substances can be studied by the microwave techniques provided their vapour pressures are above the value of 0.01 mm of mercury.

4 **Detector** : A quartz crystal is generally used as a detector. It is mounted on a ~~cat~~ cartiridge made up of a tungsten whisker held in point contact with the crystal. In place of crystal detector, an ordinary superheterodyne radio receiver can be used provided it may be tuned to the appropriate high frequency. But a simple quartz crystal is more sensitive and easier to use.

5 **Spectrum analyser** : It consists of an amplifier of detected energy and an indicator which may be either a cathode ray oscillograph or a pen - and ink recorder. The vibrations emitted by the quartz crystal produce an electrical signal which is amplified and then displayed as a pattern on an oscilloscope screen or a recording on a chart by the pen-and-ink recorder

simplified diagram of microwave spectrometer



Working: Monochromatic radiations of various wavelengths in the microwave region emitted by klystron valve are allowed to pass through the sample space containing the gaseous sample of the substance under investigation. Then, the radiations are made to conduct along a rectangular tube called a waveguide. After this the radiations are received by the quartz crystal detector which is situated at the far end of the waveguide. After receiving the radiations from the wave guide it vibrates and produces an electrical signal which is amplified by amplifier and then displaye either as a recording on a chart or as a pattern on an oscilloscopic screen. The pattern obtained on the chart or on the screen of the oscillograph enables one to determine the frequenc or the range of frequencies of to detected

The Rotation of molecules

Notes

The rotational of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through its 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.

1. **Linear molecules** - Molecules in which all the atoms are arranged in a straight line.

eg - HCl (Hydrogen chloride

OCS (carbon oxysulphide)

The three directions of rotation may be taken as

ⓐ about the bond axis

ⓑ end over end rotation in the plane of the paper

c) end over end rotation at right angles to the plane

The moments of ⓑ and ⓒ are 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

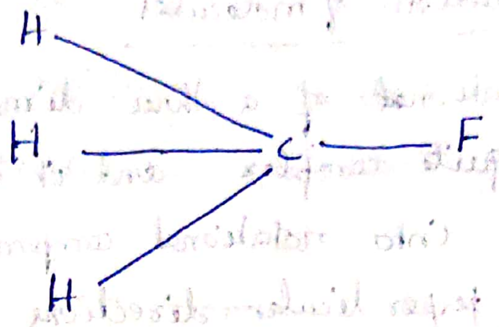
$$I_B = I_C \quad , \quad I_A = 0$$

H — Cl

O — C — S

2. Symmetric tops.

e.g methyl fluoride



The three hydrogen atoms are bonded tetrahedrally to the carbon. 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 $I_B = I_c$. The moment of inertia about the C–F bond axis (choosen as the main rotational axis since the centre of gravity lie along it) is now negligible, however it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis cane be imagined as a top, and hence the name of the class. We have then:

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

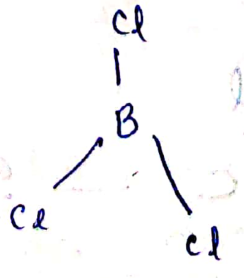
Two sub division.

[illegible]

I. $I_B = I_C > I_A$, then the molecule is called a prolate symmetric top ; (eg) CH_3F

[illegible]

$I_B = I_C < I_A$, it is referred to as oblate (e.g) BCl_3



Planar and Symmetrical

In this case $I_A = 2I_B = 2I_C$

3. Spherical tops. When a molecule has all three moments of inertia identical, it is called a spherical top e.g CH_4

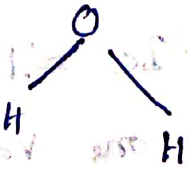
Spherical tops : $I_A = I_B = I_C$

They have no dipole moment 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 :

$$I_A \neq I_B \neq I_C$$

e.g H_2O and Vinyl chloride $CH_2 = CHCl$



Rotational spectra Microwave Spectroscopy

Linear polyatomic molecules

Linear polyatomic molecules can also be treated similar to the diatomics. Since $I_a = 0$, $I_b = I_c$ as for diatomics the energy levels E_J are given by a formula identical to that of diatomics.

The selection rule is $\Delta J = \pm 1$ and the frequency of the $J \rightarrow J+1$ transition is

$$\bar{\nu}_J = 2B(J+1) - 4D(J+1)^3 \; cm^{-1} \quad J = 0, 1, 2, \ldots$$

(The moment of inertia for the end - to - end rotation of the Polyatomic linear molecule is considerably greater)

The spectrum will show the same 2B separation modified by the distortion constant. In fact, whole of the discussion on diatomic molecules applies equally to all linear molecules; three points however should be underlined

1. Since the moment of inertia for the end over end rotation of a polyatomic linear molecule is considerably greater than that of a diatomic molecule, the B value will be much smaller, and the spectral lines more closely spaced.

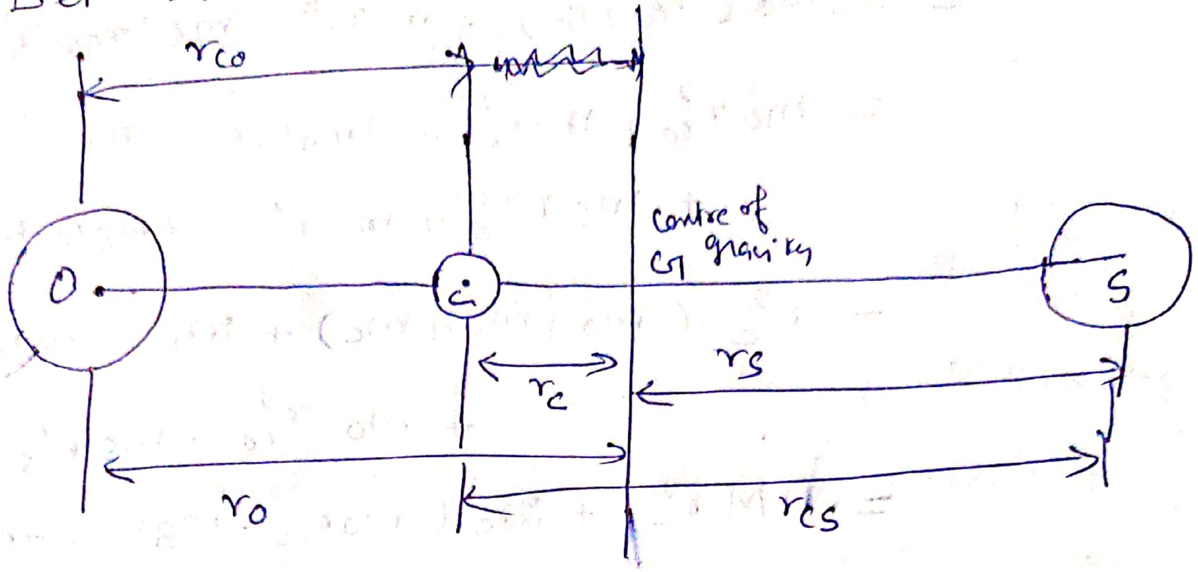
Thus B values for diatomic molecules are about 10 cm^{-1}, while for triatomic molecules they can be 1 cm^{-1} or less, and larger molecules still smaller.

2. The molecule must possess a dipole moment in order to exhibit a rotational spectrum. Thus OCS will be microwave active OCO will be microwave in active.

Linear Polyatomic molecule

3. A linear molecule containing n atoms altogether has (n−1) individual bond lengths to be determined. Thus in a triatomic molecule OCS there is the CO distance r_{CO} and the CS distance r_{CS}. But experiment i.e from the spectrum ~~we can find out the~~ there is only one moment of inertia for the end-over-end rotation of OCS. However if we study a isotopically substituted molecule we will have a different moment of inertia with the same bond lengths. Hence for the determination of r_e (inter nuclear distance) r_{CO} and r_{CS} Parameters we requires a study of isotopically substituted molecule.

Let us consider the rotation of OCS in detail



r_o, r_c and r_s represent the distances of the atoms from the centre of gravity.

Consideration of moments of OCS molecule

$$m_o r_o + m_c r_c = m_s r_s \quad \text{———} \quad ①$$

The moment of inertia is

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad \text{———} \quad ②$$

$$\left.\begin{aligned} r_o &= r_{co} + r_c \\ r_s &= r_{cs} - r_c \end{aligned}\right\} \quad \text{———} \quad ③$$

Substituting ③ in ①

$$m_o(r_{co} + r_c) + m_c r_c = m_s(r_{cs} - r_c)$$

$$m_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$$

$$m_o r_{co} - m_s r_{cs} = -r_c(m_s + m_c + m_o)$$

$$M r_c = m_s r_{cs} - m_o r_{co} \quad \text{———} \quad ④$$

M total mass of the molecule

Substituting ③ in ②

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

$$= m_O r_{CO}^2 + m_O r_C^2 + 2m_O r_{CO} r_C + m_C r_C^2$$

$$+ m_S r_{CS}^2 + m_S r_C^2 - 2m_S r_{CS} r_C$$

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

$$+ m_O r_{CO}^2 + m_S r_{CS}^2$$

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

Substituting the value of r_C from eqn ④ and simplifying we get

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

This is the eqn for ${}^{16}O\,{}^{12}C\,{}^{32}S$ —— ⑤

Considering now the isotopic molecule

${}^{18}O\,{}^{12}C\,{}^{34}S$

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

—— ⑥

We can solve eqn ⑤ and ⑥ and find out the value of r_{CO} and r_{CS} provided if we know the value of I' from the microwave spectrum of isotopic molecule

The extension of the above discussion with more than three atoms is straight forward; it suffices to say here that microwave studies have led to very precise determination of many bond lengths in such molecules.

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The intensities of spectral lines The selection rule for rotational spectra is $\Delta J \pm 1$

The propability of all changes with $\Delta J = \pm 1$ is almost same. This does not mean, However all spectral lines are not equally intense. Although the intrinsic propability that a single molecule in the $J=0$ state will move to $J=1$ is same as that of a single molecule moving from $J=1$ to $J=2$ in an assembly of molecules, There will be different number of molecules in each level. Therefore different total number of molecule will carry out transitions between the various levels. In fact since the intrinsic propabilities are identical; the line intensities will be directly proportional to the initial number of molecules in each level.

According to Boltzman distribution the number of molecules in any higher state is given by

$$\because \quad EJ = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\frac{N_J}{N_0} = \exp\left[-\frac{E_J}{kT}\right] \qquad B = \frac{h}{8\pi^2 Ic}$$

$$= \exp\left[-\frac{Bhc\, J(J+1)}{kT}\right] \quad \text{—— ①}$$

No - no of molecules at the lowest energy level (for $J=0$)

Energy level expression

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) = \frac{h^2}{2 \times 4\pi^2 I} J(J+1)$$

$$2EI = \frac{h^2}{4\pi^2} J(J+1) \qquad \because E = \tfrac{1}{2} I\omega^2$$

$$EI = \tfrac{1}{2} I^2\omega^2$$

$$\sqrt{2EI} = \frac{h}{2\pi}\sqrt{J(J+1)} \qquad 2EI = I^2\omega^2$$

$$P = I\omega$$

$$P = \sqrt{J(J+1)}\,\frac{h}{2\pi} \qquad 2EI = P^2$$

$$= \sqrt{J(J+1)} \text{ units} \qquad P = \sqrt{2EI}$$

$\frac{h}{2\pi}$ is the fundamental unit of angular momentum.

Thus we see that like E, P is also quantised.

If $J = 1$

$P = \sqrt{2}$

The vector length $\sqrt{2}$ have three integral or zero components i.e 1, 0 and −1. Thus the angular momentum vector can be oriented in only three direction with respect to reference direction. All three direction are associated with the same angular momentum and hence the same rotational energy: the $J=1$ level is thus three fold degenerate.

If $J = 2$, $P = \sqrt{6}$, it is five fold degenerate.

If $J = 3$ ~~P=~~ the level is seven fold degenerate.

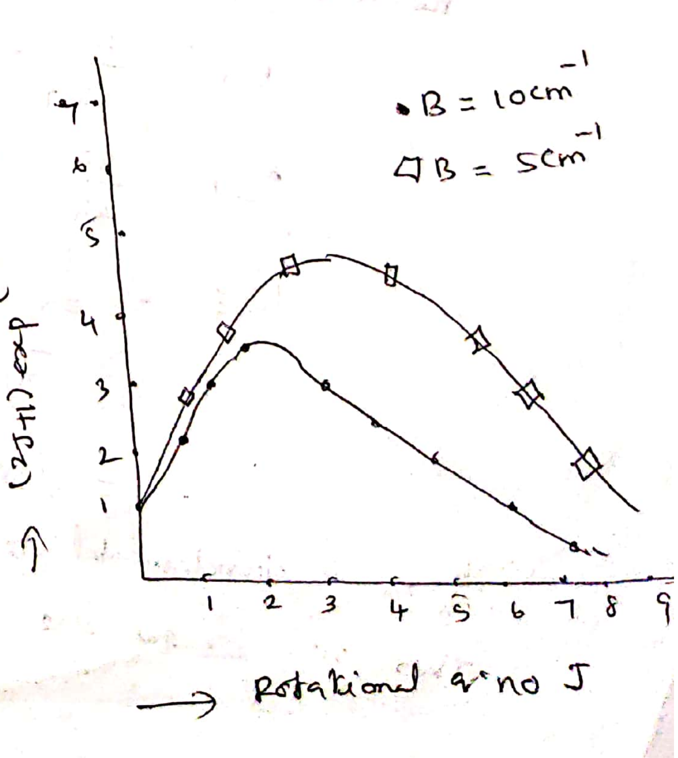
from eq① it is clear that the molecular population in each level decrease exponentially. The number of degenerate levels available increases rapidly with J. The total relative population ~~and~~ at an energy E_J will be

$$\text{population} \propto (2J+1)\exp^{(-E_J/KT)} \quad \text{—} ②$$

When population is plotted against J we can notice that population rises to a maximum and then diminishes. Differentiating eqn 2 we get Maximum population

$$J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2} \quad \text{—} ③$$

We have seen that line intensities are directly proportional to the population of the rotational levels, hence it is plain that transition between levels with very low or very high J values will be small intensities while the intensity will be maximum at or near the J value giving eqn③



Jmax J value

adjacent lines is $2B$. As the rotational levels are closely spaced compared with kT, many of the lower levels will have reasonable population leading to a spectrum with sufficient lines (k is Boltzmann constant). The energy levels and the allowed transitions are shown schematically in Figure 6.3. The value of B can be deduced from the spacing between the observed spectral lines. Use of Eqs. (6.9) and (6.5) immediately gives the internuclear distance of the diatomic molecule.

6.4 ISOTOPE EFFECT IN ROTATIONAL SPECTRA

An atom when replaced by one of its isotopes, the interbond distance remains the same as the electron charge distribution does not change. However, the mass of the nucleus changes leading to a change in the moment of inertia.

Denoting the frequency of the isotopically substituted molecule by single prime,

$$\bar{\nu}' = 2B'(J + 1)$$

$$\Delta\bar{\nu} = \bar{\nu} - \bar{\nu}' = 2(J + 1)\ (B - B')$$

$$= 2(J + 1)\ \frac{h}{8\pi^2 Ic}\left(1 - \frac{I}{I'}\right)\text{cm}^{-1} \tag{6.11}$$

Writing,

$$\frac{I}{I'} = \frac{\mu}{\mu'} = \rho^2$$

$$\Delta\bar{\nu} = 2B(J + 1)\ (1 - \rho^2) \tag{6.12}$$

As $\rho \simeq 1$ in most of the cases, the shift will be extremely small. When there is a mass increase, $\rho^2 < 1$ giving a positive value for $\Delta\bar{\nu}$. It is evident from Eq. (6.12) that isotope shift increases with the value of J. The effect of ^{13}C isotope substitution on the rotational spectrum of diatomic molecule $^{12}C\ ^{16}O$ is illustrated in Figure 6.4.

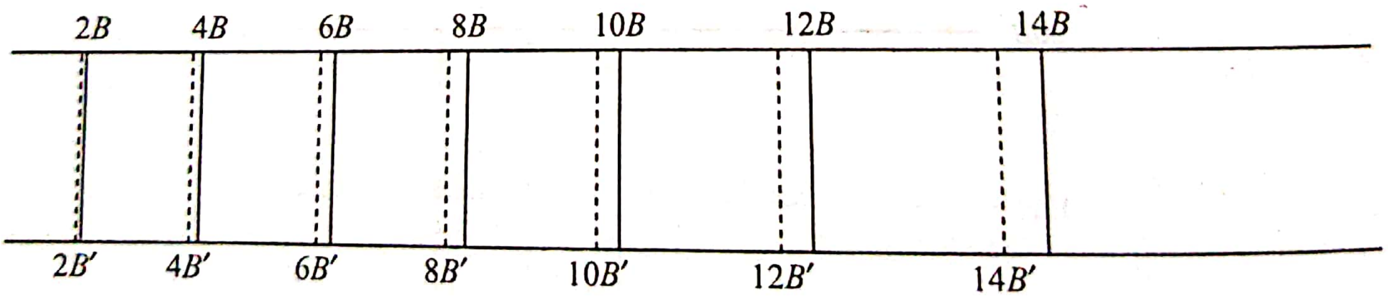


Figure 6.4 Rotational spectrum of (a) diatomic molecule (continuous lines), and (b) isotopically-substituted diatomic molecule having a mass increase.

Measurement of isotope shift allows precise determination of atomic weight of atoms. From the observed spectra of $^{12}C^{16}O$ and $^{13}C^{16}O$, the ^{13}C atomic weight was estimated as 13.007 which is within 0.02% of the best value obtained by other methods.

6.5 INTENSITY OF ROTATIONAL LINES