Spectroscopy

2

Introduction

Spectroscopy is a branch of science dealing with the study of interaction of electromagnetic radiation with matter. The most important consequence of such interaction is that energy is absorbed or emitted by matter in discrete amounts called quanta. The absorption and emission process extends throughout the electromagnetic spectrum ranging from the gamma ray region to the radio frequency region. When the radiation frequency is measured experimentally, it gives the value for change of energy involved, from which one can conclude that matter has a set of possible discrete energy levels. The frequency or wavelengths of absorbed or emitted radiation are experimentally measurable and the energy levels can be deduced.

Spectroscopy offers one of the most powerful tools available for the study of atomic and molecular structure. The study of spectroscopy can be discussed under the following heads.

(a) Atomic spectroscopy

This study is concerned with the interaction of electromagnetic radiation with atoms which are normally in their lowest energy state called the ground state.

Monoatomic substances generally exist in the gaseous state and are able to absorb radiation and result in transition of electrons from one electronic energy level to another. Absorption of electromagnetic radiation can occur only if it has an energy which is equal to the difference in energy between two quantized energy levels given by $\Delta E = h\gamma$ where ΔE represents energy difference between two quantum levels and γ is the frequency of radiation which can result in the electronic excitation.

(b) Molecular Spectroscopy.

This study details with the interaction of electromagnetic radiation with molecules. As a result of interaction transitions are induced between rotational and vibrational energy levels in addition to electronic transitions. The nature of molecular changes that are responsible for the process of absorption and emission makes the spectra of molecules more complicated than those of atoms.

Spectra of molecules extend from the visible region through infrared into microwave region. From molecular spectra, quantitative values of molecular parameters can be determined. Detailed and exact measurements of the size, shape, flexibility,and electronic arrangements can be obtained by spectral studies.

Spectral lines of atoms and molecules may be spread over different regions of the electromagnetic spectrum. Hence it is necessary to have an idea of the electromagnetic spectrum.

Regions of electromagnetic spectrum.

Careful investigation by spectroscopist has led to the classification of electromagnetic spectrum into various regions. In increasing order of frequency or energy the regions are:

1. Radio frequency region : 3×10^6 to 3×10^{10} Hz : 10m to 1cm wavelength.
2. Microwave region : 3×10^{10} to 3×10^{12} Hz : 1cm - 100 μm (micrometers) wavelength.
3. Infrared region : 3×10^{12} to 3×10^{14} Hz : 100 μ m - 1 μm wavelength.
4. Visible and ultraviolet regions : 3×10^{14} to 3×10^{16} Hz : 1μm - 10 nm wavelength.
5. X-ray region : 3×10^{16} to 3×10^{18} Hz : 10nm - 100pm wavelength.
6. $\gamma-$ray region : 3×10^{18} to 3×10^{20} Hz : 100pm - 1pm wavelength.

Emission spectra

Emission spectra are of three types (i) Continuous spectrum (ii) Line spectrum and (iii) Band spectrum.

Incandescent materials (electric light) give a continuous spectrum having all the colours from red to violet. It is not possible here to clearly specify where one colour ends and the other begins.

The light emitted by hot vapours of elements, when seen through a spectroscope gives a spectrum which consists of bright lines. This spectrum is known as 'Line spectrum' or 'atomic spectrum' and is characteristic of the atom. For example, sodium gives two yellow lines of wavelength 589nm and 589.6nm which are characteristic of the elements.

'Band spectrum' is characteristic of molecules. It consists of groups of lines closely packed together giving the appearance of a luminous band.

Absorption spectra.

An absorption spectrum is obtained by placing the substance between the light source and the spectroscope. Dark lines appear in the spectroscope at the same wavelengths as the bright lines of the emission spectrum of the same substance. For example, if a sodium flame is placed between the white light source and the spectroscope, the continuous spectrum of the white light is crossed by two dark lines in the yellow region of the spectrum. If the white light source is now removed, the continuous spectrum disappears leaving behind two bright lines occupying the position of the two dark lines originally present. The two dark lines are a part of the 'absorption line spectrum '.

Absorption spectra are also produced when white light is passed through liquids or solutions of salts. For example, a solution of $KMnO_4$ gives five dark lines in the green region.

The solar spectrum contains a large number of dark lines known as the 'Fraunhoffer lines' . The dark lines are due to the selective absorption of appropriate wavelengths of the white light by the vapours of the elements in the chromosphere of the sun.

The chemist is primarily interested in the structure of matter and the absorption spectra are convenient for this study. The regions of the electromagnetic spectrum that are most useful for this study are the Microwave and Infrared region.

Molecular spectra

Three types of molecular spectra are recognized in structural studies. They are :

(a) Rotational spectra.

(b) Vibrational spectra and vibration - rotation spectra.

(c) Electronic band spectra.

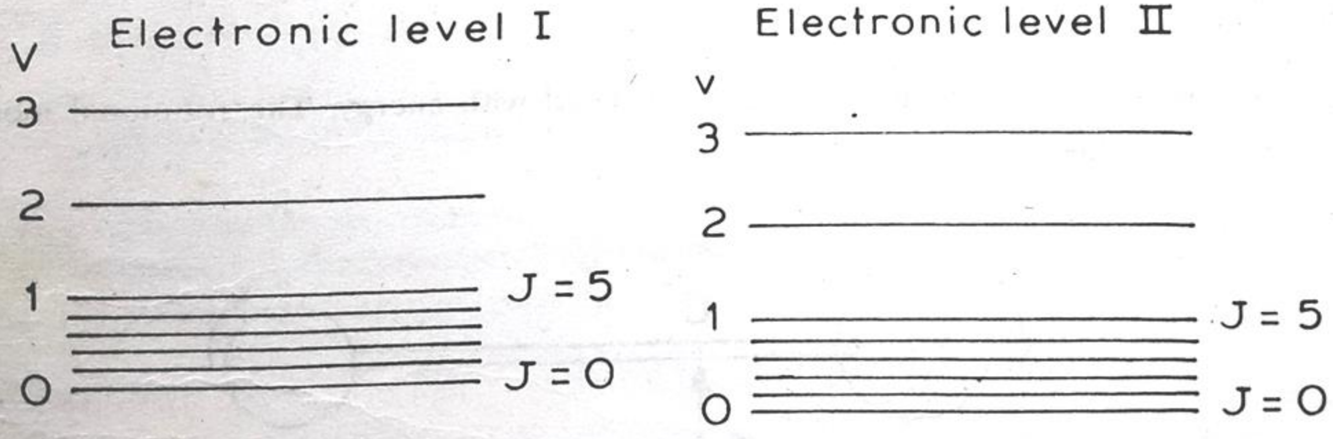

Fig. 2 . 1 : Energy levels

When the normal molecule in the state A absorbs energy, and when this energy is sufficient to raise an electron from state A to an excited state B, one would expect that a single line would appear in the absorption spectrum due to the electronic transition. In practice, however, each electronic transition is accompanied by vibrational and rotational transitions. In each electronic state the molecule can have a series of vibrational sub-levels indicated by v = 0,1,2 etc. Each vibrational level has a set of rotational sub-levels indicated by J = 0,1,2 etc. v and J are the vibrational and rotational quantum numbers respectively. The various sub-levels of the two states I and II have been represented diagramatically in fig. 2 .1

Rotational energy changes are very small and are of the order of 0.005 ev. Since these are small, rotational lines will be closely spaced as shown in the Fig. 2.1 . Such energies are equivalent to radiations in the far infrared or microwave region. Vibrational energy changes are of the order of 0.1 ev, which is about 1.6×10^{-20} J per molecule. the corresponding spectral lines have a frequency

$$\gamma = \frac{1.6 \times 10^{-20}\ \mathrm{J}}{6.6 \times 10^{-34}\ \mathrm{J}} = 3 \times 10^{14}\ Hz$$

Radiations accompanying purely vibrational transitions should therefore appear in the near infrared region of the electromagnetic spectrum. In practice, however, vibrational changes are always accompanied by rotational energy changes. This results in vibration-rotation bands being produced in the near infrared region.

The electronic energy quantum is about 5 ev. Electronic transition therefore appear in the visible and ultraviolet regions.

Pure rotation and vibration spectra in the infrared are exhibited only if a molecule has a resultant dipole moment. Consequently homopolar diatomic molecules like H_2, O_2, Cl_2,N_2etc., do not have pure rotation or vibration-rotation spectra. However, in an electronic transition, vibration and rotation lines are found, even if the molecule is homopolar in its ground state.

Rotational spectra

Rotational motion of molecules is associated with energy. The rotational motion of a diatomic molecule is shown in Fig. 2. 2

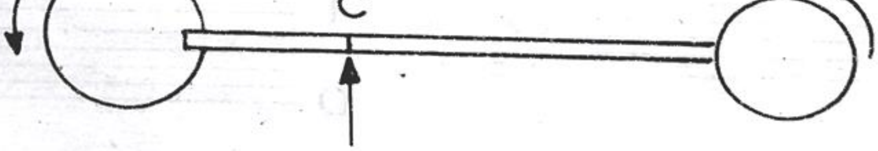

Fig 2 . 2 : Rotational spectra

The centre of gravity does not shift during rotation (rigid rotation) unlike translational motion where the centre of gravity shifts.

Rotational energy is related to the moment of inertia and the square of the angular velocity of the molecule. The term angular velocity is commonly applied to cases of rotation. It is then a vector, whose magnitude is the time rate of change of the angle θ rotated through, i.e., $\frac{d\theta}{dt}$. Monoatomic gases do not give a microwave absorption spectrum, as they have their mass concentrated at the nucleus and hence have no moment of inertia.

The interaction of radiation with the molecule results in a rotational transition only if the molecule has a dipole moment. Molecules with a resultant zero dipole moment (O_2, Cl_2, etc.) do not give rotational spectra. A molecule like HCl gives a rotational spectrum. This is due to the fact that the electric dipole of the HCl molecule enables the oscillating field of radiation to effect the necessary twist on the molecule resulting in the rotational spectrum.

By the use of Schrodinger equation, it can be shown that the rotational energy of a diatomic molecule is given by the expression

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules, where J} = 0, 1, 2, 3, \ldots.. \qquad (2.1)$$

where h is the Planck's constant, J is the rotational quantum number having only integral values, 0, 1, 2, etc. This restriction to integral values for J arises out of the solution of Schrodinger equation and by no means arbitrary and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule. I is the moment of inertia, given by

$$I = \mu r_0^2 \qquad (2.2)$$

where μ is the reduced mass defined by

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} \qquad (2.3)$$

m_1 and m_2 are the masses of two atoms, r_0 is the equilibrium internuclear distance.

In order to discuss the spectrum we now need to consider differences between rotational energy levels particularly in the corresponding frequencies γ and also in the wave number $\overline{\gamma}$, when there is transition from one rotational level to another, say J'' to J'.

We know that

$$\Delta E = h\gamma = hc\overline{\gamma} = h\frac{c}{\lambda} = hc\frac{1}{\lambda} = hc\overline{\nu} \qquad (2.4)$$

Since $\gamma = c\overline{\gamma}$ where $\overline{\gamma}$ is the wavenumber in m^{-1} and c is the velocity of light in ms^{-1}

$$\overline{\gamma} = \frac{\Delta E}{hc} \; m^{-1} \qquad (2.5)$$

Using equation 2.1

$$\Delta E = E_J' - E_J'' = \bar{\gamma} = \frac{h^2\left[J'\left(J'+1\right) - J''\left(J''+1\right)\right]}{8\pi^2 Ihc} \quad \mathrm{m}^{-1} \tag{2.6}$$

or

$$\bar{\gamma} = \frac{h\left[J'\left(J'+1\right) - J''\left(J''+1\right)\right]}{8\pi^2 Ic} \quad \mathrm{m}^{-1} \tag{2.7}$$

This equation is usually abbreviated to

$$\bar{\gamma} = B\left[J'\left(J'+1\right) - J''\left(J''+1\right)\right] \quad \mathrm{m}^{-1} \tag{2.8}$$

where 'B' is the rotational constant and is given by

$$B = \frac{h}{8\pi^2 Ic} \quad m^{-1} \tag{2.9}$$

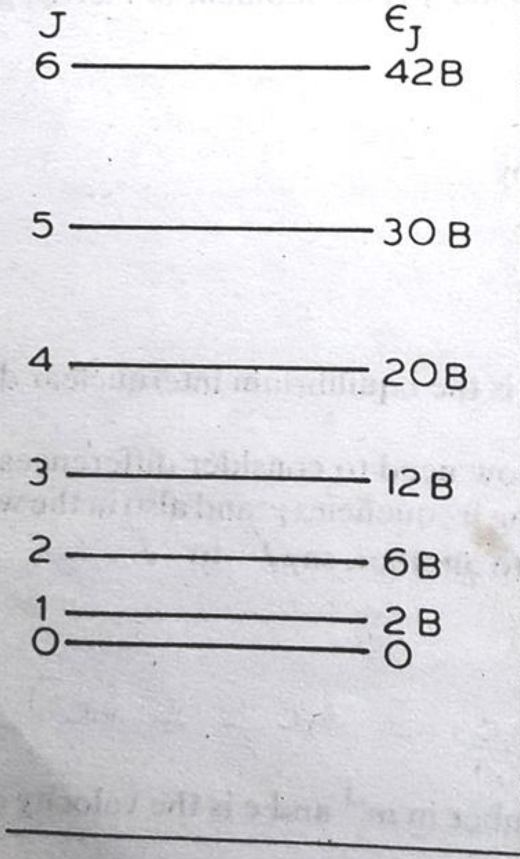
J
ϵ_J
6
42B
5
30 B
4
20B
3
12 B
2
6B
1
2 B
0
0

Fig. 2.3 The allowed rotatioal energy levels of a diatomic molecule

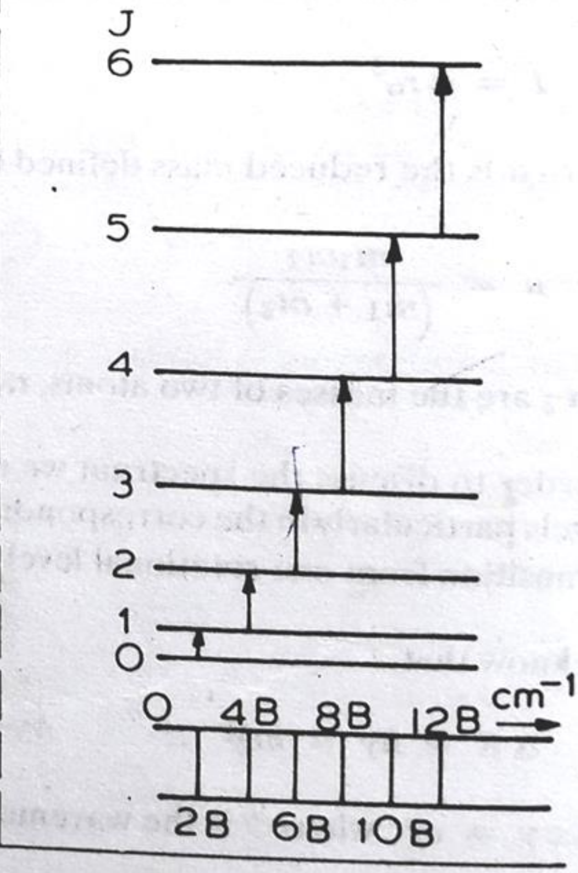
J
6
5
4
3
2
1
0
0
4B
8B
12B
cm^{-1}
2B
6B
10B

Fig. 2.4 Allowed transition between the energy levels of a rigid diatomic molecule and the spectrum arising from them

As a general rule, rotational transitions are restricted to those in which J = +1 so that $J' - J'' = 1$. If molecule in the state of J = 0 (ground state in which no rotation occurs) is raised to a state J = 1, then

$$\bar{\gamma}_{J=0->J=1} = B\left[1\left(1+1\right) - 0\left(0+1\right)\right]$$
$$= 2B \ m^{-1} \qquad (2.10)$$

This means an absorption line will appear at 2B m^{-1}. If the molecule is raised from J = 1 to J = 2, an absorption line will now appear at 4B m^{-1}. In general, to raise the molecule from the state J to the state J + 1, we have

$$\bar{\gamma}_{J->J+1} = B(J+1)(J+2) - BJ(J+1)$$
$$= B\left[\left(J^2 + 3J + 2 - J^2 + J\right)\right]$$
$$= 2B\left(J+1\right) \ m^{-1} \qquad (2.11)$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of a series of lines at 2B, 4B, 6B, 8B, etc., such a spectrum is shown in Figs 2 . 3 and 2 . 4 . The spacing between any two successive lines is the same i.e.,2B.

From the Schrodinger equation it is established that J changes by one unit i.e., ΔJ = ±1. This result is called a 'selection rule'. Hence we see that it is possible to get the whole spectrum from the equation (2 .11).

Rotation spectra are not observed with liquids and solids, due to interference of neighbouring molecules on each other's rotation. The most important application of the rotational spectra is the calculation of bond lengths and the moment of inertia of heteronuclear diatomic molecules. The problem given below illustrate this point.

Problem

The first absorption line (J = 0 to J = 1) in the rotation spectrum of CO was found to be 384.2 m^{-1}. Calculate the moment of inertia of the molecule and the bond length of the carbon-oxygen bond.

Solution.

$$\bar{\gamma}_{J=0->J=1} = 384.2 \ m^{-1} = 2B \ m^{-1}$$

$$B = \frac{384.2}{2} = 192.1 \ m^{-1}$$

We know that $$B = \frac{h}{8\pi^2 Ic} \ m^{-1}$$

$$I_{co} = \frac{h}{8\pi^2 \cdot c \cdot B} = \frac{6.62 \times 10^{-34}\, J \cdot s}{8 \times (3.14)^2 \times 3 \times 10^{-10}\, ms^{-1} \times 192.1\, m^{-1}}$$

$$= 14.6 \times 10^{-47}\, kg\, m^2 \quad (\text{since } J = kg \cdot m^2 s^{-2})$$

$$I = \mu r_o^2$$

$$= 14.6 \times 10^{-47}\, kg\, m^2 = \frac{\frac{12 \times 10^{-3}}{6.02 \times 10^{23}} kg \times \frac{16 \times 10^{-3}}{6.02 \times 10^{23}} kg}{\frac{(12 + 16) \times 10^{-3}}{6.02 \times 10^{23}} kg} \times r_o^2$$

$$= \frac{12 \times 16 \times 10^{-3}}{28 \times 6.02 \times 10^{23}}\, kg \times r_o^2$$

$$r_o^2 = 1.28 \times 10^{-20}\, m^2$$

$$r_{co} = 1.13 \times 10^{-10}\ \text{m} = 0.113\ \text{nm} = 1.13\ \text{A}^\circ$$

Vibrational spectra

A vibration is a to and fro motion. Vibration involves the interconversion of potential and kinetic energies. In a diatomic molecule, vibrations cause a stretching and compression of the molecule. This is the only mode of vibration possible here and so it gives a comparatively simple spectrum.

The extension and compression of a bond may be linked to the behaviour of a spring and by analogy the bond, like spring may be assumed to obey Hooke's law. We may write

$$f = -k(r - r_{eq}) \tag{2.12}$$

where f is the restoring force, k is the force constant, and r is the internuclear distance. $r - r_{eq}$ is a measure of displacement from equilibrium distance. In this case the energy is parabolic and has the form

$$E = \frac{1}{2} k (r - r_{eq})^2 \tag{2.13}$$

This model of a vibrating diatomic molecule forms an excellent starting point for the discussion of vibration spectra.

Simple harmonic oscillator

If we plot the energy according to equation 2 .13 as a function of internuclear distance, the parabolic variation in the energy is observed (Fig.2 .5)

The energy of the oscillator is zero at $r = r_{eq}$ and any energy in excess of this say ε_1, arises because of bond extensions and compressions. The figure shows that if one atom (A) is fixed on $r = 0$ axis then the other will oscillate between B' and B". If the energy is increased to ε_2 the degree. of the extension and compression will become more vigorous but the frequency of vibration will not change. An elastic bond like a spring shows a vibrational frequency dependance on mass of the system and force constant but independent of the amount of distortion.

Classically it is easy to show that the frequency of oscillation to be

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{k/\mu}\ \text{Hz} \tag{2.14}$$

Where μ is the reduced mass of the system. To convert this into wave numbers, the unit most frequently used in vibrational spectroscopy, we must divide by the velocity of light c, expressed in ms^{-1}

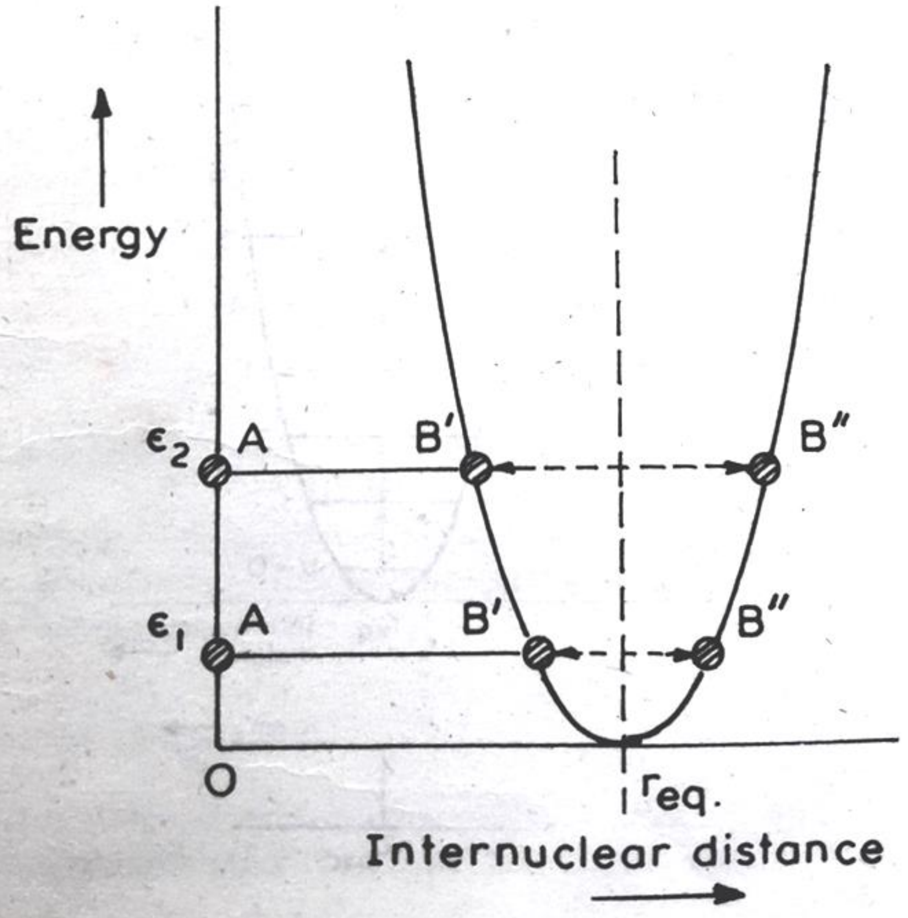

Fig 2. 5 : Parabolic curve of Energy Plotted aganist Internuclear Distance

$$\overline{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{k/\mu} \qquad (2.15)$$

Vibrational energies like rotational energies are also quantised and the allowed vibratio energies for a system can be calculated using Schordinger equation.

For a simple harmonic oscillator we have

$$E_V = \left(v + \frac{1}{2}\right) h\,\omega_{osc} \text{ Joules } (v = 0,1,2) \qquad (2.\ 16)$$

where v is the vibrational quantum number. Converting it into wave number unit cm^{-1} we have

$$\varepsilon_v = \frac{E_V}{hc} = \left(v + \frac{1}{2}\right) \overline{\omega}_{osc} \qquad (2.17)$$

This equation represents the energies allowed to a simple harmonic vibrator as shown figure 2 .6

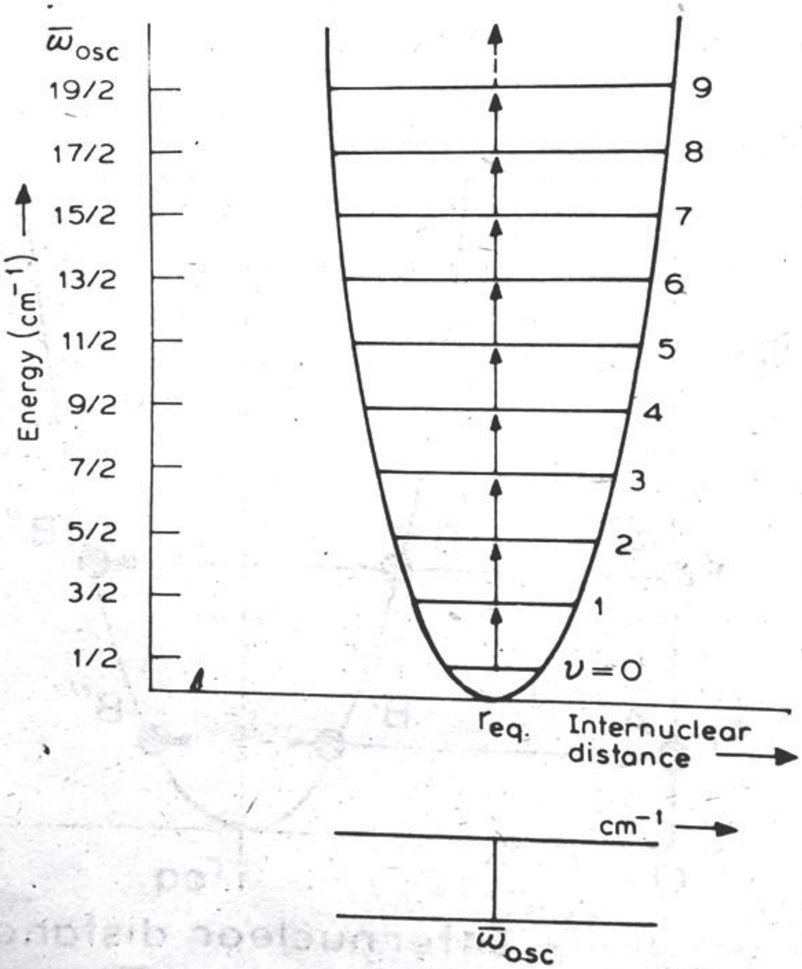
$\overline{\omega}_{osc}$
19/2
17/2
15/2
13/2
11/2
9/2
7/2
5/2
3/2
1/2
Energy (cm^{-1})
9
8
7
6
5
4
3
2
1
$\upsilon = 0$
$r_{eq.}$
Internuclear distance
cm^{-1}
$\overline{\omega}_{osc}$

Fig 2.6 : The allowed vibraional energy levels and transiion beween them for a diatomic simple harmonic vibrator

In this model we see immediately that the lowest vibrational energy obtained by putting v = 0 in equation 2.16 or 2.17 is

$$E_o = \frac{1}{2} h\,\omega_{osc} \quad Hz$$

$$\varepsilon_o = \frac{1}{2} \overline{\omega}_{osc} \quad cm^{-1} \tag{2.18}$$

This implies that the diatomic molecule can never be completely at rest and have zero vibrational energy. The quantity $\frac{1}{2} h\,\omega_{osc}$ or $\frac{1}{2} \overline{\omega}_{osc}$ is known as the " Zero point energy". This zero point energy depends only on the vibrational frequency and hence on the strength of the chemical bond and the atomic masses. The prediction of the zero point energy is the only basic difference between quantum mechanical and classical approaches to molecular vibrations.

By utilization of Schrodinger equation one can calculate the vibrational energies of a molecule using a simple selection rule that vibrational quantum number changes by one unit i.e.,

$$\Delta v = \pm 1 \tag{2.19}$$

The various vibrational energy levels are shown in Fig 2.6 which are obtained for different values of v from 0 upwards in equation 2.17

Applying the selection rule for emission we have

$$\varepsilon_{v+1->v} = \left(v + 1 + \frac{1}{2}\right) \overline{\omega}_{osc} - \left(v + \frac{1}{2}\right) \overline{\omega}_{osc} \tag{2.20}$$

$$= \overline{\omega}_{osc} \quad cm^{-1}$$

and

$$\varepsilon_{v->v+1} = \overline{\omega}_{osc} \quad cm^{-1} \tag{2.21}$$

for absorption , whatever the initial value of v.

Since the vibrational energy levels are equally spaced, transition of molecules between any two vibrational states results in the same energy change and hence shows a single frequency for absorption or emission.

$$\overline{\gamma}_{spec} = \varepsilon = \overline{\omega}_{osc} \quad cm^{-1} \tag{2.22}$$

Vibrational spectra will be observable only in heteronuclear diatomic molecules and not in homonuclear diatomic molecules. This is because homonuclear molecules have no dipole moment.

One of the most important applications of the vibrational spectrum is to calculate the force constants and hence the strength of chemical bonds.

From equation 2 .15

$$\overline{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{k/\mu}$$

Squaring both sides and rearranging we get

$$k = 4\pi^2 c^2 \overline{\omega}_{osc}^2 \mu \qquad (2.23)$$

for a diatomic molecule

$$k = 4\pi^2 c^2 \omega_{osc}\left(\frac{m_1 m_2}{m_1 + m_2}\right) \qquad (2.24)$$

From the value of $\overline{\omega}_{osc}$ from vibration spectra, the value of force constant k, can b calculated. Table 2.1 shows the values of force constants of a few common chemical bonds.

Table 2.1 Force constants of various linkages

Bond	Force constant ($N\ m^{-1}$)
C–C-	460
C=C	950
C≡C	1580
C–O	490
C=O	1230
C≡O	1860

From the data it can be concluded that the force constant is a measure of the strength of the bond. Force constants increase approximately in proportion to the multiplicity of the bond between the bonded atoms indicating greater strength in such bonds. For example, the force constant of the bond in C_2H_2 is higher than that of C_6H_6 and C_2H_4 indicating the greater strength of the triple bond in acetylene

Problem

The spectrum of HCl shows an intense absorption at a frequency of 8.7×10^{13} Hz. Calculate the force constant of the bond (μ for HCl is 1.628×10^{-27} kg).

Solution

$$\gamma_{spec} = c\,\overline{\gamma}_{spec}$$

$$\overline{\gamma}_{spec} = \frac{\gamma_{spec}}{c} = \frac{8.1 \times 10^{13}\ Hz}{3 \times 10^{8}\ ms^{-1}} = 2.9 \times 10^{5}\ m^{-1}$$

Assuming that the spectroscopic line corresponds to the transition v = 0 and v = 1 then

$$\overline{\gamma} = \overline{\omega}_{vib}$$

we know that $k = 4\pi^2 \overline{\omega}^2_{osc}\, c^2 \mu$

$$k = 4 \times (3.14)^2 \times \left(2.9 \times 10^5\ m^{-1}\right)^2 \times \left(3 \times 10^8\ ms^{-1}\right)^2 \times 1.628 \times 10^{-27}\ kg$$

$$= 487\ kg\ ms^{-2}\ m^{-1}$$

$$= 487\ N\ m^{-1}$$

Since the S.I unit of force is the newton = kg m s^{-2}

For polyatomic molecules, there can be several modes of vibration. Here we can distinguish two types (a) linear and (b) non-linear molecules. For a triatomic linear molecule containing n atoms, (3n-5) vibrational modes are possible. Fig 2.7 shows the possible modes of vibrations in CO_2 molecule.

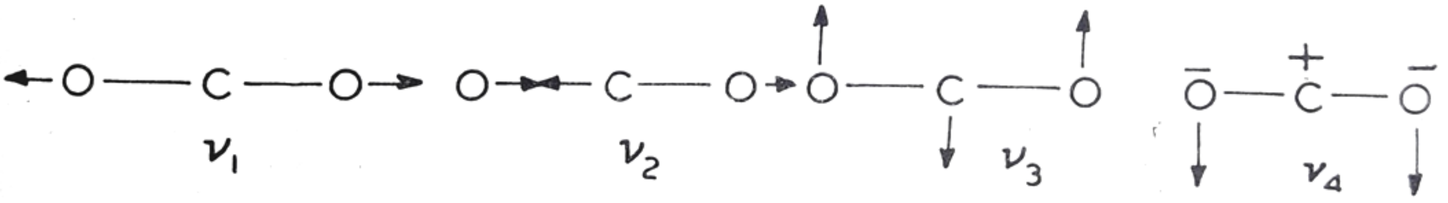

Fig. 2.7 Vibrational modes of CO_2 molecules

γ_3 in fact consists of two bending vibrations, one involves the displacement in plane of paper and the other out of plane. These two vibrations are identical in all respects except direction and are termed degenerate. A triatomic linear molecule should have 3×3 - 5 = 4 modes of vibration. Since one of these is doubly degenerate in CO_2 there are only three different normal modes of vibrations with corresponding frequencies $\gamma_1, \gamma_2, \gamma_3$, as shown in fig 2 .7 .Out of 3n-5 vibrations, (n-1) are stretching vibrations and 2n-5 are bending vibrations.

A non-linear triatomic molecule for example H_2O, has (3n-6) fundamental vibrations. Out of this, (n-1) are stretching motions while (2n-5) are bending motions. Water has three normal mode of vibrations, none of which are degenerate. These motions are shown in fig 2 .8

$$\overline{\gamma}_{spec} = \frac{\gamma_{spec}}{c} = \frac{8.1 \times 10^{13}\ Hz}{3 \times 10^{8}\ ms^{-1}} = 2.9 \times 10^{5}\ m^{-1}$$

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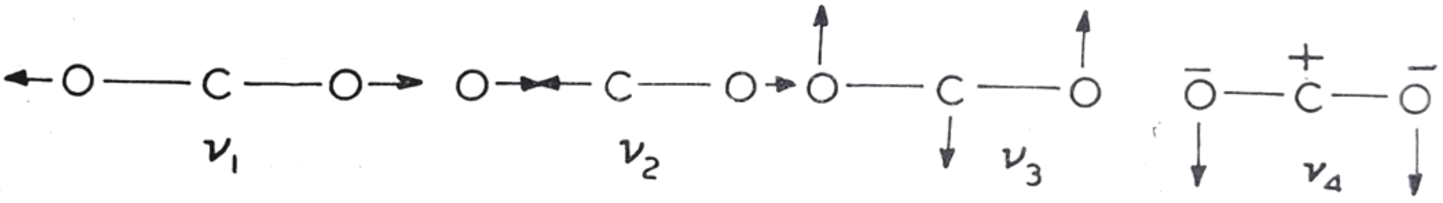

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$$J' - J'' = -\Delta J = -1 \qquad \text{P branch}$$

$$J' - J'' = \Delta J = 0 \qquad \text{Q branch}$$

As an example, the fundamental absorption band of HCl at 2886 cm^{-1} is shown in Fig 2.9

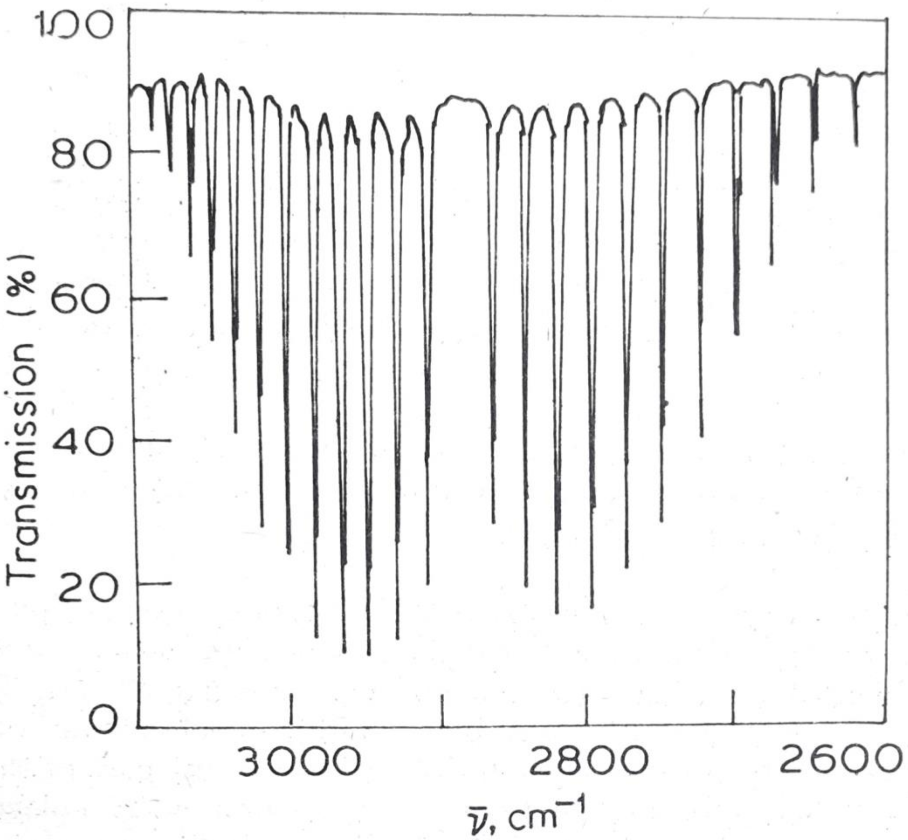

Fig 2.9 : Spectrum of HCl Molecules showing P and R Branch lines

This band occurs from transition between $v = 0$ and $v = 1$. The appearance of P and R branch lines are shown in figure at high resolution. Each line corresponds to a distinct value of J' and J''

Electronic band spectra

Electronic spectra of molecules arise from excitation of electrons from one energy level to a higher one. Electronic excitation in molecules is also accompanied by vibrational and rotational transitions.

Let E''_{ele} , E''_{vib} and E''_{rot} be the electronic, vibrational and rotational energies of the molecule prior to the transition and E'_{ele} , E'_{vib} and E'_{rot} are the corresponding quantities after change. The total energy of the molecule in the initial state is

$$E''_{ele} + E''_{vib} + E''_{rot} = E''_{total} \tag{2.27}$$

and in the final state

$$E'_{ele} + E'_{vib} + E'_{rot} = E'_{total} \tag{2.28}$$

The change in energy in electronic transition is

$$= \Delta E = (E'_{ele} - E''_{ele}) + (E'_{vib} - E''_{vib}) + (E'_{rot} - E''_{rot}) \tag{2.29}$$

$$= \Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot} \tag{2.30}$$

The frequency of radiation is given by

$$\gamma = \frac{\Delta E}{h} = \frac{\Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot}}{h} \tag{2.31}$$

The values of ΔE_{vib} and ΔE_{rot} depend on vibrational and rotational quantum numbers involved.

Electronic spectral bands are very complex but are frequently studied in preference to other types. This is because the spectra can be studied in the visible and ultraviolet region and also instrumental techniques are relatively simple.

When the electronic spectral bands of a molecule are observed, it is found that at one end of the spectrum the distance of the separation of the lines becomes smaller and smaller until at a given position the spectrum terminates (continuum). The dissociation energy for a molecule can be determined with great accuracy from this spectrum from the observance of the frequency of continuum i.e., the wave length that separates the discontinuous part of the spectrum from continuous part of the spectrum resulting from the dissociation of the molecule into two parts with various amounts of kinetic energy.

These spectra also provide information with regard to vibrational frequencies, moment of inertia, internuclear distances etc. (table 2.2). From the electronic spectral studies we can get information about vibrational and rotational motion of homopolar molecules which cannot be obtained by infrared spectral studies.

Table 2.2 Molecular constants obtained from electronic spectral measurements

Molecule	reduced mass $\mu \times 10^{27}$(kg)	moment of inertia $I \times 10^{47}$ kgm^2	$r_o \times 10^{10}$ (m)	$\gamma_o \times 10^{-12}$ s^{-1}	dissociation energy D(kJ/mole)
H_2	0.837	0.46	0.742	131.8	431.8
N_2	11.63	13.94	1.095	70.7	712.5
O_2	13.28	19.35	1.207	47.38	489.8
HCl	1.627	2.645	1.275	86.6	427.6
CO	11.4	14.4	1.128	65.05	1071.9