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KARAIKUDI – 630 003

DIRECTORATE OF DISTANCE EDUCATION

M. Sc - Physics

III - SEMESTER

34531

MOLECULAR SPECTROSCOPY

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1.1 Introduction

To tell the electronic states of molecules, it progresses necessary to study the ways in which the molecules can be built theoretically from nuclei and electrons. The mechanism that holds the atoms together in molecules was a vague fact before the beginning of wave mechanism, because bonding of oppositely charged atoms-due to the electrostatic attraction-was easy to know while the formation of a molecule with two neutral atoms cannot be understood without the help of wave mechanics. For example, hydrogen molecule is designed with the combination of two neutral hydrogen atoms. There are two wave mechanical methods to explain the construction of molecular wave function of which one is the historical valence band (VB) method developed by W.Heitler and F.London (1927) and the other is molecular orbital (MO) method developed by Milliken.

1.2 Objectives

Valence band theory is discussed, Molecular orbital theory, Heitler London theory for Hydrogen molecules are deliberated. Hybridization-SP, SP2 and SP3 hybrids are discussed

1.3 Valence Bond theory

Heitler and London were the first to explain the valency problem using the quantum mechanical approach by taking up the Hydrogen molecule

problem. In this theory, molecules are formed by bringing together atoms complete with their electrons, which are allowed to interact with each other to form a chemical bond.

1.3.1 Heitler London theory for Hydrogen Molecule:

Let two hydrogen atom A and B, with electron 1 and 2 respectively, each in the ground 1s state, be initially a large distance apart. The distance is so large that no appreciable interaction can occur between the atoms. The orbital wave functions for the separated atoms $H_A(e_1)$ and $H_B(e_2)$ would be given by $\psi_A(1)$ and $\psi_B(2)$ respectively, where H_A and H_B are the atomic Hamiltonian operators. When the two atoms together form a quantum mechanical system, the wave function is written as,

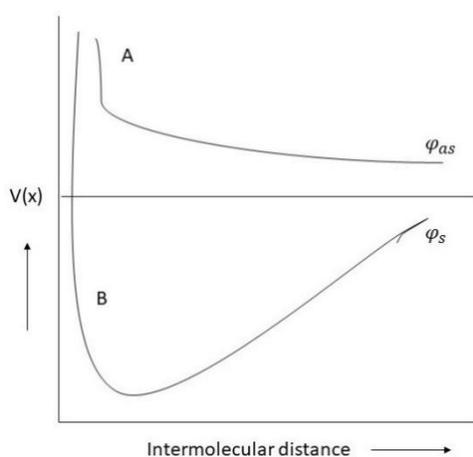
$$(H_A + H_B)\psi_A^{(1)}\psi_B^{(2)} = (E_A + E_B)\psi_A^{(1)}\psi_B^{(2)} \quad \text{-----(1.1)}$$

Therefore, the quantum mechanical system has its Hamiltonian as simply the sum of the atomic Hamiltonian operators and the wavefunction as the product of the atomic wave functions, so that,

The total energy $E = E_A + E_B$ and

The total energy wave function $\psi = \psi_A^{(1)} + \psi_B^{(2)}$ -----(1.2)

The wave function as assumed in equation (1.2) cannot be correct owing to the indistinguishable nature of the two electrons. We have supposed so far that the electrons labeled 1 and 2, could be associated with the nuclei A and B respectively. However, when the atoms are very close to each other



such that their atomic orbitals overlap, we can no longer be sure that the electron 1 will always be nearer A and electron 2 be nearer B. In fact, we cannot distinguish one electron from the other and hence there is also a chance to obtain the product $\psi_B^{(1)}\psi_A^{(2)}$ as a wave function for the joint system.

Therefore, the trial wave function ϕ for the system will contain both the possibilities,

Fig 1.1 Variation of energy with internuclear distance for the hydrogen molecule

$$\phi = C_1 \psi_A^{(1)}\psi_B^{(2)} + C_2 \psi_B^{(1)}\psi_A^{(2)} \quad \text{-----(1.3)}$$

Since an exchange of the electrons leaves the Hamiltonian H unchanged, solving the problem by perturbation method we get the wave function either to be symmetric or anti symmetric with respect to such an exchange. The symmetric ϕ_s and anti symmetric ϕ_{as} combinations are

$$\phi_s = [\psi_A^{(1)}\psi_B^{(2)} + \psi_B^{(1)}\psi_A^{(2)}] \text{-----} (1.4)$$

$$\phi_{as} = [\psi_A^{(1)}\psi_B^{(2)} - \psi_B^{(1)}\psi_A^{(2)}] \text{-----} (1.5)$$

$$C_1^2 = C_2^2 \quad \text{or } C_1 = C_2 \quad \text{and } C_1 = 1$$

The energy of the system as function of inter nuclear distance can be calculated by using the wave function ϕ_s and ϕ_{as} . The calculated energy is shown graphically in fig. (1.1) in which the curve S represents the energy curve obtained by using ϕ_s , while the curve A represents the energy curve obtained by using ϕ_{as} .

The curve S has a minimum and so it shows the formation of stable molecules while curve A has no minimum and so it shows that no stable molecule can be formed. Otherwise, ϕ_{as} represents a repulsive or non-bonding state, but ϕ_s represents a bonding state. Therefore, the antisymmetric combinations of the two possible wave functions of the system of two approaching H atoms will always lead to repulsive between the two atoms, while the symmetric combination will lead to attraction of the two hydrogen atoms so that a stable H_2 molecule can be formed. The inter nuclear distance at which the energy is minimum, represents the value of equilibrium inter nuclear separation τ_o , which was theoretically found to be 0.87\AA . The bonding energy corresponding to this separation was found to be 72 Kcal/mole.

1.2.2 Improved Trial wave functions

The structures given by ϕ_s and ϕ_{as} are referred to as the covalent structures since one electron is associated with one nucleus and second one with the other nucleus. The calculated values of τ_o and bonding energy with this covalent structures are not in good agreement with that of their corresponding experimental values, which are 0.74\AA and 109 Kcal/mole respectively. The agreement between experimental and theoretical values can be improved further by considering two additional structures in which both the electron are associated with only one nucleus. These are ionic structures. Both the electrons may be simultaneously near the nuclei A leaving B without electron loading to $H_A^- H_B^+$ or vice versa leading to $H_A^+ H_B^-$. The wave function for this ionic form of a hydrogen molecule may therefore be represented well by $\psi_A^{(1)}\psi_A^{(2)}$ or $\psi_B^{(1)}\psi_B^{(2)}$

Taking into consideration the possibility of ionic configuration, the combined wave function, for the hydrogen molecule can be written as

$$\phi_s = [\psi_A^{(1)}\psi_B^{(2)} + \psi_B^{(1)}\psi_A^{(2)}] + \lambda [\psi_A^{(1)}\psi_A^{(2)} + \psi_B^{(1)}\psi_B^{(2)}]$$

Or more conveniently as

$$\phi_s = \psi_{cov} + \lambda\psi_{ion} \text{-----(1.6)}$$

Where the coefficient λ is a measure of the degree to which the ionic forms contribute to the bonding. By varying λ between the value 0 and, the energy can be minimized and the bonding energy can be brought to very close agreement to that of the experimental value. This demonstrates strongly the validity of VB approach.

1.4 Molecular orbital theory

In the earlier VB approach, complete atoms are brought together and allowed to interact, but the Molecular orbital (MO) approach is quite different from the VB approach. Here, the orbitals are devised for the molecule as a whole, (i.e) by involving the nuclei of all the constituent atoms separated by fixed equilibrium distance so that the molecular orbitals will become polycentric, and then it is imagined that the electrons are fed into these molecular orbitals in accordance with Pauli's exclusion principle. This can be done in number of ways. As molecules consist of atoms, molecular orbitals may be taken as a function of atomic orbitals centered on individual atoms. The most commonly used approach for obtaining the MO is the linear combination of atomic orbitals (LCAO) approximation.

The molecular orbital (ϕ) is written as a linear combination of the atomic orbitals as,

$$\phi = C_1\psi_A + C_2\psi_B + \text{-----} \quad (1.7)$$

where ψ_A is the atomic function of one nucleus (say A) the other ψ_B of B and so on. C_1, C_2, \dots are the variable parameters which are to be selected in such a way that the energy given by ϕ is minimum. To generate an effective MO by LCAO method, the combining atomic orbitals must satisfy the following criteria:

- i) The participating atomic orbitals should have energies of comparable magnitude,
- ii) The atomic orbitals from the bonding atoms should overlap to the maximum extent, and
- iii) The combined atomic orbitals must have a symmetry consistent with that of the molecule.

Let us now consider the case of homonuclear diatomic molecules (i.e, atoms A and B are identical) for which the MO can be written as,

$$\phi = C_1\psi_A + C_2\psi_B \text{.....(1.8)}$$

Since both the combining atoms are similar, equal weights must be given to ψ_A and ψ_B on symmetry grounds, so that, $C_1^2 = C_2^2$ or $C_1 = \pm C_2$. Moreover, since the coefficients are relative quantities, we can also put $C_1 = 1$, and hence $C_2 = \pm 1$. Thus, we can have two molecular orbitals from the atomic orbitals, which are written as

$$\varphi_b = \psi_A + \psi_B \quad \dots\dots\dots(1.9)$$

$$\varphi_a = \psi_A - \psi_B \quad \dots\dots\dots(1.10)$$

The molecular orbitals φ_b has a lower energy (Fig 1.2) than that of the atomic orbitals from which it is formed; it thus leads to the formation of a stable molecule and is therefore termed as a bonding MO. The other MO, φ_a has energy higher than that of the atomic orbitals and is therefore referred to as antibonding MO.

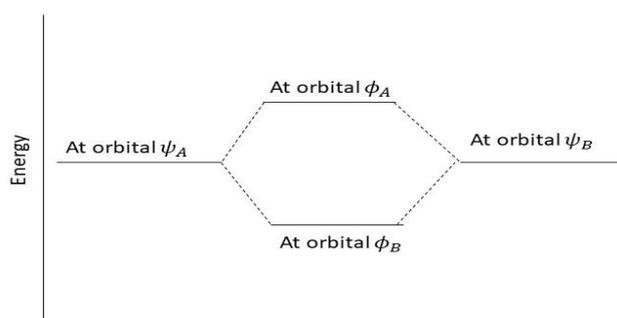


Fig.1.2 Relative energies of MO and their constituent Atomic orbitals

In the case of Hydrogen molecule, for its ground state the appropriate atomic orbitals to be employed for forming MOs are the 1s orbitals. Therefore, the bonding and antibonding MO's of hydrogen molecule are,

$$\varphi_b = H_A^{(1s)} + H_B^{(1s)} \quad \dots\dots\dots(1.11)$$

$$\varphi_a = H_A^{(1s)} - H_B^{(1s)} \quad \dots\dots\dots(1.12)$$

The wavefunction φ_b corresponds to the situation in which there is a build up of electron density between the two nuclei and a more effective screening of one nucleus from the other. In other words, a bond has been formed which is described by a bonding MO. The other possibility, φ_a corresponds to the situation in which there is a depletion of charge between the two nuclei and a larger nuclear repulsion resulting in an antibonding MO.

Fig. 1.3 shows the formation of molecular orbitals by combination of atomic orbitals and their corresponding electrons probability density contours showing the bonding and antibonding orbitals.

Molecular orbitals which are symmetrical about the internuclear axis are designated by σ and those which are not symmetrical about the internuclear axis are designated by π . The bonding orbital discussed above is given by the

symbol $1s\sigma$, since it is produced from two $1s$ atomic orbitals. The antibonding state can be given by $1s\sigma^*$, star representing higher energy. In the case of hydrogen molecule (homo nuclear diatomic molecule), the number of electrons is two.

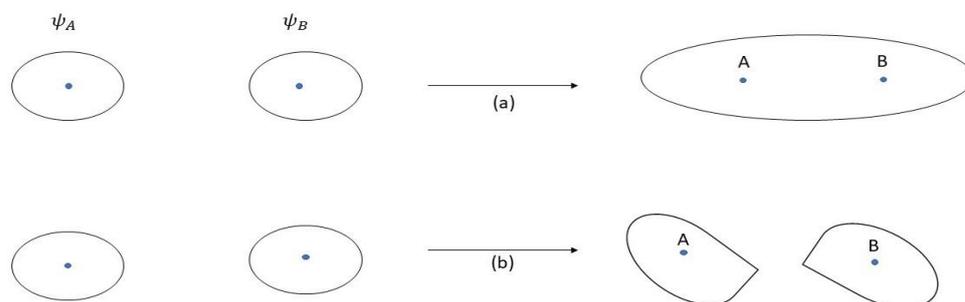


Fig.1.3 Combination of $1s$ orbitals with their contour of electron probability density forming a) bonding orbitals and b) antibonding orbital.

The MO $1s\sigma$ is formed from $2H(1s)$ atomic orbitals. As both the electrons are in the lowest bonding molecular orbital, the two electron bond of hydrogen molecule is stronger than that of a hydrogen molecule ion (H_2^+).

1.5 Directed bonds:

Why H_2O is angular, CH_4 is tetrahedral, C_2H_4 is planar etc? These questions can be answered by the application of VB theory. The localized covalent bonds, and the criterion of maximum overlap of atomic orbitals can account for the bond directions; hence the theory is also known as theory of “directed bonds”. For understanding this, one has to look at the directional characteristics of the orbitals used for bonding. The distribution of charge densities of electron is geometric in character. The s orbitals are spherically symmetrical, whereas the three p orbitals lie on the three mutually perpendicular axes with the nucleus at the centre (Fig.1.4). Being spherically symmetrical, s orbitals overlap to the same extent in all directions, whereas in the case of a p orbital the electron density is greatest along an axis, and so it overlaps to the maximum extent if the bond is formed in this direction. To understand the geometry of a molecule in simplest terms one has to look at the atomic orbitals of the central atom and see their orientations in space

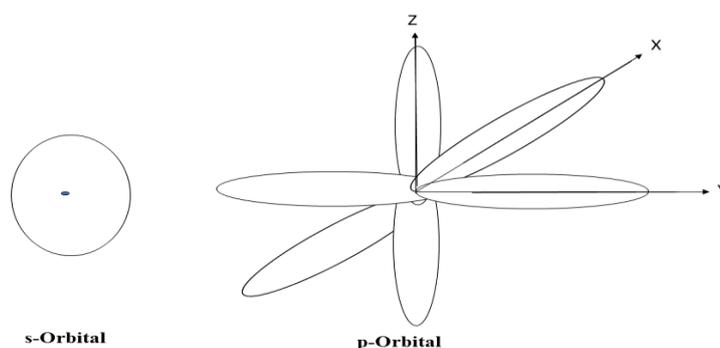


Fig.1.4 Shape of atomic orbitals s and p

For bond formation, the atoms to be bonded must approach each other along directions that lead to maximum overlap of orbitals in each bond. For example, the oxygen atom has the electronic configuration $1s^2 2s^2 2p_x 2p_y 2p_z$, which shows that there are two unpaired electrons in orbitals which are at right angles to one another. When combination with hydrogen occurs, these unpaired electrons in p_y and p_z orbitals pair up with 1s electrons of hydrogen atoms, and since p_y and p_z are at right angles to each other the resulting structure (Fig.1.5) should have two O-H bonds at 90° to each other.

However, the actual value is 104.5° . This increase has been attributed to mutual repulsion between the H atoms since the bonds are not ideally covalent but possess a partial ionic character, making the hydrogen atoms somewhat positive. Similarly, in NH_3 , N atom ($1s^2 2s^2 2p_x 2p_y 2p_z$) could form three mutually perpendicular N-H bonds (Actual value is 107°)

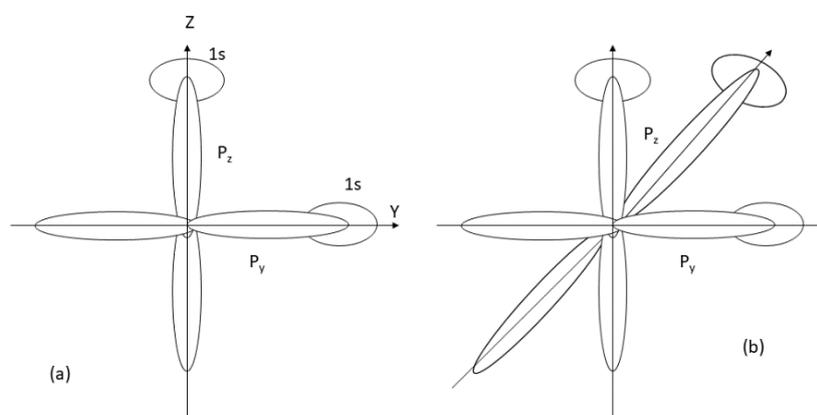


Fig.1.5 Formation of (a) water molecule and (b) ammonia molecule

1.6 Hybridization:

The concept of directed valence could explain bond angles only in certain molecules. It failed in large number of cases especially with carbon compounds. The electronic configuration of the normal state of carbon atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$.

As the lobes of the two valence electrons are perpendicular, one may expect the carbon atom to form two bonds at right angles to each other. However, in a molecule like CH_4 it is found to form four equivalent orbitals whose lobes are directed towards the corners of a regular tetrahedron. This is possible only when the 2s orbital must be promoted to the p level, thus giving the configuration $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.

The four orbitals available now for bonding will not be equivalent. However, if there is mixing of the energy of the 2s and 2p orbitals, four orbitals of the same shape and energy is possible. The general phenomenon of

such combination or mixing of pure orbitals is termed as hybridization and the resulting mixed orbitals are called hybrid orbitals or simply hybrids. There are three types of hybrid orbitals namely sp , sp^2 and sp^3 , (i.e.) those formed by combination of an s-orbital with one, two and three p-orbitals respectively. The important consideration is that the hybrid orbitals are not only orthogonal but also equivalent, which means that a symmetry operation of the molecule can transform one hybrid orbitals into another. The hybrid orbitals can form equivalent bonds.

Sp Hybrids

The simplest common type of hybridization is the sp hybridization. It has been deduced from wave mechanical treatment that a linear combination of s and p wavefunctions (or orbitals) in suitable proportions results in strong hybrid sp wavefunction or bond orbital, which is considerably stronger than both s and p orbitals.

The combination of an s and p orbital, giving two hybrid orbitals ϕ_1 and ϕ_2 may be expressed as

$$\phi_1 = a_1\psi(s) + b_1\psi(p) \text{ -----(1.13)}$$

$$\phi_2 = a_2\psi(s) + b_2\psi(p) \text{ -----(1.14)}$$

The values of the linear combination coefficients a_1, b_1, a_2, b_2 may be determined from the following considerations: (i) ϕ_1 and ϕ_2 are normalized i.e., $\int \phi_1^2 dv = 1$ and $\int \phi_2^2 dv = 1$, (ii) ϕ_1 and ϕ_2 are orthogonal $\int \phi_1 \phi_2 dv = 0$ and (iii) ϕ_1 and ϕ_2 are equivalent.

By (i)

$$a_1^2 + a_2^2 = 1 \text{ -----(1.15)}$$

$$a_1^2 + a_2^2 = 1 \text{ -----(1.16)}$$

And by (ii)

$$a_1 a_2 + b_1 b_2 = 0 \text{ -----(1.17)}$$

since the s-orbital is spherically symmetrical, and the two hybrid orbitals ϕ_1 and ϕ_2 are equivalent, the share of s functions is equal in both ϕ_1 and ϕ_2 i.e.,

$$a_1^2 = a_2^2 = 1/2 \text{ or } a_1 = a_2 = 1/\sqrt{2}$$

Then from (1.15)

$$b_1^2 = 1/2 \text{ or } b_1 = 1/\sqrt{2}$$

So that

$$\varphi_1 = 1/\sqrt{2}[\psi(s) - \psi(p)] \text{-----(1.18)}$$

Further from (1.17)

$$\frac{1}{2} + 1/\sqrt{2} b_2 = 0 \text{ or } b_2 = -1/\sqrt{2} \text{----- (1.19)}$$

Therefore

$$\varphi_2 = 1/\sqrt{2}[\psi(s) - \psi(p)] \text{-----(1.20)}$$

The directional characteristics of φ_1 and φ_2 are determined only with respect to their angular part. Using the normalized angular functions for 2s and 2p orbitals, and choosing $2P_x$, for example, as the 2p orbital, we get two sp hybrid orbitals as,

$$\varphi_1 = 1/\sqrt{2} [1/\sqrt{4\pi} + \sqrt{\frac{3}{4\pi}} \cos\theta]$$

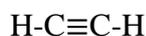
$$\varphi_2 = 1/\sqrt{2} [1/\sqrt{4\pi} - \sqrt{\frac{3}{4\pi}} \cos\theta]$$

Taking out the factor $1/\sqrt{4\pi}$, we get the functions which determine the directions of the two hybrid orbitals,

$$f_1 = 1/\sqrt{2}(1 + \sqrt{3}\cos\theta) \text{-----(1.21)}$$

$$f_2 = 1/\sqrt{2}(1 - \sqrt{3}\cos\theta) \text{-----(1.22)}$$

These functions f_1 and f_2 are maximum for $\theta=0$ (in the +z direction) and $\theta=\pi$ (in the -z direction) respectively. The value of maximum in either case is $\frac{1+\sqrt{3}}{\sqrt{2}} = 1.932$ which is greater than for the 2s pure orbitals for which $f=1$ or a 2p orbital for the 2s pure orbitals for which $f=\sqrt{3} = 1.732$. This shows that the sp orbital is stronger than pure s and p atomic orbitals. Since the simple P_z orbital is directed along +z and -z directions, an sp hybrid orbital will be directed only towards either +z or -z, making the angle between the two being 180° . The linear structure of acetylene may be accounted as the result of sp hybridization.



Sp2 hybridization:

Suppose the initial functions involved in sp2 hybridization are ones, one P_x and one P_y , then, the three sp2 hybrid orbitals formed due to the combination of an s orbital with two p orbitals can be expressed as

$$\varphi_1 = a_1\psi(s) + b_1\psi(p_x) + c_1\psi(p_y) \text{-----(1.23)}$$

$$\varphi_2 = a_2\psi(s) + b_2\psi(p_x) + c_2\psi(p_y) \text{-----(1.24)}$$

$$\varphi_3 = a_3\psi(s) + b_3\psi(p_x) + c_3\psi(p_y) \text{-----(1.25)}$$

Notes

The co-efficients a_n , b_n and c_n where $n=1,2,3$ can be determined as follows:

Since $\psi(s)$ has spherical symmetry and the three hybrids are equivalent, we can write

$$a_1^2 = a_2^2 = a_3^2 = 1/3 \text{ or } a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

If we assume ψ_1 to assigned x direction, then in (1.23), there will be no contribution from p_y i.e., $c_1=0$.

According to the normalization condition and taking $c_1=0$, we have

$$a_1^2 + b_1^2 = 1$$

$$1/3 + b_1^2 = 1$$

$$\text{Or } b_1 = \sqrt{\frac{2}{3}}$$

Thus,

$$\psi_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x \text{ -----(1.26)}$$

By orthogonality condition between ψ_1 and ψ_2 , we write

$$a_1a_2 + b_1b_2 + c_1c_2 = 0$$

$$\frac{1}{3} + \sqrt{\frac{2}{3}}b_2 = 0 \text{ or } b_2 = -\frac{1}{\sqrt{6}}$$

And by normalization of ψ_2

$$a_2^2 = b_2^2 = c_2^2 = 1$$

$$\frac{1}{3} + \frac{1}{6} + c_2^2 = 1 \text{ or } c_2 = \frac{1}{\sqrt{2}}$$

Thus

$$\psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

Similarly, by orthogonality of ψ_1 and ψ_3 .

$$a_1a_3 + b_1b_3 + c_1c_3 = 0$$

$$\text{or } 1/3 + 2/3 b_3 = 0 \text{ or } b_3 = -\frac{1}{\sqrt{6}}$$

and by orthogonality of ψ_2 and ψ_3 ,

$$a_2a_3 + b_2b_3 + c_2c_3 = 0$$

$$\text{or } \frac{1}{3} + \frac{1}{6} + \frac{1}{\sqrt{2}} c_3 = 0 \text{ or } c_3 = -\frac{1}{\sqrt{2}}$$

Thus,

$$\varphi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_z$$

The directional properties of these hybrid orbitals and their bonding strength can be determined by substituting

$$s=1$$

$$P_x = \sqrt{3} \sin\theta \sin\varphi$$

$$P_y = \sqrt{3} \sin\theta \sin\varphi$$

In 1.26, 1.27 and 1.28

The three functions defining the directional properties of the hybrid orbitals are accordingly,

$$f_1 = \frac{1}{\sqrt{3}} + \sqrt{2} \sin\theta \cos\varphi \text{ -----(1.29)}$$

$$f_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \sin\theta \cos\varphi + \sqrt{\frac{3}{2}} \sin\theta \sin\varphi \text{ -----(1.30)}$$

$$f_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \sin\theta \cos\varphi - \sqrt{\frac{3}{2}} \sin\theta \sin\varphi \text{ -----(1.31)}$$

If we consider the hybrid orbitals on xy plane, for which $\theta=90^\circ$ or $\sin\theta=1$, then

$$f_1 = \frac{1}{\sqrt{3}} + \sqrt{2} \cos\varphi \text{ -----(1.32)}$$

$$f_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos\varphi + \sqrt{\frac{3}{2}} \sin\varphi \text{ -----(1.33)}$$

$$f_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos\varphi - \sqrt{\frac{3}{2}} \sin\varphi \text{ -----(1.34)}$$

The maximum value of f_1 in (1.32) will be

$$f_1 = \frac{1}{\sqrt{3}} + \sqrt{2} = 1.992$$

which points towards x axis (i.e, $\varphi=0$).

The direction for f_2 can be determined as follows:

Let, $\cos\varphi=x$, then (1.33) can be rewritten as,

$$f_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}x + \sqrt{\frac{3}{2}}(1-x^2)^{1/2}$$

The direction for maximum f_2 can be found by differentiating the above equation with respect to x and equating it to zero.

$$\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}x + \sqrt{\frac{3}{2}}(1-x^2)^{1/2} = 0$$

$$\text{Or } \sqrt{\frac{3}{2}} \frac{\cos\phi}{\sin\phi} = -\frac{1}{\sqrt{2}}$$

$$\text{Or } \tan\phi = -\sqrt{3} \quad \text{or } \phi = 120^\circ$$

Therefore, the value of the maximum will be

$$\begin{aligned} f_2 &= \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \times \left(-\frac{1}{2}\right) + \sqrt{\frac{3}{2}} \times \frac{\sqrt{3}}{2} \\ &= \frac{1}{\sqrt{3}} + \frac{1}{2\sqrt{2}} + \frac{3}{2\sqrt{2}} = 1.992 \end{aligned}$$

Thus, a hybrid f_2 equivalent to f_1 is found to be at an angle 120° with respect to the latter.

It can be derived in the similar way for f_2 to have the same value i.e., 1.992 when $\theta=90^\circ$ and $\phi=240^\circ$. We, thus have three equivalent sp^2 hybrid orbitals that form angles of 120° with each other in the xy -plane. Such a hybridization can be found in BF_3 planar molecule. It is also found that the strength of the sp^2 hybrid orbitals (1.992) exceeds not only the strength of the pure s and p orbitals but also that of sp hybrid orbitals.

Sp3 hybridization

One s and three p orbitals will lead to a set of four sp^3 hybrid orbitals. The four hybrid functions will be

$$\psi_i = a_i\psi(s) + b_i\psi(P_x) + c_i\psi(P_y) + d_i\psi(P_z) \text{-----(1.35)}$$

where $i=1,2,3,4$

Applying the condition of normalization and orthogonality, we obtain,

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1 \quad \text{-----(1.36)}$$

And

$$a_i a_k + b_i b_k + c_i c_k + d_i d_k = 0 \text{-----(1.37)}$$

Where i and k may be 1,2,3 Or 4, but $i \neq k$

Since the four hybrid orbitals formed are equivalent, the single s orbital divides equally among the four hybrids, so that

$$a_1^2 = a_2^2 = a_3^2 = a_4^2 = \frac{1}{4}$$

Or

$$a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

Then the conditions (1.36 and 1.37) lead to,

$$b_i^2 + c_i^2 + d_i^2 = \frac{3}{4} \text{-----(1.38)}$$

$$b_i b_k + c_i c_k + d_i d_k = -\frac{1}{4} \text{-----(1.39)}$$

The first of the four hybrids can be chosen to lie in any direction, let it be along the x-axis. Along this direction,

$$c_1 + d_1 = 0 \text{ so that } b_1 = \frac{\sqrt{3}}{2}$$

Thus,

$$\varphi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x \text{-----(1.40)}$$

With respect to φ_1 , the directions of φ_2 , φ_3 and φ_4 have to be determined. Let us assumed that the plane constituted by the axes of φ_1 and φ_2 be the xz-plane. The co-efficient of φ_2 are determined as follows:

a_2 is already known to be $\frac{1}{2}$.

Since along xz-plane, the orbital p_y has no contribution, $c_2 = 0$.

By (1.39) $b_2 = -\frac{1}{2\sqrt{3}}$ and by (1.38) $d_2 = \sqrt{\frac{2}{3}}$

Thus,

$$\varphi_2 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \sqrt{\frac{2}{3}}p_z \text{-----(1.41)}$$

In view of the orthogonality of φ_1 and φ_3 (1.39) leads to

$$b_3 = -\frac{1}{2\sqrt{3}} \theta \quad c_1 = d_1 = 0$$

and because of orthogonality of φ_2 and φ_3

$$d_3 = -\frac{1}{\sqrt{6}}$$

Then, equation (1.38) leads to

$$c_3 = \frac{1}{\sqrt{2}}$$

Thus,

Notes

$$\varphi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{6}}p_z \text{-----(1.42)}$$

Similarly, by the orthogonality relations of φ_1 and φ_4 , φ_2 and φ_4 , φ_3 and φ_4 , the coefficients b_4 , d_4 and c_4 can be derived as,

$$b_4 = -\frac{1}{2\sqrt{3}}, c_4 = -\frac{1}{\sqrt{2}}, d_4 = -\frac{1}{\sqrt{6}} \text{ so that}$$

$$\varphi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{6}}p_z \text{-----(1.43)}$$

Thus, we have found the analytic expression for the four hybrid orbitals φ_1 to φ_4 . But these are not unique, because we have chosen arbitrarily the orientation of our set of coordinate axes in space, and if the choice is different. We would have got different but mathematically equivalent hybrid wave functions. But the relative directions and the maximum values of the φ_1 , may be derived as follows:

$$\begin{aligned} \varphi_1 &= \frac{1}{2} \frac{1}{\sqrt{4\pi}} + \frac{\sqrt{3}}{2} \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi \\ &= -\frac{1}{\sqrt{4\pi}} \left[\frac{1}{2} + \frac{3}{2} \sin\theta \cos\varphi \right] \end{aligned}$$

The function determining the direction of the hybrid orbital can be given by,

$$f_1 = \frac{1}{2} + \frac{3}{2} \sin\theta \cos\varphi$$

Along x-axis, $\varphi=0$ and $\theta=90^\circ$.

Therefore, the maximum value of $f_1=2.0$.

With respect to φ_1 along the x-axis, the direction of φ_2 which lies in xz plane can be derived as follows:

The equation 1.41 in terms of the function f, is given be

$$f_2 = \frac{1}{2} - \frac{1}{2\sqrt{3}}\sqrt{3} \sin\theta \cos\varphi + \sqrt{\frac{2}{3}}\sqrt{3} \cos\theta$$

In the xz plane $\varphi=0$ or 180° . The value of $\varphi=0$ determines the position of the p_x orbital, so $\varphi=180^\circ$ will determine its negative lobe which contributes to φ_2 . Then,

$$f_2 = \frac{1}{2} + \frac{1}{2} \sin\theta + \sqrt{2} \cos\theta$$

Differentiating the above with respect to θ and equating it to zero, we get

$$\tan\theta = \frac{1}{2\sqrt{2}} \text{ or } \theta = 19^\circ 28'$$

Therefore, the direction of the orbital ϕ_2 lying in the xz-plane is such that it makes an angle of $19^\circ 28'$ with z-axis or an angle of $90 + 19^\circ 28' = 109^\circ 28'$ with ϕ_1

Using this value of θ in (1.45), we get

$$f_1 = \frac{1}{2} + \frac{1}{2} \times \frac{1}{3} + \sqrt{2} \sqrt{\frac{8}{9}} = 2.0$$

Similarly, we can show that ϕ_3 and ϕ_4 to make angles of $109^\circ 28'$ with ϕ_1 and ϕ_2 and with each other and that all the four hybrid orbitals have the same maximum value (2.0). This angle corresponds to the tetrahedral angle. Accordingly, sp^3 hybridization leads to four equivalent tetrahedral oriented orbitals. If an atom uses sp^3 hybridized orbitals for forming bonds, those bonds will be directed towards the vertices of a tetrahedron with the atom at its centre. The typical example of tetrahedral bonding is CH_4 .

1.7 Let us sum up

- ❖ Valence theory dictated that molecules are formed by bringing together atoms complete with their electrons, which are allowed to interact with each other to form a chemical bond.
- ❖ Molecular orbital theory reveals that the orbitals are devised for the molecule as a whole, (i.e) by involving the nuclei of all the constituent atoms separated by fixed equilibrium distance so that the molecular orbitals will become polycentric.
- ❖ The “directed bonds” explained that localized covalent bonds, and the criterion of maximum overlap of atomic orbitals can account for the bond directions.
- ❖ The combination or mixing of pure orbitals is termed as hybridization and the resulting mixed orbitals are called hybrid orbitals or simply hybrids. There are three types of hybrid orbitals namely sp , sp^2 and sp^3

1.8 Review questions:

1. When will a molecule be said to be stable?
2. What are two wave mechanicals approached to explain the construction of molecular wave functions?
3. Explain the valence bond theory to explain the Hydrogen molecule problem.
4. How the ionic structure can improve the explanation of VB approach?
5. What is “directed bonds”?
6. What is the basic difference between valence bond and molecular orbital approach?
7. How does the directed bond approach explain the formation of water molecule and NH_3 molecules?
8. What do you understand the hybridization? What is the need for that?

9. Show that sp hybrid orbital is stronger than pure s and p atomic orbitals.
10. Find the hybridization on the oxygen atom in H₂O, where the bond angle is 104.5°. What would have been the hybridization had H₂O been a linear molecule?
11. Explain the sp² hybridization by taking suitable example.

1.9 Further reading

1. Fundamentals of Molecular spectroscopy – Colin N.Banwell and Elaine M.McCash. Fourth edition Tata McGraw Hill Education pvt.Ltd.
2. Molecular Spectroscopy- Suresh Chandra Narosa Publisher.

UNIT II ROTATIONAL SPECTRA OF DIATOMIC MOLECULE

Rotational spectra of
diatomic molecule

Notes

Structure

- 2.1 Introduction
- 2.2 Objectives
- 2.3 Rotational energy of a diatomic molecule
- 2.4 Rigid and non-rigid rotators
- 2.5 isotopic substitution.
- 2.6 Summary
- 2.7 Review questions
- 2.8 Further readings

2.1 Introduction:

We know, spectroscopy is the study of interaction of electromagnetic radiations with the matter. The matter in any form consists of molecules which undergo rotation or vibration under excited condition. Absorption of electromagnetic radiation in the rotational spectrum of a molecule arises from the interaction of molecular dipole moment with the electromagnetic field.

The rotation of a molecule can be conveniently described in terms of rotational components about three mutually perpendicular directions through the centre of gravity, called the principal axes of rotation. Thus, a body or molecule has three principal moments of inertia, one about each axis, usually designated I_a , I_b and I_c . Molecules may be classified into four groups according to the relative values of their three principal moments of inertia.

2.2 Objectives:

Here, Rotational energy of diatomic molecule is discussed. Rigid and non-rigid rotators are deliberated and also isotopic substitution is discussed.

2.3. Rotational spectra:

We have seen that rotational energy, along with all other forms of molecular energy, is quantized: this means that a molecule cannot have any arbitrary amount of rotational energy (i.e. any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values- the so-called rotational energy levels- may in principle be calculated for any molecule by solving the Schrodinger equation for the system represented by the molecule. For simple molecules the mathematics involved is straightforward for tedious, while for complicated systems it is probably impossible without gross approximations. We shall not concern ourselves unduly with this, however, being content merely to accept the results of existing solutions and to point out where reasonable approximation may lead.

We shall consider each class of rotating molecules in turn, discussing the linear molecule in most detail, because much of its treatment can be directly extended to symmetrical and unsymmetrical molecules.

2.4 Diatomic molecule as a Rigid Rotator:

A diatomic molecule with atomic masses m_1 and m_2 is connected by means of a rigid bar (the bond) whose distance remains constant. If this molecule rotates about an axis perpendicular to its molecular axis and passing through the centre of gravity is defined as a rigid rotator. The two body problem can be reduced into a single body problem by introducing the concept of reduced mass μ where,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{-----(2.1)}$$

Now, we assume the single particle of mass μ with a constant distance r_e from its centre of mass to rotate in a spherically symmetrical potential field $V(r)$ whose value is a constant and can be set equal to zero in the wave equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(r)] \psi = 0 \text{-----(2.2)}$$

So that, the equation is reduced to

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(r)] \psi = 0 \text{-----(2.3)}$$

The solution of the Schrodinger's equation for the rigid rotator gives the energy eigen values as

$$E_J = \frac{\hbar^2}{2\mu r_e^2} J(J+1) \text{ Joules} \text{----- (2.4)}$$

J-rotational quantum number

Since spectroscopic transitions are usually measured in wave number units, it is common practice to quote the rotational energy in the units of cm^{-1} . The rotational term $F(J)$ is thus given by

$$F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \text{-----(2.5)}$$

Where $I = \mu r_e^2$, the moment of inertia

(OR)

$$F(J) = B J(J+1) \text{ cm}^{-1} \text{-----(2.6)}$$

Where $B = \frac{h}{8\pi^2 I c}$ in cm^{-1} is called the Rotational constant.

According to the equation (2.6), the separation between adjacent energy levels in the rigid rotator increases linearly with J, as shown in the

figure (2.1a). These energy levels are also called the rotational states of a molecule. The transition probability between rotational state i to j is determined by the transition moment,

$$\mu_{ij} = \int \psi_i^* M \psi_j d\tau \text{ -----(2.7)}$$

Where ψ_i and ψ_j are the wave functions of the rotational states i and j , and M is dipole moment operator. The transition moment given in (2.7) is non zero only if (i) the molecule has a permanent dipole moment and (ii) the transition is between adjacent rotational states specified by the rotational quantum number J , i.e., $\Delta J = \pm 1$ (plus sign for absorption and minus for emission).

Therefore, only if the molecule is asymmetric, there will be a permanent dipole moment and hence rotational spectrum be observed. So, only the hetero nuclear diatomic molecules (O_2 , N_2 etc.) do not exhibit the spectrum since they do not possess any permanent dipole moment.

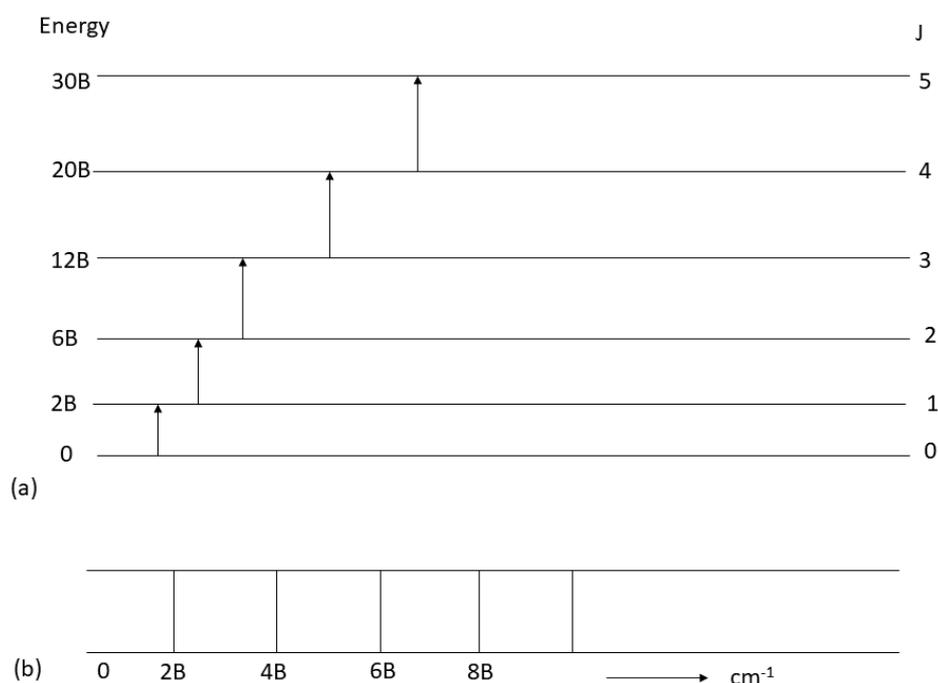


Fig.2.1 Rotational states with (a) allowed transitions and (b) the spectrum which arises from them.

The allowed rotational transitions produce a series of equally spaced spectral lines with separation $2B$ between adjacent lines, which is shown in Figure (2.1-b) as $F(J+1) - F(J) = 2B(J+1) \text{ cm}^{-1}$.

2.4.1 Non-rigid Rotator:

In the case of rigid rotator, it was found from the rotational spectrum that the rotational lines are of equal separation $2B \text{ cm}^{-1}$ between adjacent lines. But, experimentally, it is found that the separation between adjacent

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lines decreases steadily with increasing J. This observed decrease is only due to the decreased value of the rotational constant B. This shows that the bond length increases with J and we can understand that our assumption of a rigid bond is only an approximation. In fact, all bonds are elastic and the increase in length is due to the centrifugal force on the atoms of the fast-rotating molecule. This force tends to move the atoms apart and thereby increasing the bond length resulting in a reduced value of B.

Therefore, for a current treatment one has to use the complete Hamiltonian. The solution for the corresponding Schrodinger equation gives the following energy expression for the energy levels of the non-rigid rotator.

$$F_J(J) = B_J J(J+1) - D_J J^2 (J+1)^2 + \dots \quad (2.8)$$

$$J = 0, 1, 2, \dots$$

B_J is the rotational constant with respect to the vibrational level 'v' which is given by

$$B_J = B_e - \alpha_J (v + 1/2) + \dots \quad (2.9)$$

Where α_J is a small constant and B_e is the rotational constant at the equilibrium inter nuclear distance r_e .

D_v is the centrifugal distortion constant which is a small positive quantity.

In a given molecule, the effect of centrifugal distortion is to decrease the rotational energy (2.8) and found dominant for higher rotational states. The selection rule for the non-rigid rotator is again $\Delta J = \pm 1$. The fig 2.2 shows the lowering of rotational levels when passing from the rigid to non-rigid diatomic molecule. The spectra are also compared.

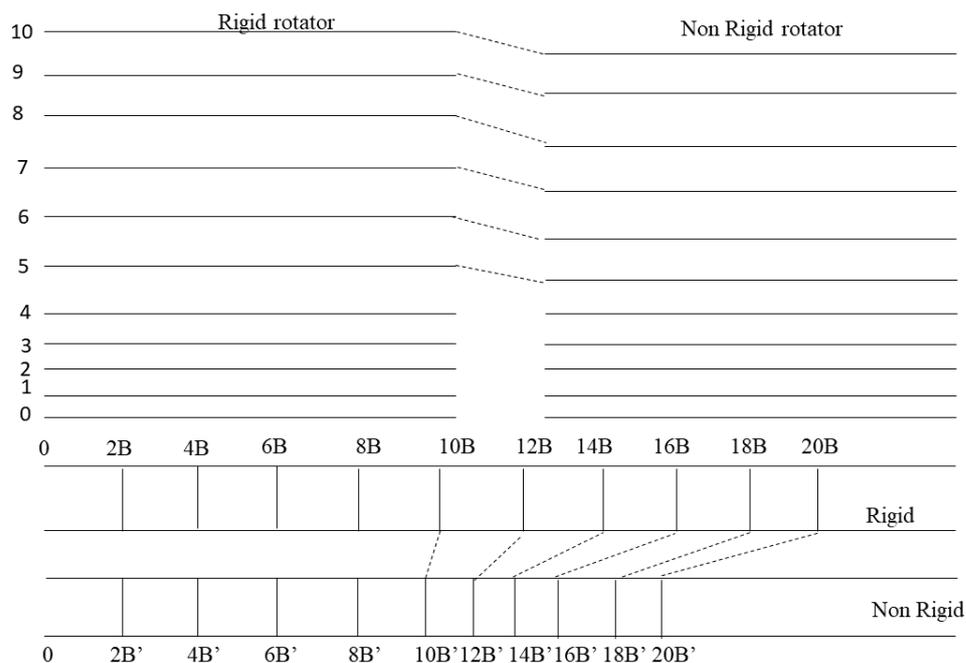


Fig.2.2 The change in the rotational levels of rigid and non-rigid rotator and the effect of their spectrum.

2.5 Isotope effect:

An atom when replaced by one of its isotope, the internuclear separation (bond) remains the same as the electron charge distribution does not change. However, due to the change in the mass of the nucleus, there will be a change in the moment of inertia, resulting in the change of its rotational constant of B, where

$$B' = \frac{h}{8\pi^2 I' C'} \quad \text{-----(2.10)}$$

Now,

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} \quad \text{-----(2.11)}$$

If the isotopic molecule has its reduced mass $\mu' > \mu$ of the original molecule, then $B > B'$. This change will reduce the separation between the energy levels and thereby the spectrum of the heavier species will show a smaller separation between the lines ($2B'$) than that of the lighter one ($2B$), as shown in fig.(2.3)

Measurement of the precise shift leads to the determination of atomic weight of the isotopes. From the intensity variation, an estimate of abundance of isotope can also be done.

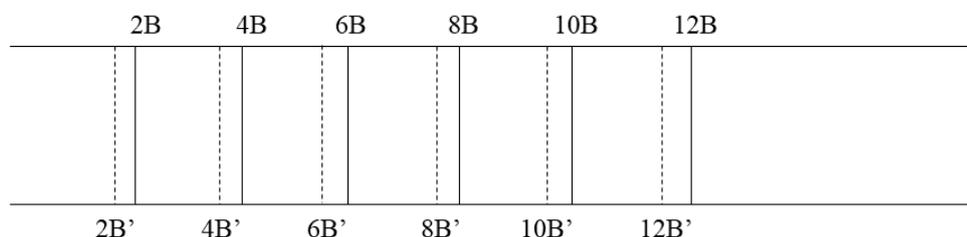


Fig.2.3 Rotational spectrum of a) diatomic molecule (continuous lines) and b) isotopically substituted diatomic molecule with heavier mass (dashed lines).

2.6 Summary

- ❖ The rotational energy is the one of the quantized molecular energy.
- ❖ A diatomic molecule with atomic masses m_1 and m_2 is connected by means of a rigid bar (the bond) whose distance remains constant. If this molecule rotates about an axis perpendicular to its molecular axis and passing through the centre of gravity is defined as a rigid rotator.
- ❖ The nonrigid rotator is found from the rotational spectrum that the rotational lines are of equal separation $2B \text{ cm}^{-1}$ between adjacent lines.
- ❖ An atom when replaced by one of its isotopes, the internuclear separation (bond) remains the same as the electron charge distribution does not change. However, due to the change.

Notes

2.7 Review questions:

1. Calculate the rotational energy of a diatomic molecule and discuss its spectra.
 2. What is the effect of isotopic substitution on the rotational spectra?
 3. Discuss in detail about the rigid rotator.
 4. Write a note on non-rigid rotator.
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2.8 Further Readings

1. Atomic and Molecular Spectroscopy M.C,Gupta, New Age Int.national Publishers.
2. Atomic and Molecular spectra and Lasers A.X.Saxena, CBS Publishers and distributors

UNIT III STARK EFFECT

Stark effect

Notes

Structure:

- 3.1 Introduction
- 3.2 Objectives
- 3.3 Stark effect
- 3.4 Its importance in microwave spectroscopy
- 3.5 Quadrupole hyperfine interaction
- 3.6 Let us sum up
- 3.7 Review questions
- 3.8 Further study

3.1 Introduction:

When the source of spectral lines is placed in an electric field. Some lines split into a number of components. This phenomenon is known as the Stark effect. Each level with the rotational quantum number J splits into $(2J+1)$ levels when the sample is subjected to electric field of several hundred volts/m.

3.2 Objectives:

In this chapter, Stark effect and its importance in microwave spectroscopy is discussed. Quadrupole hyperfine interaction is deliberated

3.3 Stark effect:

In spectroscopy, the effect of magnetic field and electric field have played very important roles in splitting the spectral lines. The interaction of molecular rotation with an external magnetic field is known as Zeeman effect, while the splitting of a rotational absorption line into various components due to the application of electric field of several hundred volts/m is known as Stark effect.

The fundamental property of Stark or Zeeman effect is that it removes the spatial degeneracy of the rotational energy levels. Stark effect is of fundamental importance in the analysis of rotational spectra.

Consider a molecule having an electric dipole moment μ placed in an electric field X . The component of the dipole moment of such a molecule along the angular momentum vector will be,

$$\mu_c = \frac{\mu K}{\sqrt{J(J+1)}} \text{-----(3.1)}$$

Except when $K=0$. The energy of such molecule in an electric field \bar{X} is found to be

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$$E_{JK} = \frac{\mu m_j K X}{J(J+1)} \text{-----(3.2)}$$

m_j is degeneracy.

With this correction, for symmetric tops the energy is given by,

$$E_{JKm} = B\hbar c J(J+1) + (A-B)\hbar c K^2 - \frac{\mu K m_j X}{J(J+1)} \text{-----(3.3)}$$

$$J=0,1,2,\dots\dots\dots K=0,\pm 1,\pm 2 \dots\dots \pm J, \quad m_j = 0, \pm 1, \pm 2 \dots\dots \pm J$$

The selection rule $\Delta J = +1$, $\Delta K = 0$ and $\Delta m_j = 0$ gives the first order correction $\Delta\nu^{(1)}$ to the transition frequency.

From the equation (3.2)

$$\Delta E^{(1)} = \frac{2\mu X K m_j}{J(J+1)(J+2)} \text{-----(3.4)}$$

Where, J is the rotational quantum number of the lower state.

$$\Delta\nu^{(1)} = \frac{\Delta E^{(1)}}{h} = 0.5035 \mu X \frac{2K m_j}{J(J+1)(J+2)} \text{ MHz} \text{-----(3.5)}$$

Here μ is expressed in Debyes and X in volts/cm. In the absence of the field a single line results for the $J=1, K=1 \rightarrow J=2, K=1$ transition. However, three lines are observed in the first order spectrum in Fig (3.1) whose frequencies can be easily obtained from equation (3.5)

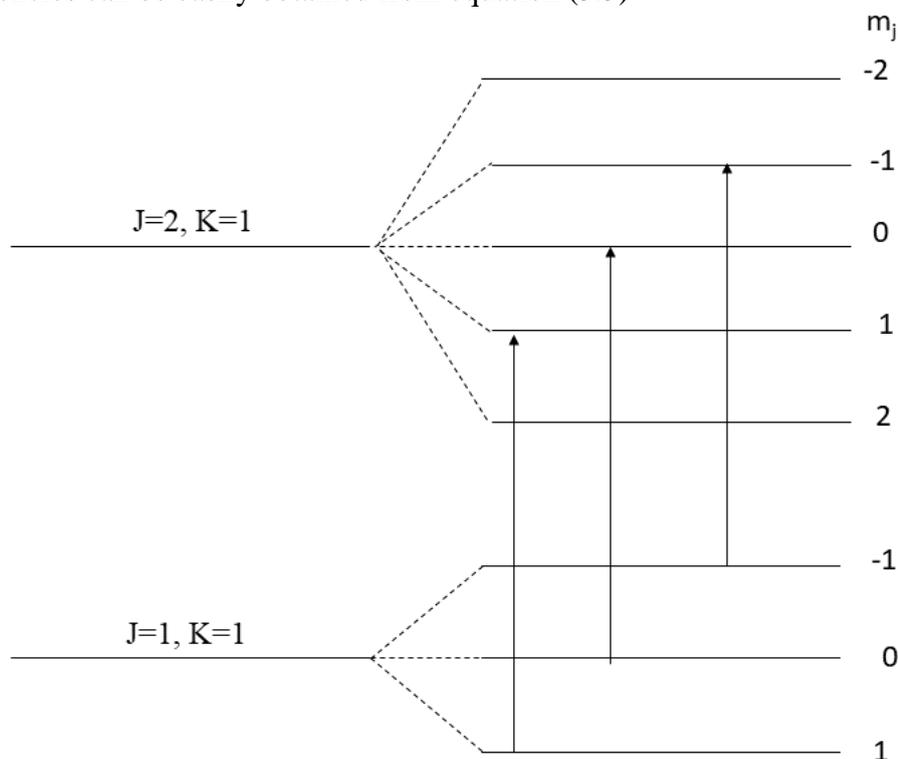


Fig.3.1 First order stark effect of a symmetric top molecule for $J=1, K=1 \rightarrow J=2, K=1$ transition.

Symmetric top molecules can have a dipole moment and degeneracy of the $\pm K$ levels and so can interact with the electric field, but possibly only when $K \neq 0$.

All linear molecules have their dipole moment vector always along the bond axis and consequently $K=0$. Thus, linear molecules and for $K=0$, the first order stark effect is not observed. Hence, the second stark effect must also be investigated for the completion purpose.

The importance of the studies on stark effect are

- (i) The stark pattern, on high resolution will reveal the J value involved in the transition.
- (ii) The lines of the various branches (P,Q,R) of rotational fine structure can be distinguished from the analysis of intensity distribution of the stark lines.
- (iii) A measurement of the stark components gives a method for the accurate determination of electric dipole moment, which is one of the most important electronic properties of a molecule. The classical way of measuring the dipole moment gives only the average value of the dipole moments of the collection of molecules in all the vibrational states, whereas, the microwave stark effect helps measuring the dipole moment of a molecule in a particular vibrational state. In addition, the microwave method gives some idea about the orientation of the magnetic dipole moment μ in the molecule.

3.4 its importance in Microwave spectroscopy

One of the most significant uses of microwave spectroscopy is in the determination of accurate dipole moments. When the electric field is applied, it interacts with the molecule dipole moment. According to classical physics, the energy of interaction is given by μE . Since both are vector quantities. If θ is the angle between the two vectors, the energy of interactions can be written as $-\mu E \cos\theta$, where μ and E are the lengths of the vectors which represents the dipole moment and the field, respectively. Another way of thinking about this is that the interaction depends on the projection of μ along the direction of the electric field.

For linear molecules, the angular momentum vector is always perpendicular to the internuclear axis and hence to the dipole moment. Thus, rotation average the dipole completely to zero, and hence there is no first order stark effect. There is, however, a second order Stark effect in the presence of strong electric fields,

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where the splitting of the energy levels goes as the square of the electric field strength.

The energy correction for the second order Stark effect of linear molecules is

$$E_{stark}^{(2)} = \frac{\mu^2 E^2 [J(J+1) - 3m_j^2]}{2hc\tilde{B}J(J+1)(2J+1)(2J+3)} \quad \text{for } J \neq 0$$

$$= -\frac{\mu^2 E^2}{6h\tilde{B}c} \quad \text{for } J \neq 0 \quad \dots\dots\dots(3.6)$$

The points to be noted are:

- (1) The splitting varies as E^2 and is hence second order.
- (2) The splitting also depends on the square of M_j , so the levels are split into $J+1$ energy level.
- (3) The splitting depends on the square of the dipole moment and hence accurate dipole moments can be determined using this technique. However, since only the square of the dipole moment can be determined with accuracy, the sign is ambiguous. Whereas in most cases it is fairly straight forward to assign the negative end of the molecule to the more electronegative atom, this is not always true. For example, the molecule CO has an extremely small dipole moment of 0.112 D. Accurate quantum mechanical calculations reveal that the carbon is the negatively charged end.

For symmetric top molecules, there is a first order Stark effect given by

$$E_{Stark}^{(1)} = -\mu E \frac{KM_J}{J(J+1)} \dots\dots\dots(3.7)$$

and this relation allows the determination of accurate dipole moments of these molecules.

3.5 Quadrupole hyperfine interaction:

When the spin of one of the nucleus in a molecule is greater than $\frac{1}{2}$, the molecule is said to possess an electric quadrupole moment eQ , and from such a molecule quadrupole hyperfine spectrum is observed. These hyperfine spectrum is observed. Thus hyperfine structures in rotational spectra arise through a coupling of nuclear spin \bar{I} with the rotational vector \bar{J} . The interaction energies of J and I and hence the rate of precession depend on the orientation angles as well as upon the coupling constant.

For symmetric rotor, if the nucleus of interest lies on the molecular symmetry axis, the first order perturbation theory gives the following correction to the rotational energy,

$$E_Q = E_{jK}^{(j)} - \frac{e^2 q Q [3K^2 J(J+1) - 1]}{2I(2I-1)(2J-1)(2J+3)} \left[\frac{3}{4} C(C+1) - I(I+1)J(J+1) \right] \text{-----(3.6)}$$

Where,

$$C = F(F+1) - I(I+1) - J(J+1) \text{----- (3.7)}$$

F=I+J, is the total angular momentum quantum number, which takes the values

$$(I+J), (I+J-1), \dots, |I-J| \text{-----(3.8)}$$

The quantity $e^2 q Q$ is usually referred to as the quadrupole coupling constant.

As an example, consider a prolate symmetric rotor having a nuclear spin $I=3/2$ along the molecular symmetry axis. For $J=0$, $K=0$, F can have the only value of $3/2$. For $J=1$, K can have the values $0, \pm 1$ and $F=1/2, 3/2$ and $5/2$. Fig (3.2) gives the possible values of J,K, F and the energy levels based on equation (3.6). The selection rules

$$\Delta J = \pm 1, \Delta K = 0 \text{ and } \Delta F = 0, \pm 1 \text{-----(3.9)}$$

Without the quadrupole interaction, we know, the $J=0 \rightarrow J=1$ transition with $\Delta K = 0$ will give a line at $2B$. With quadrupole interaction, in the place of the single line we have three lines with frequencies.

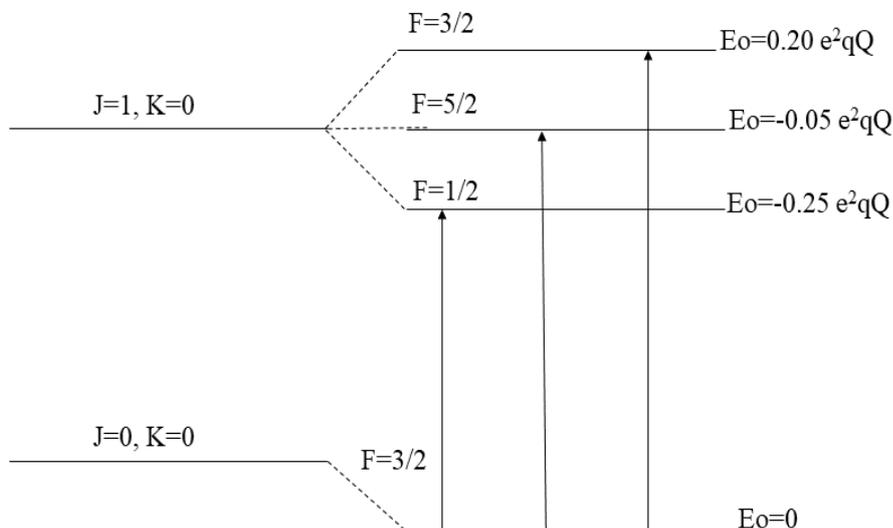


Fig.3.2 First order correction to rotational energy due to quadrupole hyperfine interaction.

$$\begin{aligned} \nu_1 &= 2B - 0.25 e^2 q Q \\ \nu_2 &= 2B - 0.05 e^2 q Q \\ \nu_3 &= 2B + 0.20 e^2 q Q \end{aligned} \quad \} \text{-----(3.10)}$$

Transition between higher J states can also be studied but becomes more complex.

Stark effect

Notes

The analysis of the quadrupole hyperfine structure gives very valuable information regarding electron distribution in molecules.

3.5 Let us sum up:

- ❖ The splitting of a rotational absorption line into various components due to the application of electric field is known as Stark effect.
- ❖ A measurement of the stark components gives a method for the accurate determination of electric dipole moment, which is one of the most important electronic properties of a molecule.
- ❖ When the spin of one of the nuclei in a molecule is greater than $\frac{1}{2}$, the molecule is said to possess an electric quadrupole moment eQ , and from such a molecule quadrupole hyperfine spectrum is observed.

3.6 Review questions:

1. What is Stark effect? Discuss the study of the first order Stark effect for the study of the symmetric top molecules.
2. Give the importance of Studies on Stark effect.
3. Give a brief account on Quadrupole hyperfine interaction.
4. Determine the dipole moment of the given molecule using microwave spectroscopy.

3.7 Further Readings

1. Fundamentals of Molecular spectroscopy – Colin N.Banwell and Elaine M.McCash. Fourth edition Tata McGraw Hill Education pvt.Ltd.
2. Atomic and Molecular spectroscopy M C Gupta, New Age Int.national Publishers.

UNIT IV ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

Rotational spectra of poly
atomic molecules

Notes

Structure:

- 4.1 Introduction
- 4.2 Objectives
- 4.3 Rotational spectra of polyatomic molecules
- 4.4 Pure rotational Raman spectra
- 4.5 Diatomic linear molecule
- 4.6 Symmetric top molecules.
- 4.7 Summary
- 4.8 Review questions
- 4.9 Further readings

4.1 Introduction:

Unlike atoms, a molecule can rotate about an axis passing through its Centre of gravity. Likewise, the electronic energy, rotational energy of a molecule also is quantized. In this chapter, we shall discuss about the rotational motion of molecules. Rotation of a three dimensional body(molecule) can be described in terms of three principal moments of inertia, I_a , I_b , I_c ($I_a \leq I_b \leq I_c$), about the three inertial axes a, b, c, passing through the Centre of mass. Based on the principal moments of inertia, the molecules are classified into four categories (i) Linear molecules, (ii) Spherical top molecules (iii) Symmetric top molecules and (iv) Asymmetric top molecules.

4.2 Objectives

Here, Rotational spectra of polyatomic molecules is discussed. Pure rotational Raman spectra and diatomic linear molecule is deliberated. Symmetric top molecule is also discussed.

4.3 Rotational spectra of polyatomic molecules:

Linear molecules

In this case, we consider molecules in which all the atoms lie on a straight line. Since for a linear molecule, we write, $I_a=0$ and $I_b=I_c$, it behaves almost like a diatomic molecule and is governed by the similar equation given in equ. 2.8. In fact, the whole of the discussion on diatomic molecule applies equally to all linear molecules but with some changes which are,

- (i) The moment of inertia for the end-to-end rotation of the linear molecule will be considerably greater than that of the diatomic molecules and hence with smaller B values. Therefore, the spectral lines will be more closely spaced.

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- (ii) In order that the molecule should possess a permanent dipole moment, only molecules of OCS type are active while the molecules of OCO (i.e CO₂) is inactive.
- (iii) From the spectrum, the only important information we get regarding the molecule is its moment of inertia. In the case of triatomic molecules, there will be two bond lengths, which can be determined with expression for the moment of inertia for the end over end rotation of such molecules. But two unknown cannot be determined with a single equation, and so the second equation is arrived by taking the isotropic molecule.

Let us consider an OCS molecule, in which the atoms are at distances r₀, r_c and r_s respectively from the centre of gravity.

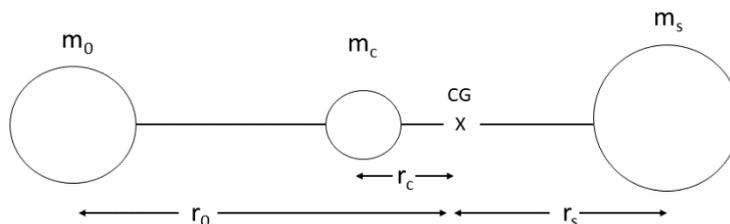


Fig.4.1 centre of gravity of OCS molecule

Taking the conservation of moments, we have,

$$m_0 r_0 + m_c r_c = m_s r_s \text{ ----- (4.1)}$$

The moment of inertia is:

$$I = m_0 r_0^2 + m_c r_c^2 + m_s r_s^2 \text{ ----- (4.2)}$$

From the figure we see,

$$R_0 = r_{c0} + r_c \text{ and } r_s = r_{cs} + r_c \text{ ----- (4.3)}$$

R_{c0} and r_{cs} are the two bond lengths in the molecule which are of our interest in determination. Substituting (4.3) in (4.1) we get,

$$(m_c + m_0 + m_s) r_c = m_s r_{cs} + m_0 r_{c0} \text{ (or)}$$

$$M r_c = m_s r_{cs} - m_0 r_{c0} \text{(4.4)}$$

Where, M is the total mass of the molecule. i.e., m_c+m₀+m_s.

Substituting (4.4) in the equation for moment of inertia (4.3) we get

$$I = m_0 (r_{c0} + r_c)^2 + m_c r_c^2 + m_s (r_{cs} + r_c)^2 \text{ -----(4.5)}$$

Expanding and rewriting we get,

$$I = M r_c^2 + 2 r_c (m_0 r_{c0} - m_s r_{cs}) + m_0 r_{c0}^2 + m_s r_{cs}^2 \text{ ----- (4.6)}$$

Substituting for r_c from equation (4.4) we get finally the moment of inertia in terms of r_{c0} and r_{cs} as,

$$I = m_0 r_{c0}^2 + m_s r_{cs}^2 - \frac{(m_0 r_{c0} - m_s r_{cs})^2}{M} \text{ -----(4.7)}$$

Considering an isotropic molecule with OCS, we write m'_o for m_o wherever it comes, so that

$$I' = m_o' r_{c0}^2 + m_s r_{cs}^2 - \frac{(m_o' r_{c0} - m_s r_{cs})^2}{M'} \text{ -----(4.8)}$$

We know already that the isotopic substitution, will only change the mass and the bond lengths will remain unaltered. By finding the values of I and I' experimentally, the bond distances r_{c0} and r_{cs} can be found by solving (4.7) and (4.8).

So, from rotational spectrum of any linear molecules, the ionic bonding distances can be accurately measured.

4.4 Pure Rotational Raman spectra:

Introduction:

More than the absorption and emission of photons, the scattering of photon also contributes a lot in the molecular spectroscopy. When the photons collide on a solid or collection of molecules, they may be mostly scattered elastically (called Rayleigh scattering) but a few undergo inelastic scattering also. These photons which are inelastically scattered have frequencies, lower or higher than its incident frequency. This was experimentally observed in 1928 by Sir C.V. Raman and is referred to as Raman scattering. The lines on the lower and higher frequency side of Rayleigh lines are called stokes and anti-stokes lines respectively. The frequency shift observed by the photons matches the vibrational or rotational energies of the molecule, and so it is comparable with the molecular energies. The spectrum observed with the modified lines in addition to the incident line is called Raman spectrum.

In order to be Raman active, a molecular vibration or rotation must cause some change in a component of molecular polarizability.

Linear molecules

The rotational energy levels of linear molecules have already been stated eq. (2.8):

$$F(J)=BJ(J+1)-DJ^2(J+1)^2\text{ cm}^{-1}\dots\dots\dots(4.9)$$

$$J=0,1,2,\dots\dots$$

But, in Raman spectroscopy, the term involving D . the centrifugal distortion constant can be omitted so that we write,

$$F(J)=BJ(J+1)\text{ cm}^{-1}\text{-----}$$

(4.10)

A quantum mechanical treatment leads to the rotational selection rule

$$\Delta J=0, \pm 2\text{-----}$$

(4.11)

Which is in contrast with the corresponding selection rule in the case of microwave spectroscopy, $\Delta J=\pm 1$. The fact that in Raman work the rotational

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quantum number changes by two units rather than one, is connected with the symmetry of the polarizability ellipsoid (A three dimensional surface whose distance from the electrical centre of the molecule is proportional to $1/\sqrt{\alpha_i}$, where α_i is the polarizability along the line joining a point I on the ellipsoid with the electrical centre). During the end-over-end rotation, for a linear molecule, the ellipsoid presents the same appearance to the observer twice in every complete rotation.

$\Delta J=0$, is a trivial transition in which there is no change in rotational energy and hence Rayleigh scattering only. Also, $\Delta J=-2$ is ignored since always there is going to be transition only from $J_{upper} \rightarrow J_{lower}$.

Therefore, applying the selection rule $\Delta J= +2$ (s-branch), we have $J'=J+2$ and $J''=J$

$$\nu = F(J+2) - F(J) = B(4J+6) \text{ cm}^{-1} \text{ -----(4.13)}$$

$$J=0,1,2,\dots\dots\dots$$

Thus, if the molecule gains rotational energy from the photon during collision, we have a series of S-lines to the low wave number side of the exciting line (Stokes lines), while if the molecule loses energy to the photon the S-branch lines appear as the high wave number side of the exciting line, called anti-stoke's lines.

$$\nu_s = \nu_{ex} - B(4J+6) \rightarrow \text{Stoke's lines}$$

$$\nu_{As} = \nu_{ex} + B(4J+6) \rightarrow \text{Anti-stoke's lines} \text{ -----(4.14)}$$

The fig. (4.2) shows the allowed transitions and the rotational Raman spectrum of a linear molecule. The Raman shift of the first Stoke's and anti-Stoke's line from the exciting line is $6B \text{ cm}^{-1}$. The separation between successive lines on either side of the excited line is $4B \text{ cm}^{-1}$. Therefore, from the observed spectral lines we can find the rotational constant B and hence the interatomic distances of the linear molecules.

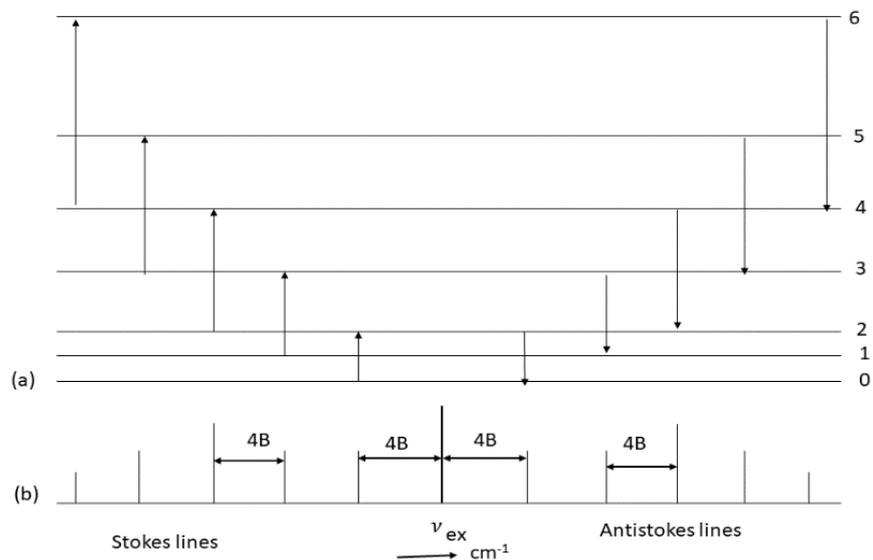


Fig.4.2 a) Allowed transitions between the rotational energy levels of a linear molecule b) predicted rotational Raman spectrum.

We have already seen that infrared and microwave spectrum can be exhibited only by heteronuclear diatomic molecules as they possess a permanent dipole moment which changes during the motion. The homonuclear diatomic molecules do not exhibit the IR and microwave spectrum. However, in the case of Raman spectroscopy, even homogeneous diatomic molecules can also be studied, since any rotation will change the polarizability.

Rotational spectra of poly atomic molecules

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4.5 Diatomic linear molecule:

In a linear polyatomic molecule, all the atoms are aligned along line called the molecular axis. A linear molecule consisting of n atoms has n-1 bonds between the adjacent atoms. A linear polyatomic molecule can also be treated in a manner similar to a diatomic molecule. For these molecules also we have $I_a=0, I_b=I_c$. The rotational motion is described by the rotational quantum number J and the selection rules for the radiation transitions are $\Delta J=\pm 1$. The wavenumber for the transition $J \rightarrow J+1$ is

$$\bar{\nu}_j = 2B(J+1) - 4D(J+1)^2 \text{ -----(4.15)}$$

Where $J=0,1,2, \dots$ Here, B and D are the rotational and distortional constants. The rotational constant B is expressed as

$$B = \frac{h}{8\pi^2 I_c} \text{ -----(4.16)}$$

Where I is the moment of inertia of the molecule about an axis perpendicular to the molecular axis and passing through the centre of mass.

4.6 Symmetric top molecules:

For symmetric top, as already seen, there are two independent moment of inertia ($I_b=I_c; I_a \neq 0$) and so there are two possible direction of rotation in which the molecules may interact with the electromagnetic radiation to absorb or emit energy. Consequent to the two moments of inertia, two quantum numbers are required to describe the rotation one for I_a and other for I_b or I_c .

For the rigid prolate symmetric top, the solution of the Schrodinger's equation gives the energy levels

$$E_{j,k} = \frac{\eta^2}{2\eta_b} J(J+1) + \left\{ \frac{\eta^2}{2I_a} - \frac{\eta^2}{2I_b} \right\} K^2 \text{ Joules -----(4.17)}$$

(or)

The rotational term may be

Notes

$$F(J) = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2 \text{ cm}^{-1} \text{ -----(4.18)}$$

For oblate type symmetric top molecules, it is

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

Where A, B and C are rotational constants given by

$$A = \frac{h}{8\pi^2 I_a C}; \quad B = \frac{h}{8\pi^2 I_b C}; \quad C = \frac{h}{8\pi^2 I_c C}$$

$$J = 0, 1, 2, 3, \dots \dots \dots K = 0, \pm 1, \pm 2, \pm 3, \dots \dots \pm J$$

The quantum number J represents that total angular momentum of the molecules while K represents only the projection of J upon the molecular symmetry axis and so K can never be greater than J. The positive and negative values of K correspond to the clockwise and anticlockwise rotation about the top axis. But since the energy depends on only K^2 values, it is immaterial whether the top spins clockwise or otherwise. Therefore, for all $K > 0$ the rotational energy levels are doubly degenerate.

The selection rule is

$$\Delta J = \pm 1 \text{ and } \Delta K = 0 \text{ -----(4.19)}$$

For a transition $F(J+1) \rightarrow F(J)$ the spectrum is given by

$$F(J+1) - F(J) = 2B(J+1) \text{ cm}^{-1} \text{ -----(4.20)}$$

From the above equation we understand the spectral lines resulting from the transition between the J-levels is independent of K and hence, rotational changes about the symmetry axis do not give rise to a rotational spectrum. The equation (4.20) shows that the spectrum is just the same as for a linear molecule and from that only one moment of inertia (for end-over-end rotation) can be determined.

4.7 Summary:

- ❖ A molecule can rotate about an axis passing through its Centre of gravity and also the electronic energy, rotational energy of a molecule also is quantized.
- ❖ In order to be Raman active, a molecular vibration or rotation must cause some change in a component of molecular polarizability.
- ❖ In a linear polyatomic molecule, all the atoms are aligned along line called the molecular axis.
- ❖ A linear molecule consisting of n atoms has n-1 bonds between the adjacent atoms.

4.8 Review questions:

1. Show that the rotational Raman spectra of a linear molecule consists of stokes and anti-stokes lines starting from $6B \text{ cm}^{-1}$ from the exciting line and equi spaced with $4B \text{ cm}^{-1}$ separation.
 2. Discuss the Raman spectrum of symmetric top molecules.
 3. Determine the moment of inertia of the symmetric top molecule.
-

4.9 Further Readings

1. Molecular spectroscopy Suresh Chandran Narosa Publishers
2. Fundamentals of Molecular spectroscopy – Colin N.Banwell Tata Mcgraw Hill Edn.

Molecular structure

Notes

UNIT V MOLECULAR STRUCTURE

Structure:

- 5.1 Introduction
 - 5.2 Objectives
 - 5.3 Molecular structure using IR and Raman spectroscopy
 - 5.4 Summary
 - 5.5 Review questions
 - 5.6 Further Readings
-

5.1 Introduction:

Determination of molecular structure using Infrared and Raman spectroscopies is done from the observed frequencies and in addition from the molecular symmetry, vibrational possibilities and the polarizability of the observed line.

A molecule of xy_2 type whether it is linear or non-linear and if linear whether symmetrical (y-x-y) or asymmetrical (y-y-x) can be concluded very easily by observing both IR and Raman spectra of the samples. If a molecule is linear and symmetrical, naturally it will possess the Centre of symmetry and so will obey the mutual exclusion principle. The reverse is also true, (ie.,) an observation of the IR and Raman spectrum of a molecule, If it is found that all the IR active vibration are Raman inactive and vice versa then the structure confirmation becomes beyond doubt. The linearity of such molecules is confirmed from some infrared bands having PR contour. In this way structure of CO_2 , CS_2 can be confirmed.

Therefore, the mutual exclusion principle and the PR contour of any of the IR bands help in identifying very easily the structure of xy_2 type molecule.

A molecule of xy_2 type will possess $(3N-6) = 6$ fundamental vibrations for these four-atomic molecules. However, if the molecular shape has some symmetry this number will be reduced by degeneracy. In particular, for the symmetric planar and symmetric pyramidal shapes, one stretching mode and one angle deformation mode are each double degenerate and so only four different fundamentals frequencies should be observed. There are stretched in Table 5.1 where their various activities and band contours or polarizations are also collected. Both molecular shapes are in fact symmetric and band contours or polarizations are also collected. Both molecular shapes are in fact symmetric tops with the main (threshold) axis passing through atom X perpendicular to the Y_3 plane. It is with the respect to this axis that the

vibrations can be described as \parallel and \perp . The symmetric models of vibration are parallel and Raman polarized while the asymmetric are perpendicular and depolarized. All the vibration of the pyramidal molecule change both the dipole moment and the polarizability. Hence all the both infra-red inactive, while asymmetric bending mode does not change the polarizability (of the discussion of the bending mode of CO_2) and so ν_2 in Raman inactive for planar AB_3 .

The overall pattern of the spectra, then, should be as follows:

Planar xy_3 : One vibration Raman active only

One vibration IR active only

Two vibrations both Raman and IR active

Pyramidal xy_3 : All four vibrations both Raman and IR active

Non-symmetric xy_3 : More than four different vibrations

With this pattern in mind we can consider the spectra of NO_3^- and ClO_3^- ions. According to spectroscopic data, without considering any assignment of the various absorption bands to particular vibration, we can see immediately that the nitrate ion fits the expected pattern for a planar system, while the chlorate ion is pyramidal.

5.2 Objectives

The molecular structure determination using IR and Raman spectroscopy is discussed,

5.3 Techniques and instrumentation:

The invention of the laser and its subsequent use as a source for Raman spectrometers revolutionized that technique. Previously, Raman measurements were taken with a mercury arc as the exciting source. But, because Raman is an inherently weak process, these sources were not intense enough for routine use, many hours sometimes being necessary to record a single spectrum.

The laser is almost ideal as a source for Raman experiments, it gives a very narrow, highly monochromatic, coherent beam, which can be focused very finely into a small sample. In addition, lasers can be extremely powerful, ranging from milliwatts to several watts, concentrated into a small energy spread. The rare gas lasers (Ar^+ , Kr^+ etc.), which are most commonly used for Raman measurements, can provide intensities as great as one million times that of sunlight.

5.3.1 Molecular structure determination using IR and Raman Spectroscopy

Molecular structure

Notes

Infrared Spectroscopy (IR): The term "infra-red" covers the range of the electromagnetic spectrum between 0.78 and 1000 mm. It is useful to divide the infra-red region into three sections; near, mid and far infra-red. The most useful I.R. region lies between $4000 - 670 \text{ cm}^{-1}$.

Table.1. Various regions of IR

Region	Wavelength range (mm)
Near	0.78 - 2.5
Middle	2.5-50
Far	50-1000

The number of normal modes of vibration of a molecule with N atoms is $3N$, but 3 of these result in translation of the whole molecule in the x, y, and z directions, and 3 results in molecular rotations. Thus the molecule has $3N-6$ normal modes of vibration. [$3N-5$ if the molecule is linear, since there is no rotation possible about the molecular axis.] The symmetry of each of the normal modes can easily be determined by Group Theory since the matrices that describe the atomic displacements have characters that form the basis for irreducible representations of the molecular point group.

A normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency during it, the Centre of Gravity of the molecule remains unchanged since a molecule having N atoms has N-1 bonds out of the $3N-6/3N-5$ vibrations N-1 would be bond stretching and $2N-5/2N-4$ would be Deformation Vibrations.

When a normal molecular motion such as a vibration, rotation, or lattice mode or a combination, difference, or overtone of these normal vibrations results in a change in the molecule's dipole moment, a molecule absorbs infrared radiation in this region of the electromagnetic spectrum. The corresponding frequencies and intensities of these infrared bands, the infrared spectrum, may be used to characterize the material. Infrared spectral information may be used to identify the presence and amount of a particular compound in a mixture.

Principle of Raman spectroscopy: When a material is illuminated, light will be scattered, reflected or transmitted. A very small part (1 in every 10^7 photons) is scattered in elastically and the resulting radiation is called Raman scatter. Specific bonds can be identified in both organic and inorganic materials, as they result in typical Raman signals.

Structural Elucidation using Raman and IR Spectroscopy:

- Raman spectroscopy is an important complement to infrared spectroscopy.
- Vibrational spectroscopy plays an important role in elucidation of molecular structure. A detailed analysis of its IR and Raman spectra provides an insight into intramolecular as well as intermolecular interactions.
- For a mode of vibration to be infrared (IR) active, it must give rise to a change in the molecular electric dipole moment.
- For a mode of vibration to be Raman active, it must give rise to a change in the polarizability of the molecule.
- For Centro symmetric molecules, the rule of mutual exclusion states that vibrations that are IR active are Raman inactive, and vice versa.
- Predictions for Fundamentals of XY₂ Type Molecule.

Table.2. Predictions for fundamentals of XY₂ type molecules using point group theory

Model		Number of fundamentals allowed in IR	Number permitted in Raman effect	Number of Raman and IR coincidences	Number of polarised Raman lines
Linear	Y-X-Y	2	1	0	1
Bent	X	3	3	3	2
	Y Y				
Linear	Y-Y-X	3	3	3	2

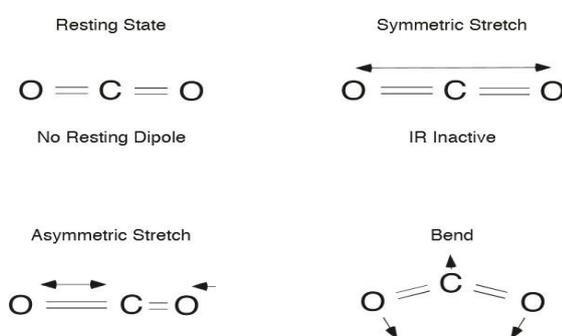


Figure.4. The fundamental vibrational modes of CO₂

5.4 Summary

- ❖ Determination of molecular structure using Infrared and Raman spectroscopies is done from the observed frequencies and in addition from the molecular symmetry.
- ❖ A change in the molecule's dipole moment, a molecule absorbs infrared radiation in this region of the electromagnetic region.
- ❖ Specific bonds can be identified in both organic and inorganic materials, as they result in typical Raman signals.

5.5 Review questions

1. How do you determine the structure of the molecule using IR spectroscopy?
2. Using Raman spectroscopy, how will you estimate the structure of the molecules.

5.6 Further Readings

1. Molecular spectroscopy- Suresh Chandran Narosa Pub.Pvt.Ltd.
2. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCASH. Tata McGraw Hill Edition.
3. Goparaju Savitri, Structural Elucidation using Raman and IR Spectroscopy, J.Chem.Pharma. Sci. ISSN:0974-2115.

BLOCK II: VIBRATIONAL PROPERTIES

UNIT VI VIBRATIONAL SPECTRA

Structure:

- 6.1 Introduction
- 6.2 Objectives
- 6.3 Vibrational spectra of diatomic molecule
- 6.4 Information on molecular constitution from IR studies.
- 6.5 Vibrational spectra of polyatomic molecule
- 6.6 Summary
- 6.7 Review questions
- 6.8 Further Readings

6.1 Introduction:

Vibrational motion is, by definition, motion of the nuclei directed along the axis of a diatomic molecule and is a function of the internuclear separation only. This vibration, when restricted within the limits of Hooke's law, can be assumed to be simple harmonic in nature and the oscillation are simple harmonic oscillation with the molecules named as harmonic oscillators. But in real cases all the molecules do not obey Hooke's law and so it is essential to assume the molecules to behave as anharmonic oscillators. Starting with simple diatomic molecules, the discussions can be extended to the complicated polyatomic molecules in this chapter.

6.2 Objectives

Vibrational spectra of diatomic and polyatomic molecules are discussed. Information on molecular constitution form IR studies is deliberated.

6.3 Vibrational energy of a Diatomic molecules

Harmonic oscillator:

Analogous to the oscillations of a vertical spring with a mass 'm' attached to its ends, the diatomic molecule can be assumed to be a dumbbell connected by means of a spring and whenever disturbed oscillates simple harmonically. If the molecules are assumed to behave as a harmonic oscillator, we know like all energies the vibrational energies are also quantized and the allowed vibrational energies for any particular system may be calculated from the Schrodinger's equation as,

$$E_v = (v + 1/2)\hbar\omega_{osc} \text{ Joules } (v=0,1,2,3,\dots) \text{ -----(6.1)}$$

Where v is called vibrational quantum number. The vibrational term value in wavenumber unit is given by

$$G(v) = \frac{E_v}{hc} = (v + 1/2)\omega_c \text{ cm}^{-1} \text{ -----(6.2)}$$

The vibrational term value $G(v)$ and hence the vibrational energy levels are quantized with values of $v=0,1,2,\dots$

When $v=0$, we get the lowest eigen state with energy $\frac{1}{2}\omega_c$. This energy is called zero-point energy. This prediction of zero-point energy makes the wave mechanical approach different from that of classical approach. In classical approach, the particle can rest at the bottom of the potential well ($r=0$) with zero energy and momentum which violates the uncertainty principle, since both position and momentum would then be exactly defined. So, this finite value position and momentum would then be exactly defined. So, this finite value of zero-point energy appears as a fundamental requirement of quantum theory of the oscillating particle, and this energy cannot be removed, even at absolute zero.

6.3.1 Spectrum of Harmonic oscillator:

A homonuclear diatomic molecule (ex. H_2 , N_2 , O_2,\dots) exhibits no vibrational spectrum (Infrared spectrum) due to the transition between the vibrational levels. It has no permanent dipole moment; its vibrations do not induce a dipole, and therefore it does not interact with radiation to produce vibrational spectrum. But a heteronuclear diatomic molecule (ex. HCl , CO,\dots) possesses a dipole moment and so involve a change in dipole moment during the vibration which will allow the vibrations to interact with the radiation. Thus, vibrational spectra will be observable only in heteronuclear diatomic molecules.

From the calculation of the transition probability using the Schrodinger's equation, we get the selection rule for the allowed vibrational transitions as,

$$\Delta v = \pm 1 \text{ ----- (6.3)}$$

However, from the equation (6.2) that separation between the successive terms of the oscillator are the same, and so all transitions occur at the same wave number ω_c . This is the same wave number at which the oscillator vibrates on the classical picture.

For most molecules, ω_c lies in the range of $200-4000 \text{ cm}^{-1}$, and the observed vibrational spectrum of a heteronuclear diatomic molecules does consist of a single intense line (under low resolution) at ω_c (Fig.6.1). But with high resolution instruments many other vibrational lines are also observed which cannot be explained with the theory of Harmonic oscillator alone

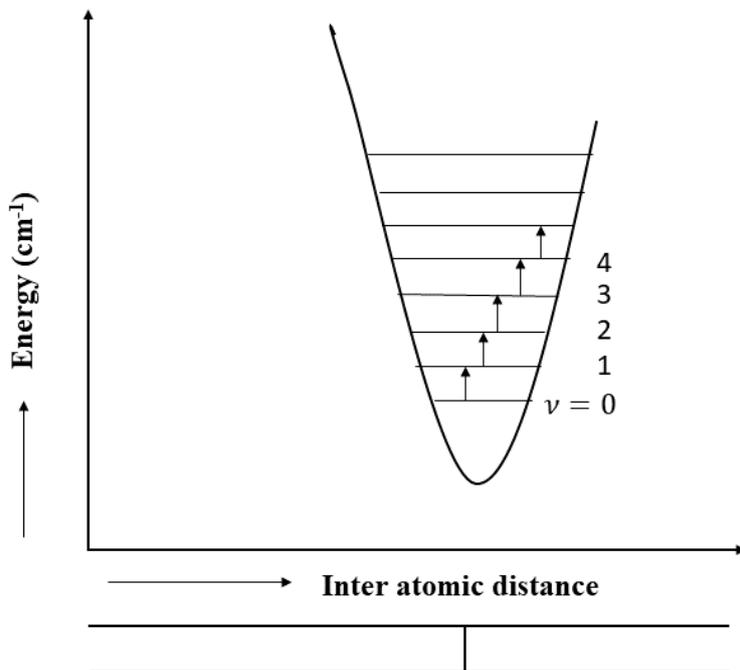


Fig.6.1 The vibrational energy levels with their allowed transition

6.3.2 The an harmonic Oscillator:

Instead of expected single intense line, other lines also appear because, real molecules do not obey Hooke's law. If the band between the atoms is stretched beyond a limit, then there will be a stage at which the molecules will no longer be intact, but will be dissociated into atoms. Therefore, the molecules can no longer be imagined to behave as a harmonic oscillator, but behaves as an anharmonic oscillator, and the shape of the energy curve can no longer be a perfect parabola as seen in Fig. 6.1, but will take a different shape as given in Fig.6.2. A purely empirical expression which fits this curve to a good approximation was derived by P.M.Morse, and is called Moorese potential energy function.

$$V(r)=D_e[1-e^{-a(r-r_e)}] \text{ -----}(6.4)$$

Where a is a constant for a particular molecule and D_e is the dissociation energy. Fig (6.2) shows a typical potential energy curve for a stable electronic state of a diatomic molecule. The main features of the curve may be summarized as follows:

- a) As $r \rightarrow \infty$ $V(r)$ tends asymptotically to a constant value equal to D_e called the dissociation energy.
- b) As $r \rightarrow 0$, $V(r)$ goes to infinity, or at least tends to a large positive value. When equ (6.4) is used in the Schrodinger equation, the pattern of the allowed vibrational energy levels is found to be

$$G(v) = (v+1/2) \omega_e - (v+1/2)^2 \omega_e X_e + (v+1/2)^3 \omega_e X_e \dots \text{cm}^{-1}$$

$(v=0,1,2,\dots) \dots \dots \dots (6.5)$

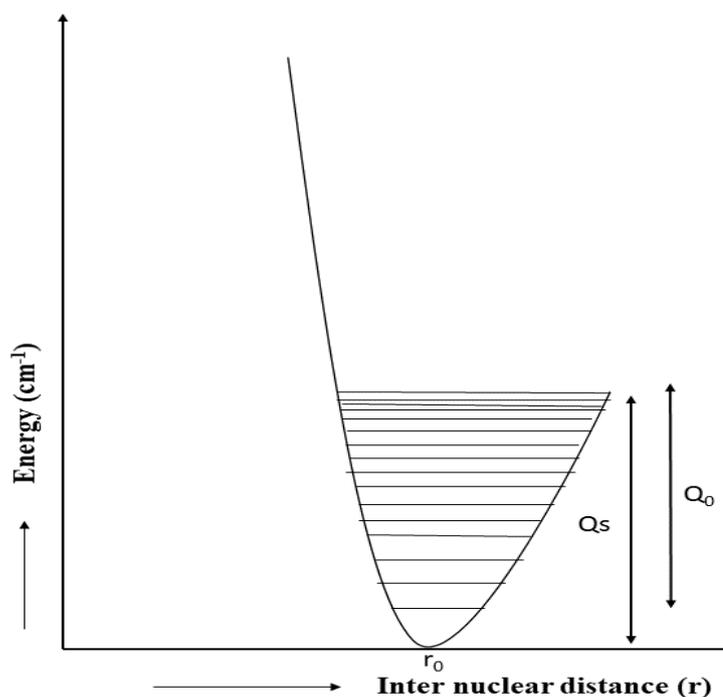


Fig.6.2 Potential energy curve and the vibrational levels of anharmonic oscillator.

Where ω_e is an equilibrium vibrational frequency, X_e and Y_e are anharmonicity constants which are always very small and positive, so that the vibrational energy levels crowd more closely together with increasing value of the vibrational quantum number 'v' (Fig. 6.2)

Unlike harmonic oscillator, the selection rules for the anharmonic oscillators are found to be

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots \dots \dots (6.6)$$

1. For a transition $v=0 \rightarrow v=1$, $\Delta v = +1$, with considerable intensity.

$$\begin{aligned} \Delta E &= G(v=1) - G(v=0) \\ &= (1 + 1/2)\omega_e - \omega_e X_e (1 + 1/2)^2 - \{1/2\omega_e - 1/4\omega_e X_e\} \\ &= \omega_e (1 - 2X_e) \text{ cm}^{-1} \dots \dots \dots (6.7) \end{aligned}$$

2. For $v=0 \rightarrow v=2$, $\Delta v = +2$, with less intensity.

$$\begin{aligned} \Delta E &= G(v=2) - G(v=0) \\ &= 2\omega_e (1 - 3X_e) \text{ cm}^{-1} \dots \dots \dots (6.8) \end{aligned}$$

3. For $v=0 \rightarrow v=3$, $\Delta v = +3$, with negligible intensity

$$\Delta E = 3\omega_e (1 - 4X_e) \text{ cm}^{-1} \dots \dots \dots (6.9)$$

4. The transition $v=1 \rightarrow v=2$, normally weak

$\Delta E = \omega_e (1 - 4X_e) \text{ cm}^{-1}$. This weak absorption is usually called hot bands since it is observed only at high temperature.

6.3.3 Diatomic vibrating Rotator:

We now consider, the actual case in which a diatomic molecule is simultaneously executing both vibrational and rotational motions. Classically the calculated periods of vibration and rotation are of the order of 10^{-14} and

10^{-12} sec, respectively. Therefore, a molecule can vibrate nearly one hundred times during a rotation. According to Born-Oppenheimer, these two types of motion can be separated and the rotational energy is calculated using a mean value of B, for rotational constant which is averaged over the changes in bond length occurring during the rapid vibrational motions of the nuclei.

$$B_v = \frac{h}{8\pi^2 c \mu} \left(\frac{1}{r^2} \right) \text{ cm}^{-1} \quad \text{-----(6.10)}$$

The energy of the vibrating rotator 'E', according to the Born-Oppenheimer approximation can be written as the sum of the vibrational and rotational energies, so that,

$$E = E_v + E_R \quad \text{-----(6.11)}$$

In wave number units, the vibration-rotation terms are expressed by,

$$T = G(v) + F(J) \quad \text{----- (6.12)}$$

Therefore, it can be viewed as each vibrational eigen state of the molecule, with vibrational quantum number 'v', has associated with it a stack of rotational energy levels.

According to the expression for the rotational energy levels, it is assumed that the nuclei are connected by a rigid bond, which is not true in real molecules undergoing anharmonic oscillators. Therefore, the following modifications are applied:

- i) We understand that the mean value of $1/r^2$ will decrease with the increase of 'v' and this decrease can be represented by

$$B_v = B_e + \alpha_e (v + 1/2) + \dots \quad \text{(6.13)}$$

Where α_e is a small constant and B_e is the rotational constant at the equilibrium internuclear distance r_e .

- ii) In any given vibrational state v, the expression for the rotational terms F(J) must include a correction for centrifugal distortion of the elastic bond between the nuclei.

$$F(J) = B_v J(J+1) - DJ^2(J+1)^2 + \dots \quad \text{(6.14)}$$

Where D is the centrifugal distortion constant which is very small constant, calculated by the following formula,

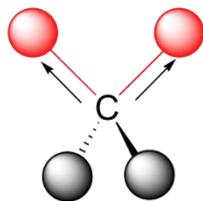
$$D = \frac{4B_e^3}{W_e^2} \quad \text{-----(6.15)}$$

6.4 Information on molecular constitution from IR studies

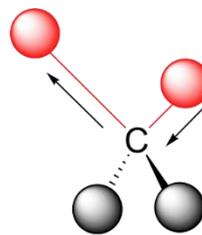
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual vibrational modes, a few of which are illustrated below.

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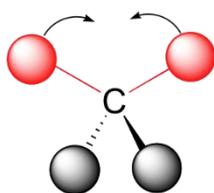
The energy of molecular vibration is quantized rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the



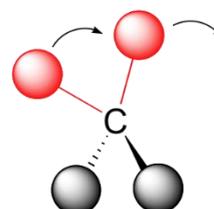
symmetric stretching



asymmetric stretching



scissoring

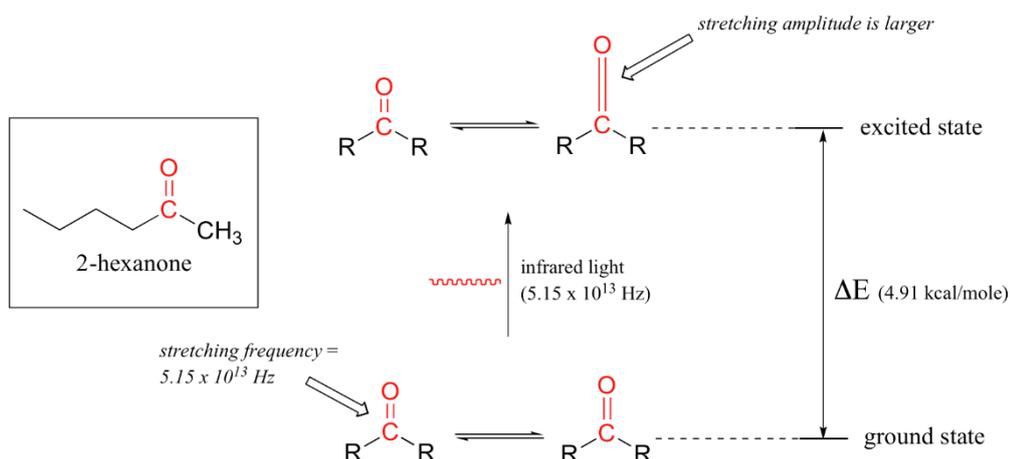


rocking

radiation and jump to a higher vibrational energy state - what this means is that the amplitude of the vibration will increase, but the vibrational frequency will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the infrared region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

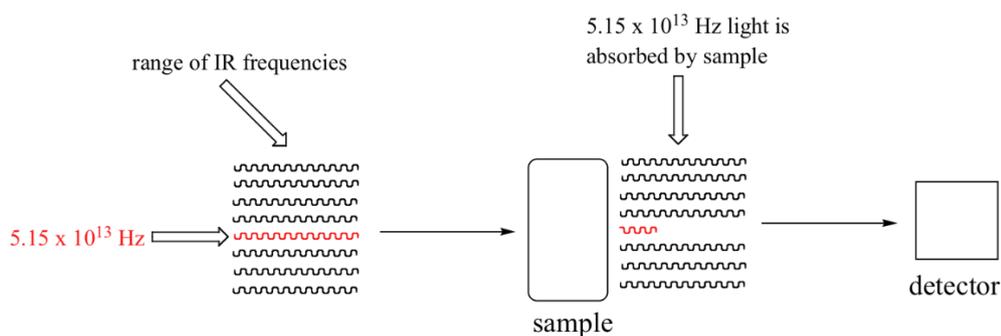
Let's take 2-hexanone as an example. Picture the carbonyl bond of the ketone group as a spring that is constantly bouncing back and forth, stretching and compressing, pushing the carbon and oxygen atoms further apart and then pulling them together. This is the stretching mode of the carbonyl bond. In the space of one second, the spring 'bounces' back and forth 5.15×10^{13} times - in other words, the ground-state frequency of carbonyl stretching for the ketone group is about 5.15×10^{13} Hz.

If our ketone sample is irradiated with infrared light, the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83×10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited not vibrational state. The value of ΔE - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91



kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not vibrational state.

remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.



With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed through our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.

Our 5.15×10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

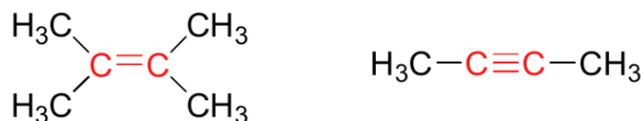
The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that different functional groups have different characteristic absorption frequencies. The

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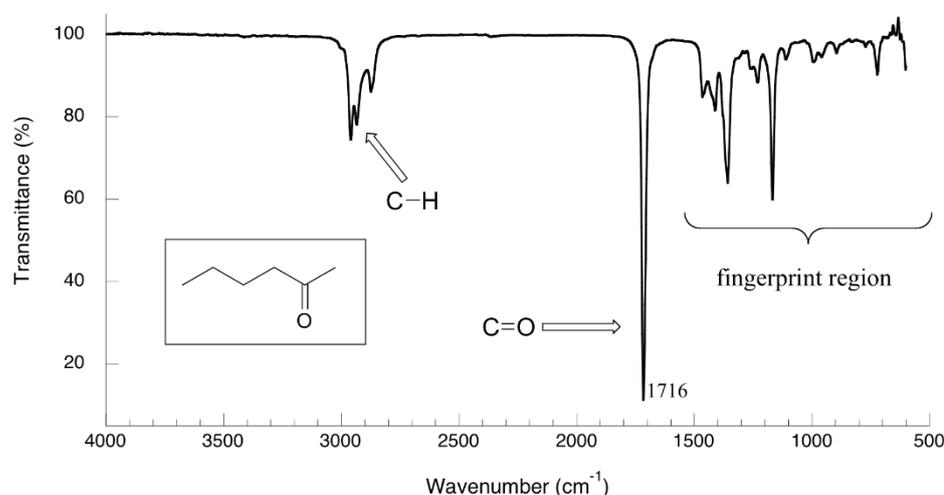
carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of $5.11 - 5.18 \times 10^{13}$ Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range $6.30 - 6.80 \times 10^{13}$ Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule. Such vibrations are said to be infrared active. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.



infrared-inactive double and triple bonds

Some kinds of vibrations are infrared inactive. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules do absorb IR light). Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called wavenumber (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see ‘% transmittance’, which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency).

6.5 Rotational -vibration spectra:

We know,

$$T = G(\nu) + F\nu (J)$$

$$= w_e(\nu + 1/2) - w_e x_e(\nu + 1/2)^2 + \dots + B\nu J(J+1) - D J^2 (J_N + 1)^2 \dots \dots (6.16)$$

The infrared spectrum consists of a series of bands due to transitions in which vibrational quantum number ν changes; and under high resolution, each of these bands is found to be composed of large number of closely spaced lines, forming the rotational fine structure.

If we define

$$\nu_0 = G(\nu') - G(\nu'') \text{ ----- (6.17)}$$

as the wave number for the transition between the two vibrational levels following the selection rule (6.6) in the absence of rotation. With the rotation also, the equation for the wave numbers of the rotation lines are given by the formula.

$$\nu = \nu_0 + B'_\nu J'(J'+1) - B''_\nu J''(J''+1) \text{ ----- (6.18)}$$

(neglecting the centrifugal distortion)

Where B'_ν and B''_ν are the rotational constants in the upper and lower vibrational states respectively. The selection rule $\Delta J = \pm 1$ produces two sets of lines called P-branch corresponding to $\Delta J = -1$ and Q-branch corresponding to $\Delta J = +1$. The frequency ν_0 is called the band centre or band origin. Applying the selection rule, the wave number of R and P branches are given by,

$$\nu_R = \nu_0 + 2B'_\nu + (3B'_\nu - B''_\nu)J + (B'_\nu - B''_\nu) J^2 \text{ ----- (6.19)}$$

$$J = 0, 1, 2, 3, \dots$$

$$\nu_P = \nu_0 - (B'_\nu + B''_\nu)J + (B'_\nu - B''_\nu)J^2 \text{ ----- (6.20)}$$

$$J = 1, 2, 3, \dots$$

Where $J = J''$ is the rotational quantum number for the lower rotational level.

Notes

When the rotational constants B'_v and B''_v are not having identical value (i.e) $(B'_v - B''_v) \neq 0$, then the series of rotational lines in both the branches can be represented by a single formula,

$$v = v_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2 \text{ -----(6.21)}$$

where m has the value (J+1) for the R-branch and (-J) for P-branch.

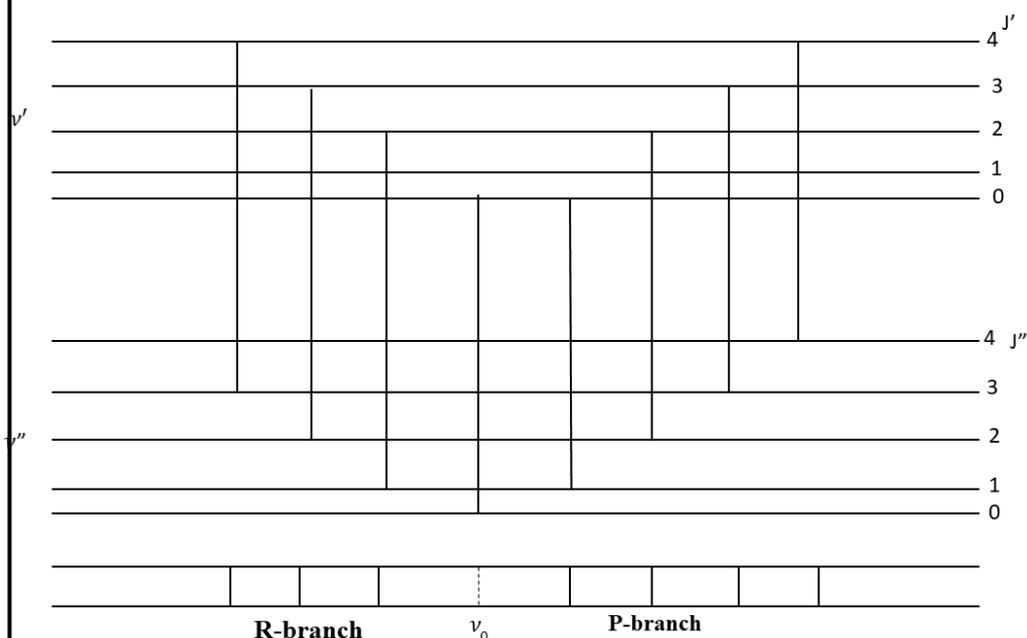


Fig.6.3 Rotational transitions accompanying vibrational transition for a diatomic molecule.

6.5.1 Vibrational of polyatomic Molecules:

We know, a molecule of 'n' number of atoms has '3n' total degree of freedom. The total degrees of freedom comprise of translational, rotational and vibrational degrees of freedoms.

Total degrees of freedom, $3n = (\text{translational} + \text{rotational} + \text{vibrational})$ degrees of freedom ----- (6.22)

Generally, the translational degrees of freedom are only '3' irrespective of molecules, but the rotational degrees of freedom are '2' for linear molecules.

(neglecting the rotational about the internuclear bond axis) and '3' for non-linear molecules.

Therefore,

- (i) For linear molecules:

$$3n = 3 + 2 + \text{vibrational degrees of freedom}$$

(or)

$$\text{No. of internal or normal vibrations} = 3n - 5 \text{(6.23)}$$

- (ii) For non-linear molecules:

$$\text{No. of normal vibrations} = 3n - 6 \quad \dots\dots\dots(6.24)$$

Notes

So, every polyatomic molecule has its own number of fundamental vibrations, depending on their number of atoms, which are all the characteristics of the molecules itself. Therefore, the study of molecular vibrations will reveal many interesting facts about the molecules such as, force constant, interatomic distance and the bond angle.

From the above equation (6.23) and (6.24) we can identify the number of fundamental vibrations possessed by any molecule.

We shall consider few examples and discuss. First, if we take any diatomic molecule (Heteronuclear), we know such molecules can be only linear and so according to equation (6.23), there can be only one fundamental vibration. Next, when we consider a non-linear triatomic molecule, say H_2O and SO_2 , the equation (6.24) gives that there can be only 3 allowed vibrational modes ($9 - 6 = 3$). Depending on the nature of vibration, they are named as symmetric stretching vibration, asymmetric stretching vibration and symmetrical bending vibrations. The vibrations are depicted by the following figures.

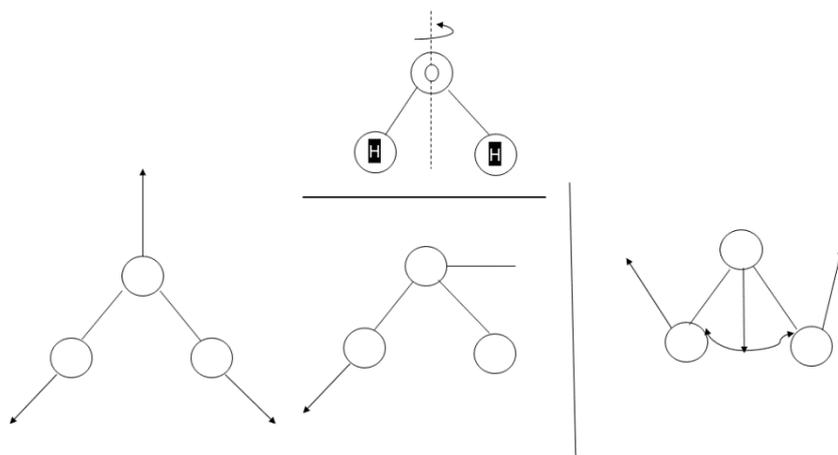


Fig.6.4 The water molecule and its fundamental vibrations

As we have seen earlier, in order that the vibrations to be infrared active, there must be a dipole change during the vibrations, and this change may be either parallel or perpendicular to the symmetry axis (C₂ axis in the figure). The third example, is a linear triatomic molecule, say CO_2 , OCS , etc., in which all

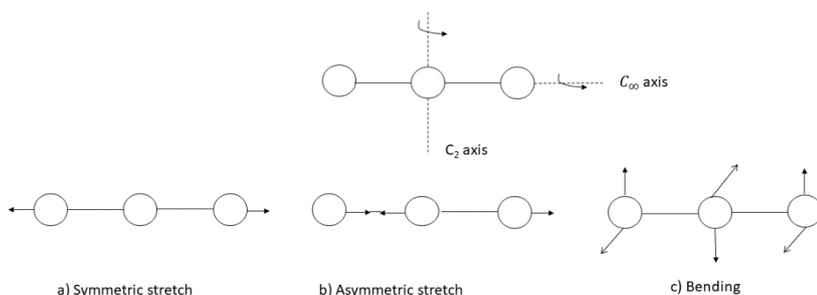


Fig.6.5 The CO_2 molecule and its fundamental vibrations

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symmetric bending vibrations are degenerative vibrations, with two kinds of vibrations of course with the same frequency. Those vibrations are depicted as follows:

The three atoms are arranged in a line. Therefore, according to the equation (6.23) there must be 4 vibrations ($9-5=4$) (i.e) we expect from fundamental vibrational modes. Apart from the symmetric stretch and asymmetrical stretch, there are two degenerate vibrations, one in the planes of the paper and the other perpendicular to the plane of the paper, but both with the same frequency. Only the asymmetric stretch and bending vibrations of CO_2 cause a change in dipole moment and hence IR active while the symmetric stretch is IR inactive.

A complex molecule has a large number of normal modes of vibrations named after this nature as, twisting, rocking, wagging, in-plane deformation and out of plane deformation, breathing etc.,

6.6 Summary:

- ❖ A homonuclear diatomic molecule (ex. H_2 , N_2 , O_2) exhibits no vibrational spectrum (Infrared spectrum) due to the transition between the vibrational levels.
 - ❖ Instead of expected single intense line, other lines also appear because, real molecules do not obey Hooke's law.
 - ❖ Diatomic molecule is simultaneously executing both vibrational and rotational motions. Classically the calculated periods of vibration and rotation are of the order of 10^{-14} and 10^{-12} sec, respectively.
-

6.7 Review questions

1. What is the condition for a molecule to exhibit vibrational spectrum? Why?
 2. Assuming a harmonic oscillator be assumed to behave as anharmonic oscillator?
 3. When will an oscillator be assumed to behave as anharmonic oscillator?
 4. Discuss the effect of anharmonicity in the case of diatomic vibrating rotator.
 5. How many normal modes of vibration can be expected in SO_2 and CO_2 molecules? Which of them are IR active? Why?
-

6.8 Further Reading

1. Atomic and Molecular spectra and Lasers A.K.Saxena, CBS Publication.
2. Fundamentals of Molecular spectroscopy – Colin N.Banwell and Elaine M.McCash. Fourth edition, Tata McGraw Hill Education Pvt.Ltd.,

UNIT VII VIBRATIONAL RAMAN SPECTRA

Vibrational Raman spectra

Notes

Structure:

- 7.1 Introduction
- 7.2 Objectives
- 7.3 Vibrational Raman spectra
- 7.4 Vibrational course structure
- 7.5 Rotational course spectra
- 7.6 Summary
- 7.7 Review questions
- 7.8 Further Readings

7.1 Introduction:

Vibrational motion is, by definition, motion of the nuclei directed along the axis of a diatomic molecule and is a function of the internuclear separation only. This vibration, when restricted within the limits of Hooke's law, can be assumed to be simple harmonic in nature and the oscillations are simple harmonic oscillations with the molecules named as harmonic oscillators. But in real cases all the molecules do not obey Hooke's law and so it is essential to assume the molecules to behave as a harmonic oscillator. Starting with simple diatomic molecules, the discussions can be extended to the complicated polyatomic molecules.

7.2 Objectives:

Vibrational Raman spectra is discussed. Vibrational course structure and Rotational course spectra are deliberated.

7.3 Vibrational Raman spectra:

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

$$\epsilon = \bar{\omega}_e (v+1/2) - \bar{\omega}_e X_e (v+1/2)^2 \text{ cm}^{-1} \quad (v=0,1,2,\dots) \quad \text{-----}$$

(7.1)

where, as before $\bar{\omega}_e$ is the equilibrium vibrational frequency expressed in wavenumbers and X_e is the anharmonicity constant. Such an expression is perfectly general, whatever the shape of the molecule or the nature of the vibration. Quite general, too, is the selection rule:

$$\Delta v=0, \pm 1, \pm 2 \dots \dots \dots (7.2)$$

Vibrational Raman spectra

Notes

Which is the same for Raman as for infra-red spectroscopy, the probability of $\Delta v = \pm 2, \pm 3, \dots$

Decreasing rapidly.

Particulating, now, to Raman active modes, we can apply the selection rule to the energy level expression (7.1) and obtain the transition energies

$$v=0 \rightarrow v=1; \Delta \epsilon_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v=0 \rightarrow v=2; \Delta \epsilon_{\text{overtone}} = 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

$$v=1 \rightarrow v=2; \Delta \epsilon_{\text{hot}} = \bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1} \dots \dots \dots (7.3)$$

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. This is not to say that active overtones and hot bands cannot be observed, but they add little to the discussion here.

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

$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \Delta \epsilon_{\text{fundamental}} \text{ cm}^{-1} \dots \dots \dots (7.4)$$

Where the minus sign represents the stoke’s lines (i.e for which the molecule has gained energy at the expense of the radiation) and the plus sign refers to the anti-stokes’ lines. The latter are often too weak to be observed, since as we saw earlier, very few of the molecules exist in the $v=1$ state at normal temperatures.

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.

As an example, we illustrate the Raman spectrum of chloroform, CHCl_3 , a symmetric top molecule. The exciting line in this case is the 488 nm argon ion laser line (at a power of 100 mW), and a wavenumber scale is drawn from this line as zero. Raman lines appear at 262.366, 668, 761, 1216 and 3019 cm^{-1} on the low-frequency (stokes’) side of the exciting line while the line at 262 cm^{-1} on the frequency (anti-stokes’) side of the exciting line while the line at 262 cm^{-1} on the frequency (anti-stokes’) side is included for a comparison of its intensity.

The range of the instrument used precluded measurements below 600 cm^{-1} , but we see clearly that strong (and hence fundamental) lines appear in the spectrum at wavenumbers corresponding very precisely with those of lines in the Raman spectrum but with very different relative intensities.

For this molecule, containing five atoms, nine fundamental vibrations (that is $3N-6$) are to be expected. The molecule has considerable symmetry, however, and three of these vibrations are doubly degenerate leaving six different fundamental absorptions, we see that these all active in both the infra-red and Raman. The immediate conclusion, not at all surprisingly, is that the molecule has no centre of symmetry.

7.3 Vibrational course spectra:

If a molecule has little or no symmetry it is a very straightforward matter to decide whether its vibrational modes will be Raman active or inactive: in fact, it is usually correct to assume that all its modes are Raman active. However, when the molecule has considerable symmetry it is not always easy to make the decision. Since it is sometimes not clear, without detailed considerations whether or not the polarizability changes during the vibration.

We consider first the simple asymmetric top molecule H_2O whose polarizability ellipsoid was shown in Fig. earlier. In Fig.7.2 we illustrate in (a), (b), and (c) respectively, the three fundamental modes ν_1, ν_2 and ν_3 , sketching for each mode the equilibrium configuration in the centre with the extreme positions to right and left. The approximation shapes of the corresponding polarizability ellipsoids are also shown.

During the asymmetric stretch, in Fig.7.2.a the molecules as a whole increase and decrease in size, when a bond is stretched, the electrons forming it are less firmly held by the nuclei and so the bond becomes more polarizable. Thus the polarizability ellipsoid of H_2O may be expected to decrease in size while the bonds stretch, and to increase while they compress, but to maintain an approximately constant shape. On the other hand, while undergoing the bending motion, in Fig.7.2.b, it is the shape of the ellipsoid which changes most; thus if we imagine vibrations of very large amplitude, at one extreme (on the left) the molecule approaches the linear configuration with a horizontal axis, while at the other extreme (on the right) it approximates to a diatomic molecule (if the two H atoms are almost coincidental) with a vertical axis. Finally in Fig.7.2.c, we have the asymmetric stretching motion, ν_3 , where both the size and shape remain approximately constant, but the direction of the major axis change markedly. Thus all three vibrations involve obvious changes in at least one aspect of the polarizability ellipsoid, and all are Raman active. Now consider the linear transition molecule CO_2 , whose three fundamental vibrational modes have been shown in Fig. In the first three columns of Fig we illustrate the extreme and

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equilibrium configuration of the molecule and their approximate polarizability ellipsoids. The question of the Raman behavior of the symmetric stretching mode, ν_1 , is easily decided-during the motion of the molecule changes size, and so there is a corresponding fluctuation in the size of the ellipsoid; the motion is thus Raman active. It might be thought that the ν_2 and ν_3 vibrations are also Raman active, because the molecule changes shape during each vibration and hence, presumably, so does the ellipsoid; however, both these modes are observed to be Raman inactive. We must, then, consider this example rather more carefully.

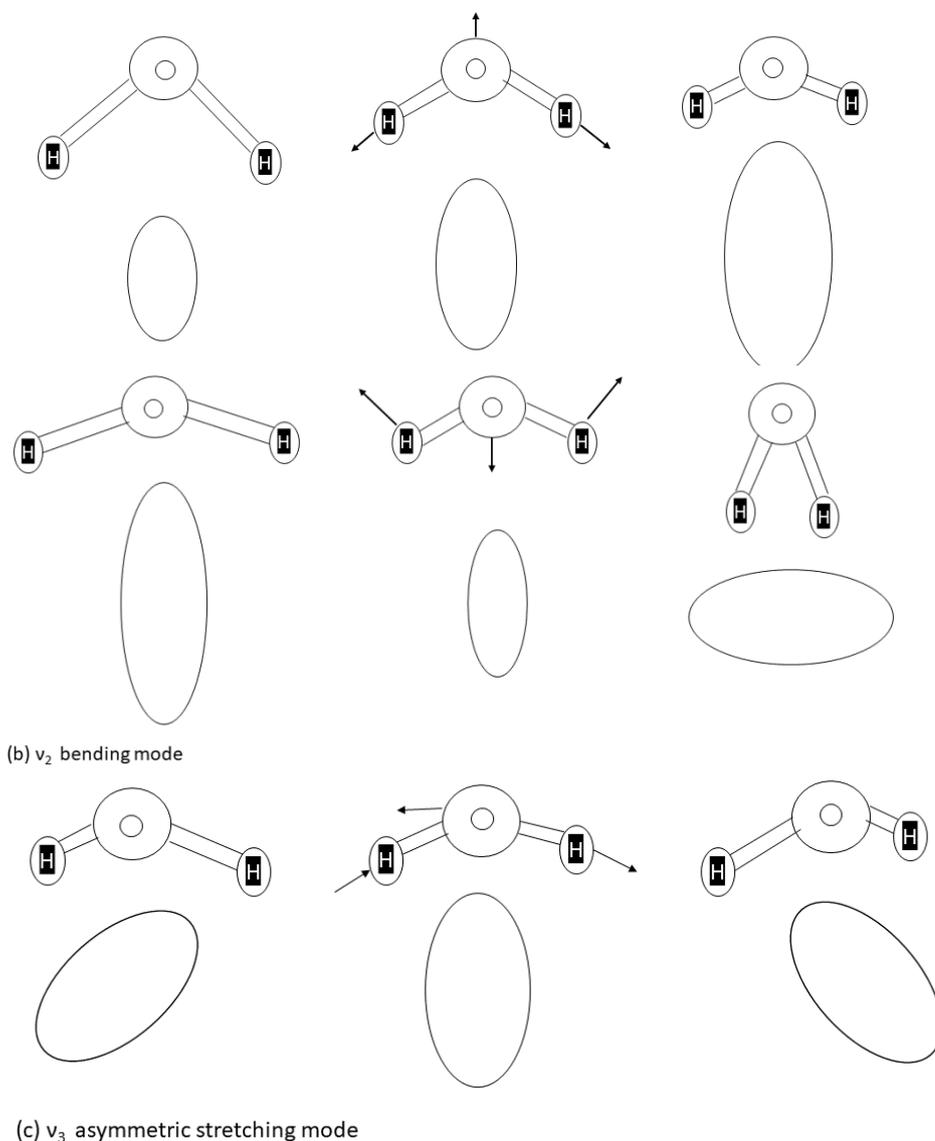


Fig.7.2 The change in size, shape, or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes. The centre column shows the equilibrium position of the molecule, which to right and left are the (exaggerated) extremes of each vibration

To do this it is usual to discuss the change of polarizability with some displacement coordinate, normally given the symbol ξ . Thus for a stretching

motion ξ is a measure of the extension (positive ξ) or compression (negative ξ) of the bond under consideration, while for a bending mode, ξ measures the displacement of the bond angle from its equilibrium value, positive and negative ξ referring to opposite displacement directions.

Consider, as an example, the ν_1 stretch of carbon dioxide sketched in Fig.7.3.a. If the equilibrium value of the polarizability is α_0 (second picture) then, when the bonds stretch (ξ positive), α increases (remember that the extent of the ellipsoid measures the reciprocal of α). While when the bonds contract (negative ξ) α decreases. Thus we can sketch the variation of α with ξ as shown on the right of Fig.7.3. The details of the curve are not important since we are concerned only with small displacement: it is plain that near the equilibrium position ($\xi=0$) the curve has a distinct slope, that is $d\alpha/d\xi \neq 0$ at $\xi=0$. Thus for small displacements the motion produces a change in polarizability and is therefore Raman active.

If we now consider the situation for ν_2 , the bonding motion of Fig.7.3.b, we can count a downwards displacement of the oxygen atoms as negative ξ and an upwards displacements as positive. Although it is not clear from the diagrams whether the motion causes an increase or a decrease in polarizability (actually it is an increase) it is plain that the change is exactly the same for both positive and negative ξ . Thus we can plot α against ξ on the right of Fig.7.3.b with, as before, $\alpha=\alpha_0$ at $\xi=0$. Now for small displacement we evidently have $d\alpha/d\xi=0$ and hence for small displacement there is effectively no change in the polarizability and the motion is Raman inactive.

Exactly the same argument applies to the asymmetric stretch, ν_3 , shown in Fig.7.3.c. Here the polarizability decreases equally for positive and negative ξ , so the plot of polarizability against ξ has the appearances shown. Again $d\alpha/d\xi=0$ for small displacements and the motion is Raman inactive.

We could have followed the same reasoning for the three vibrations of water discussed previously. In each case we would have discovered that the α versus ξ curve has the general shape of Fig.7.3.a or its mirror image, in other words, in each case $d\alpha/d\xi \neq 0$ and the motion is Raman active. In general, however, the slopes of the three curves would be different at $\xi=0$, that is $d\alpha/d\xi=0$, would have different values. Since we have seen that the Raman spectrum is forbidden for $d\alpha/d\xi=0$ but allowed for $d\alpha/d\xi \neq 0$ we can imagine that the 'degree of allowedness' varies $d\alpha/d\xi$. Thus if the polarizability curve has a large slope at $\xi=0$ the Raman line will be strong; if the slope is small it will be weak; and if zero, not allowed at all. From this stems the following very useful general rule:

Symmetric vibrations give rise to intense Raman lines; non-symmetric ones are usually weak and sometimes unobservable. In particular, a bending motion usually yields only a very weak Raman line; e.g. the ν_2 motion of H_2O

(Fig.7.2.b) although allowed in the Raman, has not been observed, nor has ν_3 for which $d\alpha/d\xi$ is also small.

Vibrational Raman spectra

Notes

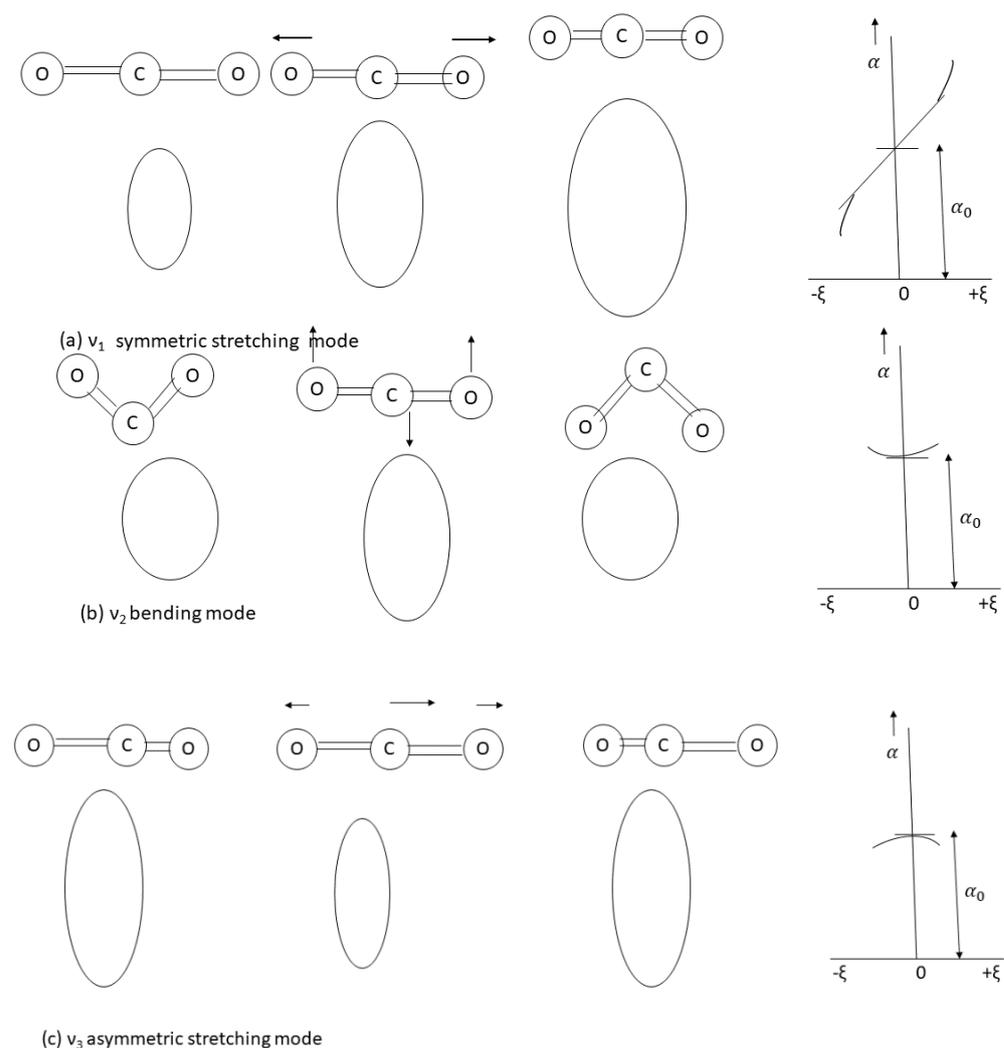


Fig.7.3 The changes in the polarizability ellipsoid of carbon during its vibrations, and a graph showing the variation of the polarizability, α with the displacement coordinate, ξ , during each vibration.

7.4 Rotational RAMAN Spectra:

Linear Molecules

The rotational energy levels of linear molecules have already been stated

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

but, in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D , the centrifugal distortion constant. Thus we take the simple expression

$$\epsilon_J = BJ(J+1) \text{ cm}^{-1} \quad (J=0,1,2,\dots) \dots\dots\dots(7.5)$$

to represent the energy levels.

Transition between these levels follow the formal selection rule for microwave spectroscopy. $\Delta J = \pm 1$. The fact that in Raman work, the rotational quantum number changes by two units rather than one is connected with the symmetry of the polarizability ellipsoid. For a linear molecule, such as is depicted in Fig. (7.4), it is evident that during end-over-end rotation the ellipsoid presents the same appearance to an observer twice in every complete rotation. It is equally clear that rotation about the bond axis produces no change in polarizability and hence, as in infra-red and microwave spectroscopy, we need concern ourselves only with end-over-end rotations.

If, following the usual practice, we define ΔJ as ($J_{\text{upper state}} - J_{\text{lower state}}$) then we can ignore the selection rule $\Delta J = -2$ since, for a pure rotational change, the upper state quantum number must necessarily be greater than that in the lower state. Further, the 'transition' $\Delta J = 0$ is trivial since this represents no change in the molecular energy and hence Rayleigh scattering only.

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

$$\begin{aligned} \Delta \varepsilon &= \varepsilon_{J'=J+2} - \varepsilon_{J'=J} \dots\dots\dots(7.6) \\ &= B(4J+6) \text{ cm}^{-1} \end{aligned}$$

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

$$\Delta \varepsilon_s = B(4J+6) \text{ cm}^{-1} \quad (J=0,1,2,\dots\dots\dots)$$

Where J is the rotational quantum number in the lower state.

Thus if the molecule gains rotational energy from the photon during collision we have a series of S branch lines to the low wavenumber side of the exciting line (Stoke's lines). While if the molecule loses energy to the photon the S branch lines appear on the high wavenumber side (anti-stokes lines). The wavenumbers of the corresponding spectral lines are given by

$$\bar{\nu}_s = \bar{\nu}_{ex} \pm \Delta \varepsilon_s = \bar{\nu}_{ex} \pm B(4J+6) \text{ cm}^{-1} \dots\dots\dots(7.8)$$

Where the plus sign refers to anti-stokes' lines, the minus to stokes' lines, and $\bar{\nu}_{ex}$ is the wavenumber of the exciting radiation.

The allowed transitions and the Raman spectrum arising are shown schematically in Fig.7.3. Each transition is labelled according to its lower J value and the relative intensities of the lines are indicated assuming that the population of the various energy levels varies according to equ and Fig . In particular it should be noted here the Stokes' and anti-stokes' lines have comparable intensity because many rotational levels are populated and hence downward transitions are approximately as likely as upward ones.

When the value $J=0$ is inserted into Equ(7.8) it is seen immediately that the separation of the first line from the exciting line is $6B \text{ cm}^{-1}$, while the

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separation between successive lines is $4B\text{cm}^{-1}$. For diatomic and light triatomic molecules, the rotational Raman spectrum will normally be resolved and we can immediately obtain a value of B , and hence the moment of inertia and bond length for such molecules. If we recall that homonuclear diatomic molecules (for example O_2 , H_2) give no infra-red or microwave spectra since they possess no dipole moment, whereas they do give a rotational Raman spectrum, we see that the Raman technique yields structural data unobtainable from the techniques previously discussed. It is thus complementary to microwave and infra-red studies, not merely confirmatory.

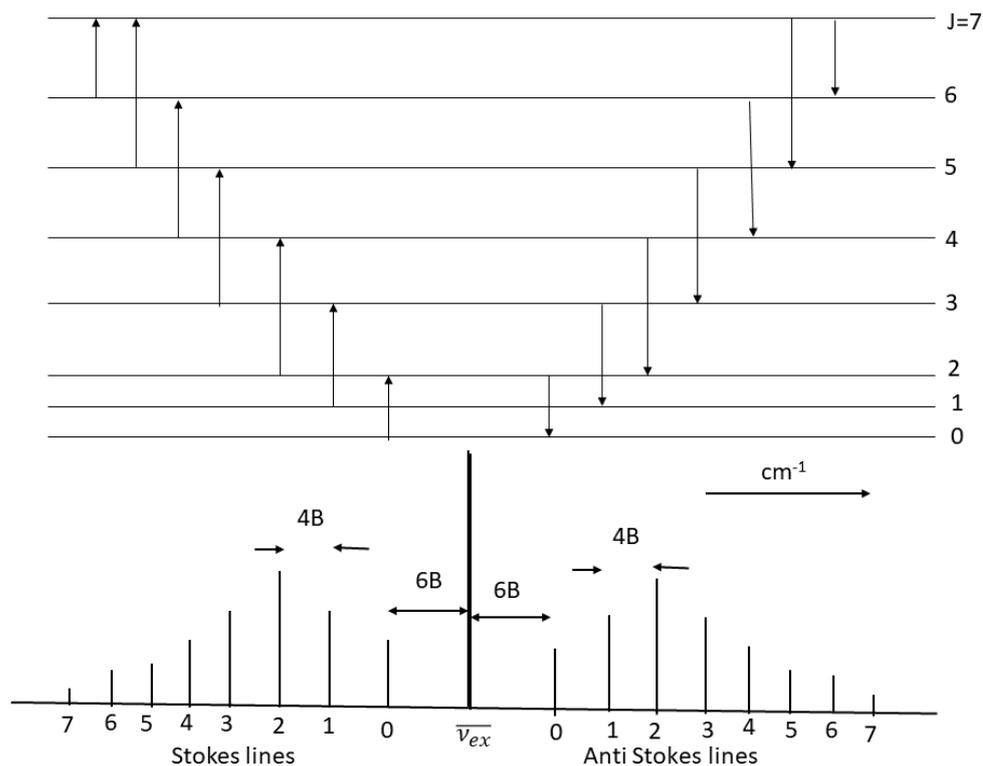


Fig.7.3 The rotational energy levels of a diatomic molecule and the rotational Raman spectrum arising from transitions between them. Spectral lines are numbered according to their lower J values.

It should be mentioned that, if the molecule has a centre of symmetry (as, for example, do H_2 , O_2 , CO_2), then the effects of nuclear spin will be observed in the Raman as in the infra-red. Thus for O_2 and CO_2 (since the spin of oxygen is zero) every alternate rotational level is absent; for example, in the case of CO_2 (since the spin of oxygen is zero) every alternate rotational level is absent; for example, in the case of O_2 , every level with even J values is missing, and thus every transition labelled $J=0, 2, 4, \dots$ in fig is also completely missing from the spectrum. In the case of H_2 and other molecules composed of nuclei with non-zero spin, the spectral lines show an alternation of intensity.

Linear molecules with more than three heavy atoms have large moments of inertia and their rotational fine structure is often unresolved in the Raman

spectrum. Direct structural information is not. Therefore, obtainable, but we shall see shortly that, taken in conjunction with the infra-red spectrum, the Raman can still yield much very useful information.

7.5 Summary

- ❖ Vibrational motion is, by definition, motion of the nuclei directed along the axis of a diatomic molecule and is a function of the internuclear separation only.
- ❖ If a molecule has little or no symmetry it is a very straightforward matter to decide whether its vibrational modes will be Raman active or inactive.
- ❖ The rotational quantum number changes by two units rather than one is connected with the symmetry of the polarizability ellipsoid

7.6 Review questions

1. What is the condition for a molecule to exhibit vibrational spectrum? Why?
2. Explain about the vibrational course spectra.
3. Discuss about the rotational Raman spectra in detail

7.7 Further Reading

1. Molecular spectroscopy – Suresh Chandra, Narosa Publisher.
2. Atomic and Molecular spectra and Lasers- Saxena, CBS Publishers.

Vibrational Raman spectra

Notes

UNIT VIII FRANCK-CONDON PRINCIPLE

Structure:

- 8.1 Introduction
- 8.2 Objectives
- 8.3 Franck – Condon principle
- 8.4 Intensity distribution
- 8.5 Portrait parabola
- 8.6 Disassociation
- 8.7 Pre disassociation
- 8.8 Mutual exclusion principle.
- 8.9 Summary
- 8.10 Review questions
- 8.11 Further studies

8.1 Introduction:

We are going to discuss about the vibrational electronic transitions (0, 0), (1, 0), (2, 0)..... It is found that in some cases the (0, 0) transitions is the most intense whereas in other cases some other transition is the most intense. Hence, the intensity distribution of the lines in the electronic spectra of molecules is not the same. The intensity variations are readily explained on the basis of the Frank-Condon principle.

8.2 Objectives

Franck-Condon principle is defined. Intensity distribution and Portrait parabola are deliberated. Dissociation and pre disassociation concepts are discussed. Mutual exclusion principle is defined.

8.3 Franck-Condon principle:

Classically we have seen that in general only the transitions vertically upward or downward in the potential energy curve correspond to the most intense bonds. This was confirmed by Condon through his wave mechanical treatment.

From quantum mechanics, we know, the probability of a transition between two states is proportional to the square of the corresponding matrix element of the electric moment.

$$R = \int \psi'^* M \psi'' d\tau \dots\dots\dots(8.1)$$

We know already $\psi = \psi_e \psi_v$ and $M = M_e + M_v$

Substituting the values of ψ and M the integral becomes,

$$R = \iint \psi_e'^* \psi_v'^* (M_e + M_v) \psi_e'' \psi_v'' d\tau_e d\tau_v$$

$$= \int \psi_e'^* \psi_e'' d\tau_e \int \psi_v'^* M_n \psi_v'' d\tau_v + \int \psi_v'^* \psi_v'' d\tau_v \int \psi_e'^* M_n \psi_e'' d\tau_e \dots\dots\dots(8.2)$$

Since the electronic states are orthogonal, we can have,

$$\int \psi_e'^* \psi_e'' d\tau_e = 0 \dots\dots\dots(8.3)$$

Substituting this in equ, R reduces to

$$R = I_c \int \psi_v'^* \psi_v'' d\tau_v \dots\dots\dots(8.4)$$

Where, I_c -is the electronic transition moment

Since the intensity will be proportional to the square of R, it means that the band intensities are proportional to the square of the overlap integral $\int \psi_v'^* \psi_v'' d\tau_v$. The more the minima are separated from each other, the smaller is the overlap integral and therefore the smaller is the intensity of the 0-0 band (Fig.8.1)

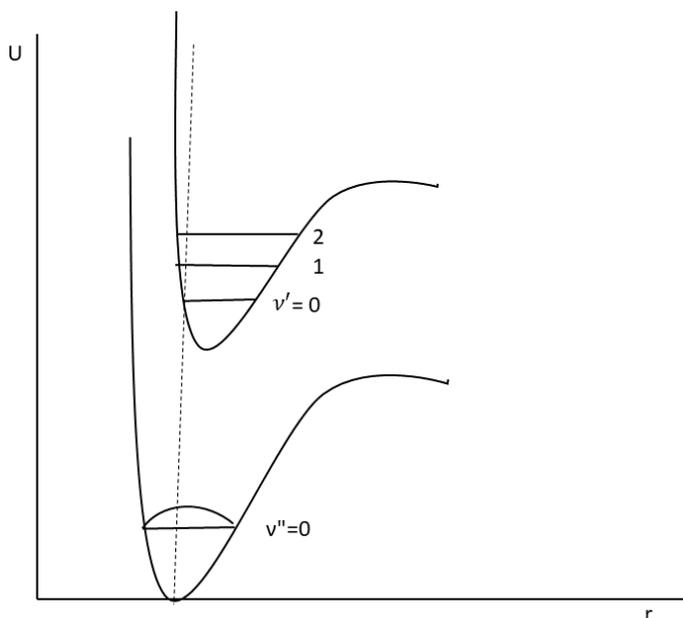


Fig.8.1 Franck-Condon principle according to wave mechanics

8.4 Intensity distribution:

Three typical cases of intensity distribution in absorption band series of electronic band spectra have been observed Fig.8.2 In the first case, coming from long wavelengths, the first band, the 0-0 band of the system is very intense. Joining onto it a new further bands of the $v'' = 0$ progression appear with very rapidly decreasing intensities. Such a case is observed for the

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atmospheric oxygen bands which appear in the red part of the solar spectrum. In the second case, the intensity of the bands in the progression $v''=0$ at first increases somewhat with decreasing wavelength and then decreases slowly. Example for this is shown by absorption bands of CO. In the third, there is a long progression of absorption bands whose intensity rises gradually from zero at the long wavelength end. The observed band is usually not 0-0 band. Toward shorter wavelengths the bands draw closer together until they come to a convergence limit where it joins to a continuum. This kind of intensity distribution is observed in the I_2 absorption spectrum.

These different cases of intensity distribution are explained in an easily visualized manner by the Frank-Condon's principle. Frank's main idea, which was developed mathematically and later given a wave-mechanical basis by Condon is the following:

“ The electron jump in a molecule takes place so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump”.

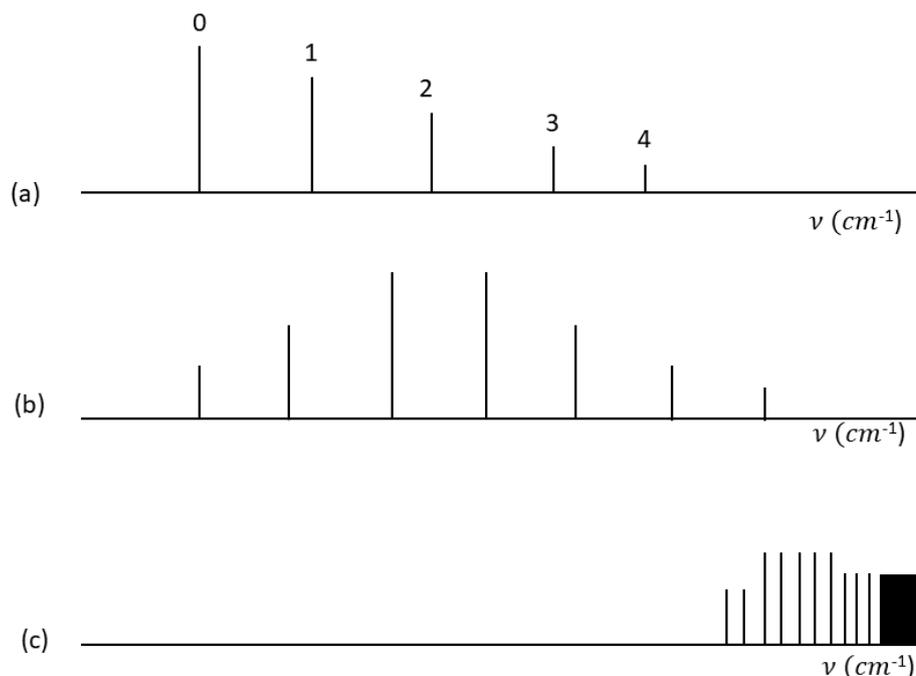


Fig.8.2 Three types of intensity distributions

In the fig.8.3(a) the potential curves of the two electronic states have been so chosen that their minima lie very nearly one above the other (i.e with equal inter nuclear distance). In absorption, the molecule is initially at the minimum of the lower potential curve, if we disregard the zero- point vibration. It can be seen that for a transition to the minimum of the upper potential curve (0-0) band, the requirement of the Franck-Condon principle that the change of position and momentum be small, is satisfied (i.e. vertical transition). On the other hand, a transition into a high vibrational state CD would be possible only when, at the moment of the electronic jump, either the position or the velocity or both alter to an appreciable extent. At the point E of

course, the molecule has the amount of kinetic energy EB . Only at the turning point C or D are the velocity and kinetic energy zero, as the initial state at A. Thus, on the basis of the Franck-Condon principle, a transition from $v''=0$ to such a high vibrational level is forbidden or at least highly improbable. For the level $v''=1$, the necessary alternation of the position or of the velocity during the electron jump is comparatively small. Therefore the 1-0 band will still appear, though with much smaller intensity than the 0-0 band. For the 2-0, 3-0... Bands the necessary alteration of position and velocity increases, and consequently a rapidly decreasing intensity is to be expected. Thus, the intensity distribution described in the first case is explained.

In fig.8.3(b) the minimum of the upper potential curve lies at a somewhat greater 'r' value than that of the lower. Therefore, the transition from minimum to minimum (0-0) band is no longer the most probable. Since the internuclear distance must alter somewhat in such a transition. The most probable transition. The most probable transition is that from A to B (i.e vertically upwards). For this transition there is no change in the internuclear distance at the moment of "jump" and change of the velocity. For still higher vibrational levels an appreciable change of the internuclear distance or velocity must take place, as a result of which the intensities at the bands decrease again with increasing v'' . Thus, the intensity distribution in the second case is explained.

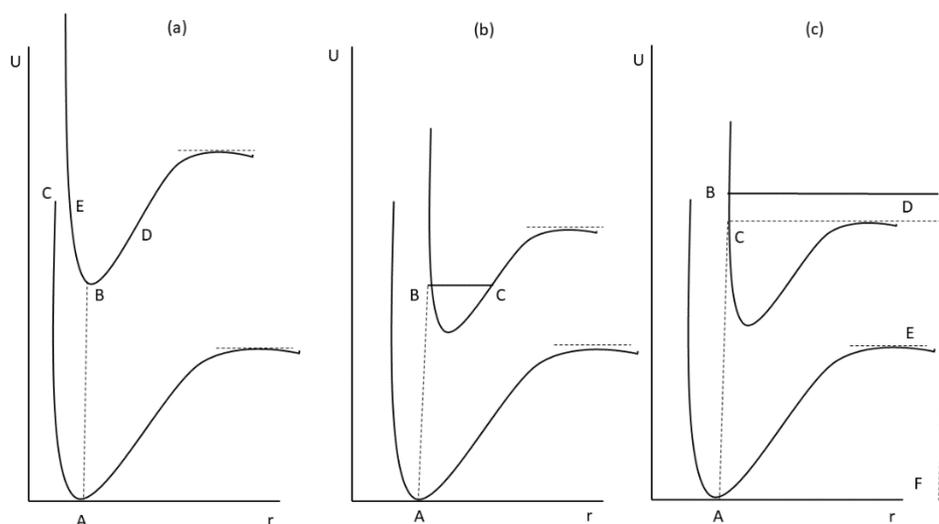


Fig.8.3 Potential curves Explaining the Intensity distribution in absorption according to the Franck-Condon Principle.

In fig.8.3(c) the minimum of the upper potential curve lies at a still greatest internuclear distance. If the vertical jump, according to the Franck-Condon's principle is to be followed, the most probable transition can be only to B from A. However, the point B lies above the dissociation limit and therefore it corresponds to the continuum region. After such an electron jump the atoms will fly apart. Transitions to points somewhat below B with discrete

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lines and somewhat above B, with continuum region are also possible. In this way the third case of intensity distribution is explained.

Condon has shown a wave-mechanical treatment which confirms in a general way the basic assumption of the Franck-Condon principle that transitions vertically upward or downward in the potential energy diagram correspond to the most intense bands. The wave mechanical treatment of Condon is explained.

8.5 Portrait parabola:

In the vibrational course structure of the electronic spectra, under high resolution each line in the spectrum consists of a set of closed spaced lines caused by rotational fine structure of electronic vibration transition. To study the vibrational course structure we started with the approximation of rotation less states, but no study the rotational fine structure, we must take the rotational energy also into account.

For any given vibrational transition, the changes in the rotational states gives,

$$v = v_e + v_v + v_r \dots\dots\dots (8.5)$$

$v_e + v_v$ is a constant

$$v = v_0 + F'(J') - F''(J'') \dots\dots\dots (8.6)$$

Where v_0 -Band origin

$$v = v_0 + B'_v J'(J' + 1) - D'_v J'^2 (J' + 1)^2 + \dots\dots\dots$$

$$-[B''_v J''(J'' + 1) - D''_v J''^2 (J'' + 1)^2 + \dots\dots\dots] \dots\dots\dots (8.7)$$

Selection rule

A selection rule,

$$\Delta J = J' - J'' = 0, \pm 1 \dots\dots\dots (8.8)$$

is applied, when one of the two participating electronic states is with $A \neq 0$.

If $A=0$ in both the electronic states, (ie) $\Sigma-\Sigma$ transition, then $\Delta J=0$ is forbidden and only $\Delta J=\pm 1$ appears

For $\Delta J=+1$, R-branch : $v_R = v_0 + F'_v(J' + 1) - F''_v J''$

For $\Delta J=+1$, Q-branch : $v_Q = v_0 + F'_v(J') - F''_v J''$

For $\Delta J=+1$, P-branch : $v_P = v_0 + F'_v(J' - 1) - F''_v J'' \dots\dots\dots (8.9)$

Substituting the expression for F'_v and F''_v , we have

$$\begin{aligned} \nu_R &= \nu_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2 \\ \nu_Q &= \nu_0 + (B'_v - B''_v)J + (B'_v - B''_v)J^2 \\ \nu_P &= \nu_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2 \dots\dots\dots(8.10) \end{aligned}$$

We can write a general formula for P & R branches, as

$$\nu_Q = \nu_0 + (B'_v - B''_v)m + (B'_v - B''_v)m^2 \dots\dots\dots(8.11)$$

Where, $m = J + 1$ for R branch

$m = -J$ for P branch

If we represent the equation (8.11), with ν as abscissa and m as ordinate, we get a Parabolic parabola corresponding to P and R branches. From the parabola we can understand how the band head is formed. The vertex of the parabola corresponds to the head.

The m value corresponding to the vertex of the parabola is obtained putting,

$$\begin{aligned} \frac{d\nu}{dm} &= 0 \text{ in equation (8.11). This gives,} \\ m_{\text{vertex}} &= - \frac{B'_v + B''_v}{2(B'_v - B''_v)} \dots\dots\dots(8.12) \end{aligned}$$

By substituting this in equation (8.11), we get,

$$\nu_{\text{head}} - \nu_0 = - \frac{(B'_v + B''_v)^2}{4(B'_v - B''_v)} \dots\dots\dots(8.13)$$

If $(B'_v - B''_v)$ is negative, the band head appears in the R branch on the high wave number side; such a band is said to be degraded (or shaded) towards the red. If on the other hand, $(B'_v - B''_v)$ is positive, the band head appears in the P-branch and such a Band is shaded towards violet.

8.6 Dissociation:

What a stable molecule is supplied with an energy than a particular value, the molecule will dissociate into its constituent atoms. That energy required to a stable diatomic molecule AB into two atoms A and B is known as dissociation energy. The dissociation energy if it is measured from the zero-point energy of a state (ie from $\nu=0$), then it is named D_0 . The equilibrium dissociation energy D_c is represented by,

$$D_c = D_0 + \text{zero point energy} \dots\dots\dots(8.14)$$

Normally, the electronic band spectra of diatomic molecules consist of a series of vibrational course structure with or without rotational fine structure followed by a continuous. The lower end of the continuous represents the

energy required just to dissociate the molecule into atoms without any kinetic energy. The measurement of D_0' , D_0'' , D_e and E_{ex} are shown in the Fig.8.4.

The wave number corresponding to continuum limit can be represented as

$$\nu_{\text{cont limit}} = \nu_{00} + D_0' \dots\dots\dots(8.15)$$

$$D_0'' = \nu_{00} + D_0' - E_{ex} \dots\dots\dots(8.16)$$

The value of ν_{cont} limit can be accurately measured from electronic spectroscopy and E_{ex} from atomic spectroscopy. From these values the dissociation energy can be easily estimated.

We know, the vibrational term value of a diatomic molecule given by

$$G(v) = \omega_c (v + 1/2) - \omega_c x_c (v + 1/2)^2 \dots\dots\dots(8.17)$$

The separation between successive vibrational levels ΔE .

$$\Delta E = G(v+1) - G(v) = \omega_c [1 - 2x_c (v+1)] \text{ cm}^{-1} \dots\dots\dots(8.18)$$

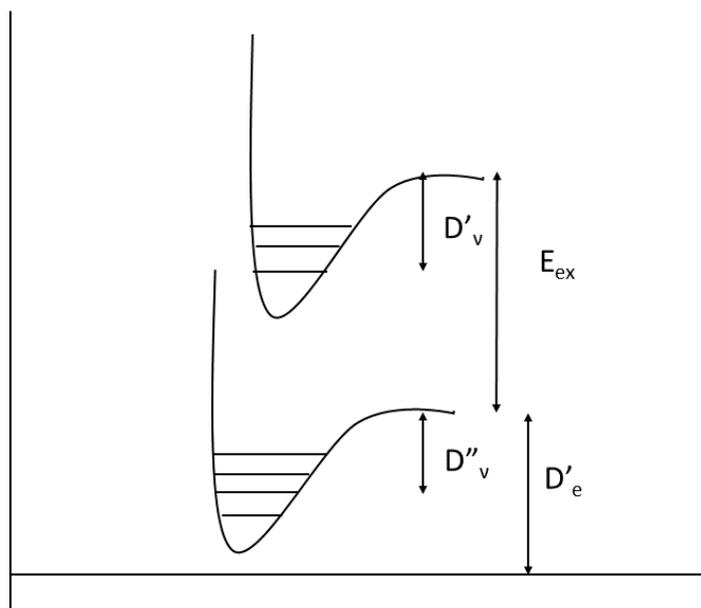


Fig.8.4 Dissociation energies of ground and excited electronic states

The separation between successive vibrational levels decreases linearly with increasing value of vibrational quantum number 'v' and tends to zero when the dissociation limit is reached. Denoting the value of v corresponding to the dissociation limit ($\Delta E=0$) by ν_{max} , we have,

$$\omega_c [1 - 2x_c(\nu_{\text{max}} + 1)] = 0 \dots\dots\dots(8.19)$$

$$\nu_{\text{max}} = \frac{1}{2x_c} - 1 \dots\dots\dots(8.20)$$

The vibrational energy for $v=v_{\max}$ corresponds to the dissociation energy D_e . Substituting the expression (8.20) in to equation (8.17), we get the expression for dissociation energy D_e .

$$D_e = \left(\frac{1}{2x_e} - \frac{1}{2}\right)\omega_e - \left(\frac{1}{2x_e} - \frac{1}{2}\right)^2\omega_e x_e \dots \dots \dots (8.21)$$

$$= \frac{\omega_e}{4x_e} - \frac{1}{4}\omega_e x_e \approx \frac{\omega_e}{4x_e} \text{ cm}^{-1} \dots \dots \dots (8.22)$$

The value of D_e may be estimated from the known values of ω_e and x_e from which the value of D_v can be evaluated.

8.7 Predissociation:

With ordinary dissociation, the electronic spectra jumps the continuum at the high wave number side. But in some cases, the rotational fine structure is diffused of a complete continuum is observed for intermediate transition of vibration levels. This kind of occurrence of diffuse structure or complete continuum below the actual dissociation limit is known as predissociation. It was observed in the electronic spectrum of S2.

With more potential energy curve of stable and unstable electronic states fig.8.5, this predissociation can be easily explained.

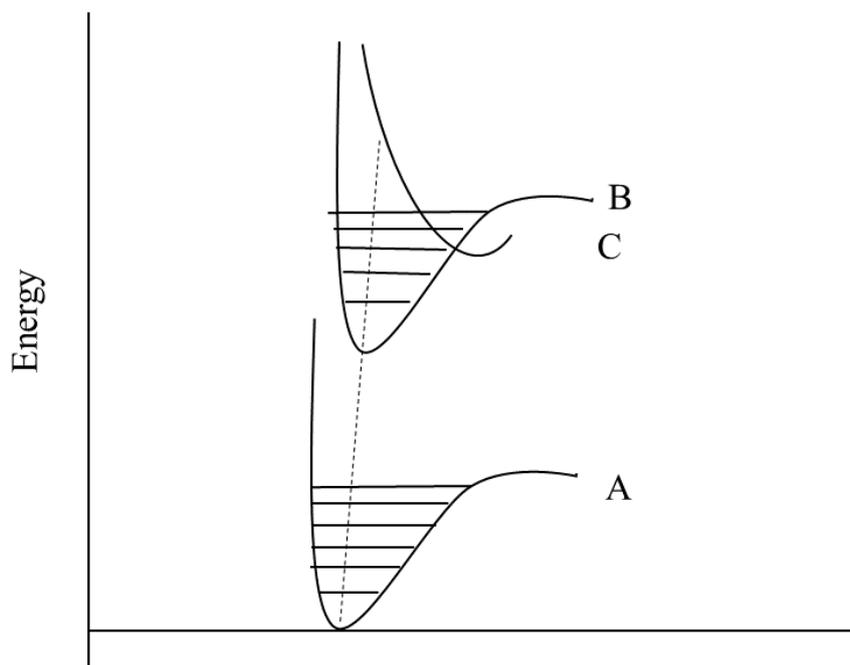


Fig. 8.5 Predissociation occurring due to intersected unstable

Consider a transition is taking place from a curve A to curve B upto the transition to the levels $v'=0,1,2,3$, in the upper stable state B, we get the normal vibrational electronic spectrum with rotation fine structure also. When the transitions goes to $v'=4$, there is a possibility that the molecule will cross over transition from curve B to curve C takes place, there will not be any

rotation of the molecule, since the time required for molecular vibration is very small compared to that for a molecular rotation. However, the transition to the levels $v'=5,6,7,\dots$ will give normal vibrational electronic spectrum with rotational fine structure.

8.8 Mutual exclusion Principle:

A further extremely important general rule has been established whose operation may be exemplified by carbon dioxide. We can summarize our conclusions about the Raman and infra-red activities of the fundamental vibration of the molecule in Table and we see that, for this molecule, no vibration is simultaneously active in both Raman and infra-red. The corresponding general rule is

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

The converse of this rule is also true, i.e., the observance of Raman and infra-red spectra showing no common lines implies that the molecule has a centre of symmetry: but have cautions is necessary since, as we have already seen, a vibration may be Raman active but too weak to be observed. However, if some vibrations are observed to give coincident Raman and infra-red absorption it is certain that the molecule has no centre of symmetry. Thus extremely valuable structural information is obtainable by comparison of the Raman and infra-red spectra of a substance.

8.9 Summary

- ❖ we have seen that in general only the transitions vertically upward or downward in the potential energy curve correspond to the most intense bands.
- ❖ The electron jump in a molecule takes place so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump.
- ❖ In the vibrational course structure of the electronic spectra, under high resolution each line in the spectrum consists of a set of closed spaced lines caused by rotational fine structure of electronic vibration transition.
- ❖ The energy required to a stable diatomic molecule AB into two atoms A and B is known as dissociation energy.
- ❖ This kind of occurrence of diffuse structure or complete continuum below the actual dissociation limit is known as predissociation.
- ❖ *If a molecule has a centre of symmetry then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry*

then some (but not necessarily all) vibrations may be both Raman and infra-red active.

8.10 Review questions

1. State the Franck-Condon principle and explain how it accounts for the three types of intensity distributions observed in electronic band spectra.
2. What is dissociation energy? Arrive an expression for the maximum number vibrational levels below the dissociation limit.
3. Explain predissociation.
4. What is rule of mutual exclusion? Explain with examples.

8.11 Further Reading

1. Atomic and Molecular spectroscopy M.C.Gupta, New Age Int.national Publishers.
2. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCASH. Tata McGraw Hill Edition.

**BLOCK III: NON LINEAR SPECTROSCOPIC
PHENOMINA**

UNIT IX HYPER RAMAN EFFECT

Structure:

- 9.1 Introduction
- 9.2 Objectives
- 9.3 Non linear Raman Phenomena
- 9.4 Hyper Raman effect- Classical treatment
- 9.5 Experimental techniques
- 9.6 Stimulated Raman Scattering
- 9.7 Let us sum up
- 9.8 Review questions
- 9.9 Further readings

9.1 Introduction:

Laser plays a vital role in spectroscopy, not only in giving high intensity source but also in introducing a host of non-linear phenomena. According to the classical theory of the Raman effect, when a molecule is put into a static electric field it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field and the electrons to the positive. This separation forms a dipole which causes an induced dipole moment to be associated with that of the radiation passing through the medium, the induced dipole moment P can be written as

$$P = \alpha E \quad \dots\dots\dots(9.1)$$

Where α is called the polarizability of the molecule, which is also a tensor. This equation (9.1) is considered when the source is with normal intensity. But, if the intensity of the light increases, we know the electric field associated with the light also will increase. Nowadays, it is possible to generate 1MW pulses of laser lasting a few tenths of nanoseconds. This can produce an electric field strength of 3×10^7 V/m. At such high fields, the relationship between the electric polarization P and the field strength E ceases to be linear and many non-linear effects come to the fore.

Alternately, the equation (9.1) can be written as the dipole moment per unit volume for ordinary source

$$P = \epsilon_0 \chi E \quad \dots\dots\dots(9.2)$$

Where χ is the polarizability of the medium or dielectric susceptibility. For high intensity, radiation, the relation becomes,

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots\dots\dots(9.3)$$

$\chi^{(2)}$, $\chi^{(3)}$etc. are degree of non-linearity and known as non-linear susceptibilities.

Media which impose their characteristic frequencies on the incident light wave are called active media. In these media, the interval vibration modifies

the internal structure and so they present a periodically varying polarizability to the electromagnetic field. Non-linear optical phenomena in active media led to the discovery of a large number of spectroscopic phenomena and propelled Raman spectroscopy into its present popularity. Some of the non-linear spectroscopic phenomena are:

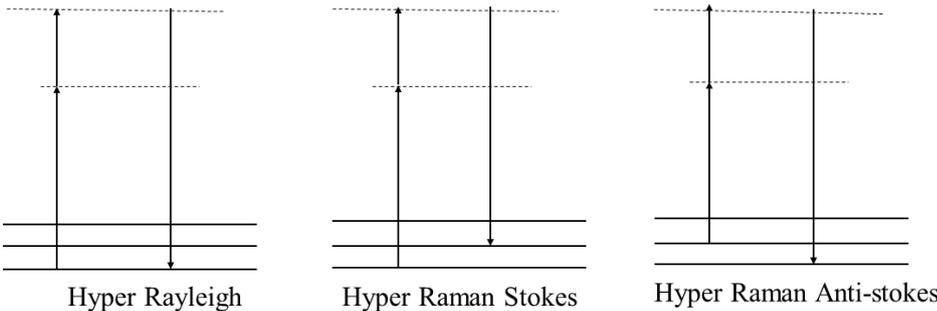
- i) Hyper Raman effect
- ii) Stimulated Raman scattering (SRS)
- iii) Coherent Raman scattering (CARS)
- iv) Inverse Raman scattering (IRS)
- v) Photo Acoustic Raman scattering (PARS)

9.2 Objectives:

Here, Non-linear phenomena is discussed. Hyper Raman effect and its experimental techniques are deliberated. Stimulated Raman scattering is also discussed.

9.3 Hyper Raman Effect:

It has been found that when a system is illuminated with radiation of wave number ν_0 from a focused giant-pulse laser, it gives rise to a scattered radiation at twice the incident frequency $2\nu_0$ (elastic scattering) and at displaced frequencies $2\nu_0 \pm \nu_m$ (inelastic scattering) where ν_0 corresponds to Raman active vibration of the molecule. These elastic and inelastic scatterings are now referred to as hyper-Rayleigh and hyper Raman scattering respectively. If the electric field E associated with the incident radiation is extremely high, we can observe the additional scattered with the incident radiation is extremely high, we can observe the additional scattered radiations at frequencies $3\nu_0$ and $(3\nu_0 \pm \nu_m)$. Hyper Rayleigh and hyper Raman scattering are three photon process with two incident photons and one scattered photon.



Classical treatment

We have seen in equation (9.3), that the second order induced dipole is given by,

$$P^{(2)} = \epsilon_0 \chi^{(2)} E \cdot E \dots\dots\dots(9.4)$$

The time dependence of the electric field E associated with the incident radiation can be written as

$$E = E_0 \cos 2\pi\nu_m t \dots\dots\dots(9.5)$$

For a molecule oscillating with frequency ν_m in the simple harmonic approximation, we write,

Notes

$$Q=Q_0\cos 2\pi\nu_m t \dots\dots\dots(9.6)$$

Where Q is the displacement. The dependence of $\chi^{(2)}$ on Q, to a first approximation is given by,

$$X^{(2)}=\chi_0^{(2)} + \frac{\partial\chi^{(2)}}{\partial Q}Q \dots\dots\dots(9.7)$$

Substituting (9.5), (9.6) and (9.7) in (9.4), we have,

$$\begin{aligned} P^{(2)} &= \epsilon_0 \left\{ \chi_0^{(2)} + \frac{\partial\chi^{(2)}}{\partial Q} Q_0 \cos 2\pi\nu_m t \right\} E_0^2 \cos^2 2\pi\nu t \\ &= \epsilon_0 \left\{ \chi_0^{(2)} + \frac{\partial\chi^{(2)}}{\partial Q} Q_0 \cos 2\pi\nu_m t \right\} E_0^2 \left(\frac{1+\cos 4\pi\nu t}{2} \right) \\ &= 1/2 \epsilon_0 \chi_0^{(2)} E_0^2 + 1/2 \epsilon_0 Q_0 \left(\frac{\partial\chi^{(2)}}{\partial Q} \right) E_0^2 \cos 2\pi\nu_m t + 1/2 \epsilon_0 \chi_0^{(2)} E_0^2 \cos 4\pi\nu_m t \\ &\quad + 1/2 \epsilon_0 Q_0 \left(\frac{\partial\chi^{(2)}}{\partial Q} \right) E_0^2 \cos 2\pi\nu_m t \cos 4\pi\nu_m t \\ &= 1/2 \epsilon_0 \chi_0^{(2)} E_0^2 + 1/2 \epsilon_0 Q_0 \left(\frac{\partial\chi^{(2)}}{\partial Q} \right) E_0^2 \cos 2\pi\nu_m t + 1/2 \epsilon_0 \chi_0^{(2)} E_0^2 \cos 4\pi\nu_m t \\ &\quad + 1/4 \epsilon_0 Q_0 \left(\frac{\partial\chi^{(2)}}{\partial Q} \right) E_0^2 [\cos 2\pi(2\nu+\nu_m)t + \cos 2\pi(2\nu-\nu_m)t] \dots\dots\dots(9.8) \\ &= P_{(\nu=0)}^{(2)} + P_{(\nu_m)}^{(2)} + P_{(2\nu)}^{(2)} + P_{(2\nu\pm\nu_m)}^{(2)} \end{aligned}$$

The first term gives the static field: the second produces radiation at the molecular frequency; the third gives rise to a radiation at 2ν (hyper Rayleigh scattering) and the last term accounts for the radiation for the radiation at $(2\nu\pm\nu_m)$. Stokes and anti-stokes hyper-Raman scattering.

9.4 Experimental Techniques for Hyper Raman effect:

As already mentioned, only with giant pulse lasers, one can observe effects due to the nonlinear susceptibility χ_2 . A typical nanostructured pulse from a giant pulse laser would deliver about 10^{17} photons to the sample at frequency ν_0 . But the number of photons of frequency $2\nu_0-\nu_m$ which the detector would receive ranges from a few photons per laser pulse down to 1 photon for every 100 laser pulses depending on the sample. There are two methods of observing the scattered radiations of such low intensities (i) single channel detection (ii) multichannel detection. In both cases, radiations from a giant pulse laser is focused on to the sample and the radiations scattered at right angles to the laser beam is collected with a wide angle lens and fed to a grating system which disperse the radiation.

In single channel detection, the grating dispersion system works as a monochromator. The monochromator is set to pass radiation over a narrow frequency range. The intensity of the scattered radiation in this range is found by averaging the photoelectrons produced over a large number of laser pulses (usually 50 to 100). This procedure is then repeated, spectral element by spectral element over the whole frequency range of interest. This method is very time consuming and very hard on the laser and observer. For covering 1000 spectral elements one requires about 15 hours and about 50,000 laser shots.

In the multichannel method, the informations from all the spectral elements over the desired spectral region is received for each laser shot. The

grating dispersion system then operates as a spectrograph. The exit slit and photomultiplier are replaced by an image intensifier which intensify the complete spectrum to a level at which it can be scanned by a television camera. The information is stored in the digital form so that it can easily be combined with information from other laser shots and then averaged. At the end of the experiment, the stored data can be displayed in analogue form on an oscilloscope or plotter. Fig (9.1) gives the block diagram a multichannel instrument. Often several intensifier tubes are used in cascade to have a high photon gain. The television camera tube has the main advantage of direct beam read out of the image elements and transfer of information onto a magnetic tape, a magnetic disc or the memory of a computer. Though the procedure is more complicated, the same result can be achieved in much less time. The Laser wear and tear is also much less.

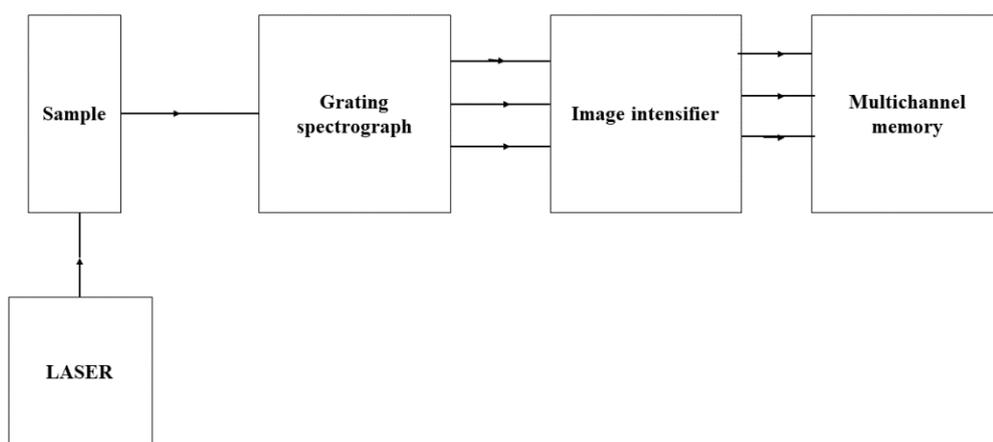


Fig.9.1 Block diagram of multichannel Raman spectrometer

9.5 Stimulated Raman Scattering

The giant-pulse or Q-switched laser system commonly used for the investigations of non-linear spectroscopy are ruby laser emitting at $\lambda=6943.3\text{\AA}$ and neodymium-glass laser with an output at $\lambda=10600\text{\AA}$. The outputs of these lasers are of short duration and of very high powers. The pulses extend over about 10 to 100 nanoseconds.

While experimenting with a Q-switched ruby laser, provided with a nitrobenzene- filled Kerr cell as shutter, it was observed besides the stimulated emission 6943.3\AA , an additional intense radiation at 7670\AA . This additional emission also displayed several characteristic properties of stimulated emission such as: i) a marked threshold occurred both when the ruby laser power and the length of the liquid column were varied, (ii) the line width was found to decrease with increasing input intensity; (iii) emission showed sharp directionality. The line 7670\AA was later identified as a line of the Raman spectrum of nitro benzene. By subsequent investigations with Raman active material placed inside the cavity of a Q-switched ruby laser, it was confirmed that the high power pulse induces gain in the medium at Stokes frequencies $\nu_0 - n\nu_m$ ($n=1,2,3,\dots$) shifted from the laser frequency ν_0 by multiples of various Raman frequencies ν_m of the medium. This process

being analogous to normal stimulated emission is called stimulated Raman scattering (SRS). Laser it was observed that if anti Stokes radiation at frequencies $\nu_0 + n\nu_M$ ($n=1,2,3,\dots$) is also generated due to an external beam from a giant pulse ruby laser when focused into cells containing Raman active liquids.

A typical arrangement for detection of stimulated Raman scattering is shown in Fig. (9.2). A giant pulse laser radiation is focused into the sample and the scattering is observed along the laser beam direction and at small angles to this direction. If the forward scattered radiation is dispersed and photographically recorded, it is found to consist of the incident wave number ν_0 and the Stokes and anti-Stokes lines at $\nu_0 \pm \nu_M$ where ν_M corresponds to just one Raman active vibration of the radiation scattered by liquid benzene, when illuminated with the focused output of a giant pulsed ruby laser, shown Stokes and anti-Stokes shifts which are exact multiples of the wave number of the strongest vibrational band in the normal Raman spectrum of benzene, viz.: 992 cm^{-1}

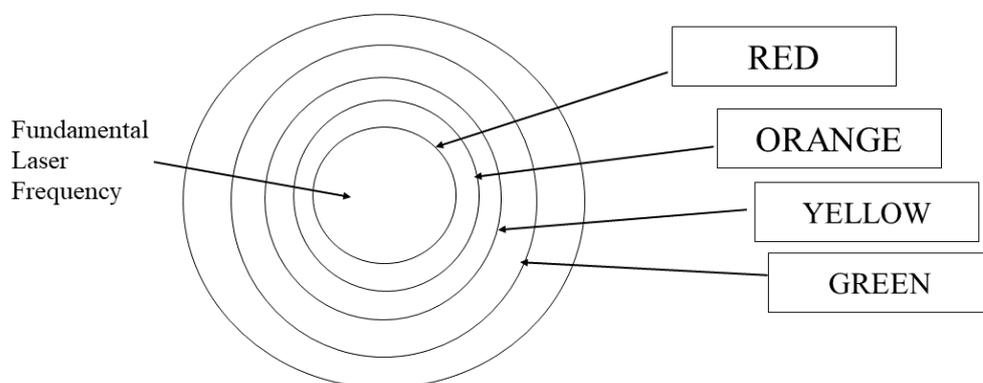


Fig.9.2 Stimulated Raman Effect on a colour sensitive film.

If the forward scattered radiation is photographed on a colour sensitive film, a striking pattern of concentric coloured rings is obtained (Fig.9.2), which reveals that stimulated Raman scattering has a spectral angular dependence. These additional wavelengths are as coherent and as well collimated as the main beam. The red spot at the centre corresponds to the ruby laser wavelengths and also to the Stokes bands which lie at lower wavenumbers and are emitted essentially along the laser beam direction. The coloured rings correspond to the successive anti-Stokes lines at higher wavenumbers which are emitted only along directions which makes specific small angles with the laser beam direction.

Investigations have revealed that the mechanism responsible for the enhancement of the stimulated Raman Stokes lines is that of parametric amplification. The power transferred to the first Stokes line at $\nu_0 + \nu_M$ is related exponentially to the power in the laser at ν_0 . The first Stokes line rapidly becomes intense enough to act as a powerful source at wave numbers $\nu_0 - \nu_M$ and another Stokes line at

$$(\nu_0 + \nu_M) - \nu_M = \nu_0 - 2\nu_M \dots \dots \dots (9.9)$$

is generated. As this line gains in intensity, it acts as another source giving rise to a third line and so on.

The generation of the anti-stokes wavenumbers does not arise as a result of downward transitions from a populated upper state. The essential difference between stimulated Raman scattering and stimulated emission in lasers is that in Raman scattering there is for inverting the population of the states. The generation for anti-stokes lines corresponds to the frequency conversion process.

One may, formally, regard the anti-Stokes photons to be created at the expense of two laser photons, Conversion of energy demands that the following relation be satisfied

$$2h\nu_0 = (h\nu_0 + h\nu_M) + (h\nu_0 - h\nu_M) \dots \dots \dots (9.10)$$

Which dictates that a Stokes line is also generated along with the anti-Stokes line. Thus, two incident photons are destructed and two photons with frequencies $\nu_0 - \nu_M$ and $\nu_0 + \nu_M$ are created so that conservation of energy is achieved. Conservation of momentum leads to the anti-stokes photons being restricted to a particular angle with the laser beam direction and consequently the emitted radiation occurs in rings around the forward scattered laser beam.

9.8 Summary

- ❖ when a molecule is put into a static electric field it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field and the electrons to the positive.
- ❖ when a system is illuminated with radiation of wave number ν_0 from a focused giant-pulse laser, it gives rise to a scattered radiation at twice the incident frequency $2\nu_0$.
- ❖ The giant-pulse or Q-switched laser system commonly used for the investigations of non-linear spectroscopy are ruby laser emitting at $\lambda = 6943.3 \text{ \AA}$ and neodymium-glass laser with an output at $\lambda = 10600 \text{ \AA}$.

9.9 Review questions

1. What is the condition for observing non-linear Raman Phenomena?
2. List some non-linear Raman phenomenon.
3. What is hyper Raman effect? Give the classical treatment of hyper Raman effect.
4. Explain the principle of stimulated Raman scattering.
5. Give some of the characteristic properties of the stimulated emissions.

9.9 Further Reading

Hyper Raman Effect

Notes

1. Fundamentals of Molecular spectroscopy – Colin N.Banwell Tata Mcgraw Hill Edn.
2. Atomic and Molecular spectroscopy M.C.Gupta, New Age International publishers.

UNIT X INVERSE RAMAN EFFECT

Structure:

- 1.1 Introduction- Inverse Raman Effect
- 1.2 Objectives
- 1.3 Coherent Anti-Stoke's Raman Scattering
- 1.4 Photo acoustic Raman Scattering.
- 1.5 Summary
- 1.6 Review questions
- 1.7 Further readings

10.1 Introduction:

Raman scattering is inelastic scattering of photons of energy $h\nu_1$ by molecules of substances. If the scattered photon has an energy $h(\nu_0+\nu_m)$, the incident photon gained an amount of energy $h\nu_m$ from the molecule. The energy balance equation for this normal anti-Stokes Raman is illustrated in Fig.10.1, If this process is inverted, the scattering molecules absorbs radiation of frequency $(\nu_0+\nu_m)$ resulting in the molecule going to a higher energy level and the emission of radiation frequency ν_0 . This phenomenon is called the inverse anti-Stokes Raman effect which is illustrated in Fig.10.1

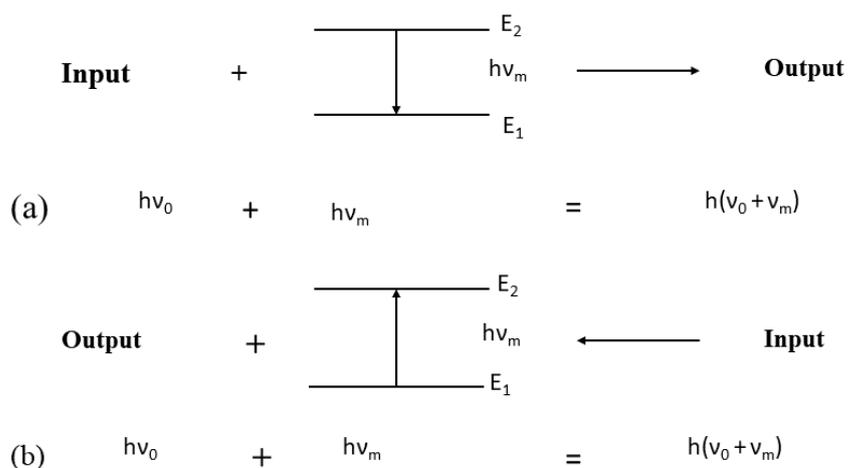


Fig.10.1 a) Anti-stokes Raman effect, b) Inverse anti-stokes Raman effect

The absorption of radiation of frequency $\nu_0-\nu_m$ by the molecule would result in a decrease in the energy of the scattering molecule by $h\nu_m$ and emission of radiation of energy $h\nu_0$. This process is inverse Raman effect which is illustrated in Fig.10.2. This complementary effect requires appropriate population of the upper state.

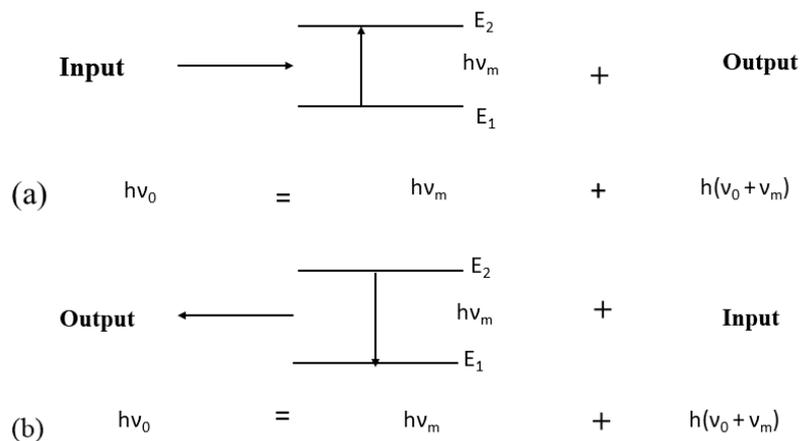


Fig. 10.2 (a) Stokes Raman effect, (b) inverse Stokes Raman effect.

It is found that absorption at frequencies $\nu_0 \pm \nu_m$ can occur only in the presence of very intense radiation a frequency ν_0 . Thus, the essential requirements for the observation of inverse Raman effect are the simultaneous irradiation of the sample with a giant pulse laser beam of frequency ν_0 and a strong continuum covering the Stokes and anti-Stokes regions in which absorptions are expected. If the continuum covers the wave number range $\bar{\nu}_0$ to $\bar{\nu}_m + 3500 \text{ cm}^{-1}$. Absorption will be observed (inverse of the anti-stokes Raman effect) in the continuum at wave numbers $\bar{\nu}_0 + \bar{\nu}_m$ where ν_m corresponds to the Raman active vibration of the system. If the continuum is extended to include the low wave number side of ν_0 , absorption at $(\bar{\nu}_0 - \bar{\nu}_m)$ with an accompanying emission at $\bar{\nu}_0$ can be observed (inverse of Stokes Raman effect).

In practice, conditions necessary for the observation of inverse Raman effect are difficult to achieve. The continuum must coincide with the laser pulse as it passes through the system. It must be of adequate intensity for detection in the duration of the experiment, which is the duration of the giant pulse (typically) 10^{-8} to 10^{-7} s). Ideally, the continuum should be strong. The first experimental arrangement which Jones and Stoicheff used in 1964 is given in Fig.10.3

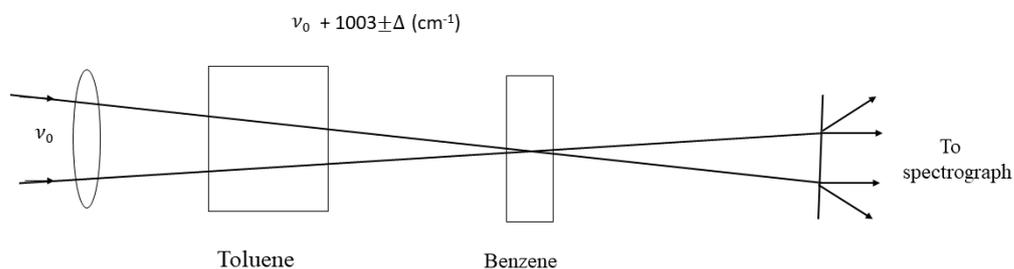


Fig.10.3 Experimental arrangement for inverse Raman effect.

The radiation from a giant pulse ruby laser is first passed through a cell containing toluene which gives a broad anti-stokes Raman band $\nu_0 + 1003 \pm \Delta \text{ cm}^{-1}$, This radiation together with the unchanged laser radiation at ν_0 (not shown) is passed through a second cell containing benzene. Since benzene has

a strong Raman active molecular frequency at 992 cm^{-1} which is within the range $1003 \pm \Delta\text{ cm}^{-1}$, a strong absorption is observed. With improved experimental techniques, inverse Raman spectroscopy offers a potential method for the study of very short-lived species and the measurement of very short lifetimes.

10.2 Objectives:

In this chapter, Inverse Raman effect is discussed. Coherent Anti-stoke's Raman scattering and Photoacoustic Raman scattering are deliberated.

10.3 Coherent Anti-Stoke's Raman Scattering:

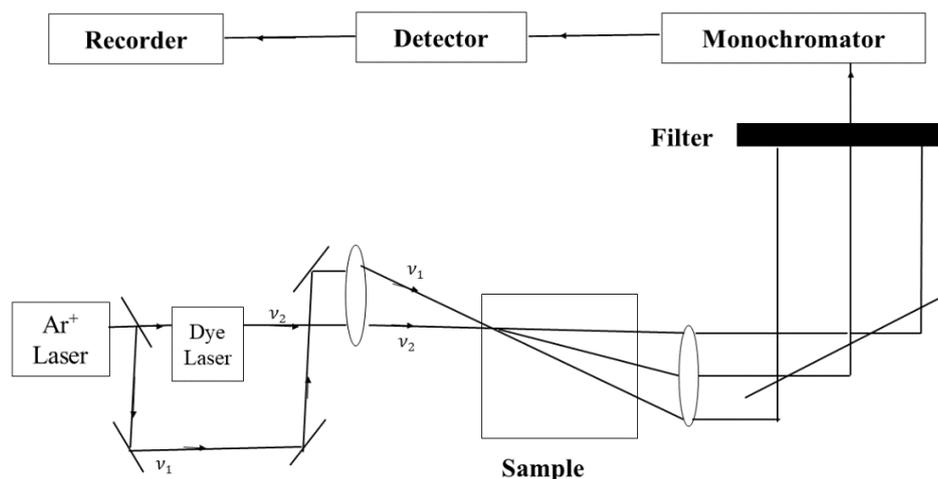
The coherent anti-stokes Raman scattering combines the advantages of stimulated Raman scattering and the general applicability of normal Raman scattering. The technique involves two powerful collinear laser beams. If a coherent radiation of frequency ν_1 is mixed in a molecular medium with coherent radiation of frequency ν_2 and their irradiation are sufficiently high, then a new coherent radiation of wave number ν_3 is generated, where

$$\nu_3 = \nu_1 + (\nu_1 - \nu_2) \dots\dots\dots(10.1)$$

If, further, ν_1 is as adjusted that $\nu_1 - \nu_2 = \nu_m$ where ν_m is a Raman active vibration of the molecule under investigation, then

$$\nu_3 = \nu_1 + \nu_m \dots\dots\dots(10.2)$$

In this case ν_3 is coincident in wave number with anti-Stokes Raman scattering associated with the molecular wave number ν_m . Radiation produced in this way is termed coherent Anti-stokes Raman scattering (CARS). CARS in the normal Raman effect, and (ii) because the radiation ν_3 is highly



coherent

Fig. 10.4 Experimental arrangements for CARS

Notes

is superior to normal Raman scattering. (i) because conversion efficiency to ν_3 in CARS is several orders of magnitude greater than the conversion efficiency and confined to a small solid angle; whereas, normal Raman scattering is incoherent and extends over a solid angle 4π .

Different experimental arrangements are available depending on the purpose for which it is used, 'Figure10.4 illustrates a typical CARS setup where the two incident radiation are provided by the 514.5 nm argon ion laser line (ν_1) and a continuous wave dye laser (ν_2) pumped by the same argon ion laser.

This CARS experiment does not require any dispersive medium. The fluorescence free nature of CARS makes it an ideal tool for high resolution spectroscopy studies of biological samples.

10.4 Photo acoustic Raman Scattering:

Photo-acoustic spectroscopy is a sensitive technique for studying absorption mainly when very small concentration of molecular species have to be detected in the presence of other components. In this technique, a laser beam is sent through an absorber cell and tuned to the absorbing molecular transition $E_a \rightarrow E_b$, part of the molecules in the lower state(a) will be excited into the upper state(b). These excited states may transfer their energy parity or completely to other molecules by collision, in the form of translational, vibrational or rotational energy. At thermal equilibrium, this energy is randomly distributed among all degrees of freedom, causing an increase in thermal energy and thereby a rise of temperature and pressure. A chopping of the laser beam at frequencies below 20 kHz produces periodical pressure variations in the absorption cell which can be the microphone is proportional to the pressure changes induced by the absorbed radiations.

Photo-acoustic Raman scattering (PARS) is a nonlinear spectroscopic phenomenon basically different from the one discussed above as there is no absorption by the sample in this case. PARS require the simultaneous illumination of the sample by two laser beams ν_p and ν_s such that $\nu_p - \nu_s = \nu_m$, a Raman active transition frequency. The PARS process is schematically illustrated in Fig. 10.5

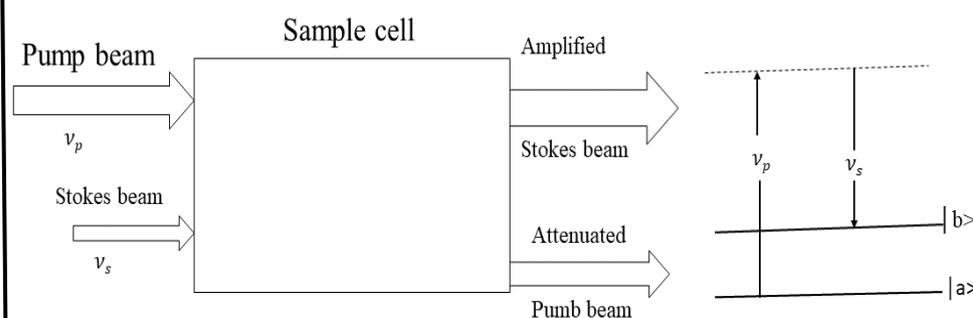


Fig.10.5 Photo acoustic Raman process

The incident laser beams with frequencies ν_p (pump beam) and ν_s (Stokes beam) interact with two energy states $|a\rangle$ and $|b\rangle$ of a molecule. By stimulated Raman scattering, the intensity of the Stokes beam increases and that of the pump beam decreases. This causes an increase in the molecular population of the upper state $|b\rangle$. For this to happen, the pump and Stokes beams must mix spatially and temporally in the gas sample. During or following the stimulated Raman scattering, collisional relaxation of these excited molecules produces a pressure change in the sample, causing an acoustic wave which is detected by a microphone. If the input lasers are modulated chopped at a rate which is slow compared to the vibrational to transitional relaxation rate, then the temperature and hence the gas pressure will vary at the modulation frequency. The modulated pressure wave is the sound wave which is detected. The Raman frequency ν_m between the states is given by $h\nu_m = (E_b - E_a)$. When the frequency of the incident lasers are adjusted such that $\nu_p - \nu_s = \nu_m$, a nonlinear interaction between ν_p and ν_s beams occurs through the third order nonlinear polarizability χ^3 of the sample. This nonlinear process is the one responsible for the amplification of the Stokes beam and the attenuation of the pump beam.

Fig.10.6 gives the schematic representation of the experimental arrangement used for obtaining PARS signal with CW laser sources. PARS differ from other nonlinear Raman techniques in the way the desired signal is detected. PARS technique involves the acoustic detection of a pressure change in the sample whereas other nonlinear Raman techniques are concerned with the measurement of an optical signal. This provides a new dimension to Raman experimental techniques and a direct way for detecting the energy deposited in the sample.

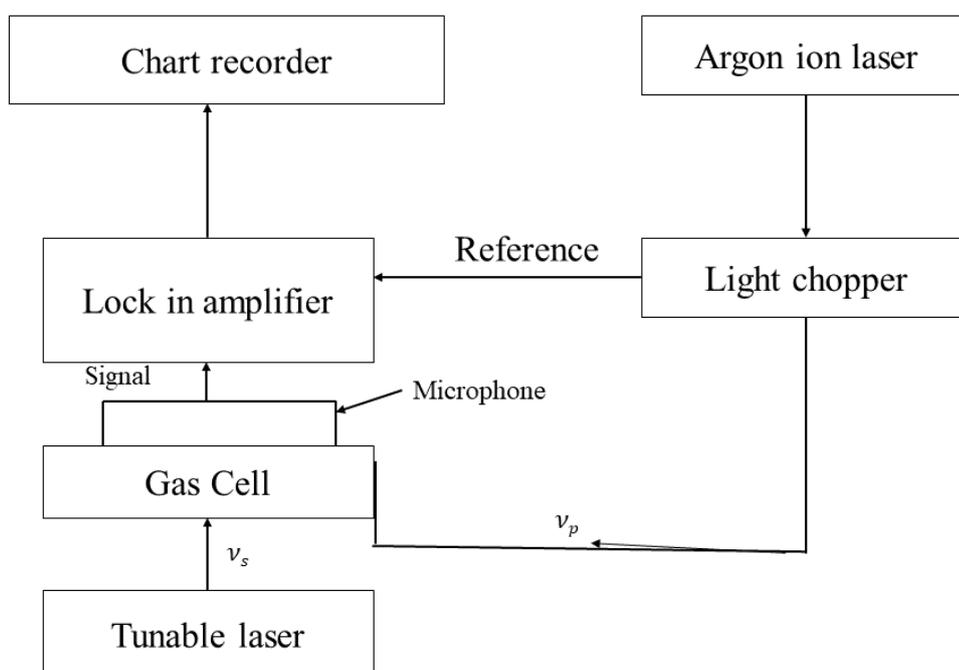


Fig.10.6 Schematic representation of the experimental set up used for PARS

Inverse Raman Effect

Notes

PARS technique has been successfully used to study pure rotational Raman transitions. The absence of the Rayleigh component is helpful in recording the low lying vibrational and rotational transitions. The high sensitivity of the technique provides a new method for the problem of trace analysis of gaseous mixture with a detection capability of about one part per million.

10.6 Let us sum up

- ❖ The scattering molecules absorbs radiation of frequency $(\nu_0 + \nu_m)$ resulting in the molecule going to a higher energy level and the emission of radiation frequency ν_0 .
- ❖ The coherent anti-stokes Raman scattering combines the advantages of stimulated Raman scattering and the general applicability of normal Raman scattering. The technique involves two powerful collinear laser beams.
- ❖ Photo-acoustic spectroscopy is a sensitive technique for studying absorption mainly when very small concentration of molecular species have to be detected in the presence of other components.

10.7 Review questions

1. Explain the principle of inverse Raman effect in detail.
2. Describe the techniques of observing the CARS.
3. Explain the principles of Photo acoustic Raman scatterings.

10.8 Further Readings

1. Molecular spectroscopy-Suresh Chandra, Narosa Publishers
2. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCASH. Tata McGraw Hill Edition.

UNIT XI MULTIPHOTON SPECTROSCOPY

Content:

- 11.1 Introduction -Multi photon spectroscopy
- 11.2 Objectives
- 11.3 Two photon absorption
- 11.4 Multiphoton absorption. X-ray spectra
- 11.5 Rotational and vibrational spectra of diatomic molecules
- 11.6 Summary
- 11.7 Review questions
- 11.8 Further readings

11.1 Introduction:

Multiphoton processes mean an interaction between radiation and matter accompanied by absorption or emission or both of two or more photons per elementary set. Though, this phenomenon was suggested theoretically with the advent of quantum mechanics, it was not exploited experimentally. Rayleigh and Raman scatterings were the only two -photon processes that could be sophisticated experimental techniques, multiphoton processes have assumed enormous importance. As a photon cannot absorb or scatter other photons, a quantum system such as an atom or a molecule possessing discrete energy levels is required for the realization of multiphoton processes. In the process, the quantum system which plays the role of an intermediary may remain in the same state or change to a different state. In Rayleigh scattering, the quantum system remains in the same state whereas in the case of Raman scattering it changes.

Multiphoton processes are explained on the basis of time dependent perturbation theory. As laser sources give very high photon flux with extremely high electric intensities, the interaction of the atom or molecule with more than one photon at the same time is possible. The interaction are described by second and higher order approximations of the perturbation theory. Detailed calculations give rise to the possibility of reaching the final state via a series of intermediate states called virtual states which are connected with the initial and final states by nonzero matrix elements. In each transition, the system absorbs or emits a photon. It may be pointed out here that, in the multiphoton process, the transitions cannot be considered as a temporal sequence of events but it must be understood as simultaneous events.

11.2 Objectives

In this chapter, Multiphoton spectroscopy is discussed. Two photon absorption and multiphoton absorption are deliberated. Rotational and vibrational spectra of diatomic molecules is discussed.

11.3 Two-Photon Absorption:

Two-photon absorption is a two-step process in which the transition occurs from the initial state $|i\rangle$ to the first state $|f\rangle$ via a virtual level $|V\rangle$. If the system absorbs one photon first and then the other, it is a case of two single-photon absorptions and not one two-photon absorption. The fictitious virtual level is represented by a linear combination of the wave functions of number of real molecular levels $|m\rangle$ which combine with $|i\rangle$ by allowing one-photon transitions. Some arguments hold for the step $|v\rangle \rightarrow |f\rangle$. If the virtual level coincides with a real intermediate level, one gets the resonant two-photon absorption. Fig.11.1 illustrates schematically three types of two-photon processes.

Consider a molecule undergoing a two-photon transition between the ground state $|i\rangle$ and the excited state $|f\rangle$ because of two photons of frequencies ν_1 and ν_2 and wave vectors k_1 and k_2 . When both waves are parallel, the Doppler width which is proportional to $|k_1+k_2|$ will become maximum and is large in comparison with the homogeneous width. When $k_1=-k_2$, there will not be any Doppler broadening leading to a pure Lorentzian line profile. This is the principle of Doppler free two-photon spectroscopy.

Fig.11.2 shows a possible experimental set-up for the observation of Doppler free two photon absorption the two oppositely travelling waves are formed by reflection of the output beam from a single mode tunable dye laser.

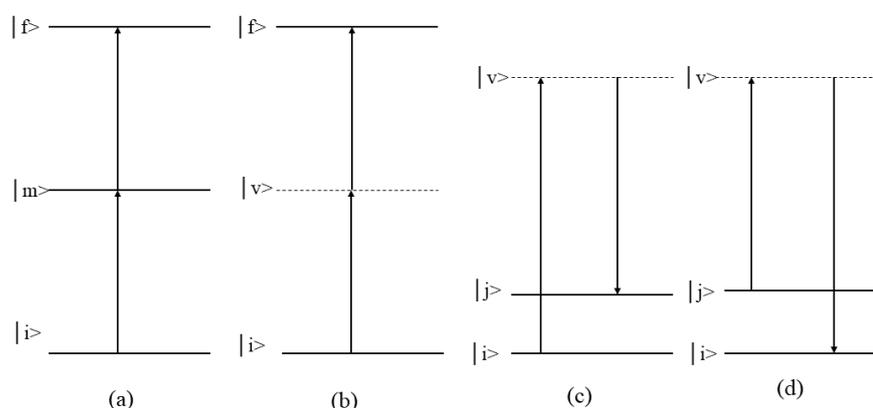


Fig.11.1 Energy level schemes of different two-photon transitions: (a) resonant two-photon absorption with a real intermediate level, (b) non-resonant two-photon absorption, (c) Raman Stokes transition, (d) anti-Stokes Raman transition.

The Faraday rotator prevents feedback into the laser. The two-photon absorption is monitored by the fluorescence emitted from the final state $|f\rangle$ into the other state $|m\rangle$.

A single photon absorption occurs between states of opposite parity. Hence, a two-photon absorption occurs between states of same parity and therefore transitions that are forbidden for one-photon absorption are allowed for two-photon absorptions.

Two-photon absorption is observed experimentally in number of cases. Fig.11.2 gives the energy levels of the cesium vapour in which a two-photon absorption is observed. The radiation from a ruby laser was focused on a cell containing cesium vapour. The filtered fluorescence output was detected by a

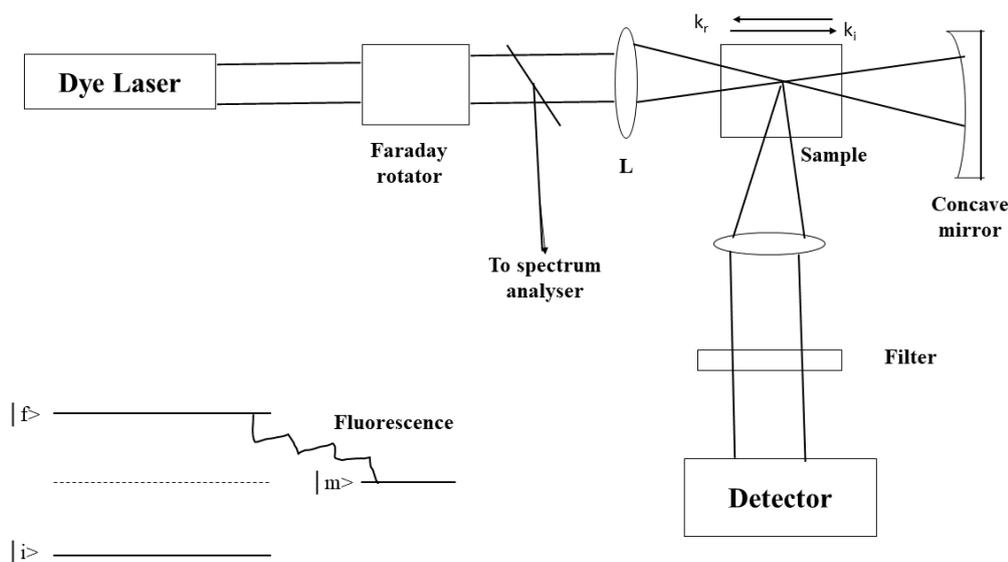


Fig.11.2. Experimental arrangement for Doppler free two-photon spectroscopy.

Notes

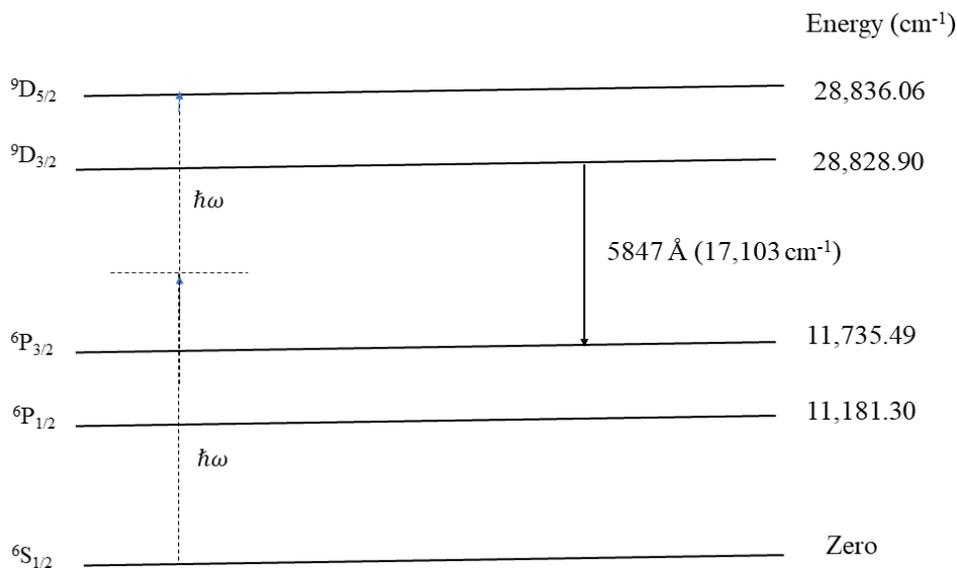


Fig. 11.3 Energy levels showing two-photon absorption in cesium vapour.

photomultiplier which was kept at right angles to the incident laser beam. No fluorescence was observed in the absence of the cesium vapour. With cesium vapour, a fluorescence was observed in the absence of the cesium vapour. With cesium vapour, a fluorescence line at 5847 Å corresponding to ⁹D_{3/2} → ⁶P_{3/2} transition was observed. Since the energy of the input radiation is only about 14,400 cm⁻¹, this emission can occur only if there is two-photon absorption.

11.4 Multi photon Absorption:

If the incident intensity is very large, a molecule may absorb several photons simultaneously, In the case of Doppler free multiphoton absorption, the following momentum and energy conservation equation have to be fulfilled

$$\sum P_i = \eta \sum k_i = 0 \dots\dots\dots(11.1)$$

$$\sum \eta \omega_i = E_f - E_i \dots\dots\dots(11.2)$$

Where E_f - E_i is the energy difference between the final and initial states. Each of the absorbed photons transfers the momentum ħk_i to the molecule. But according to equation (11.1) total momentum transfer is zero, which implied that the velocity of the absorbing molecule has not changed. That is, the photon energy $\sum_2 \hbar\omega_2$ is completely converted into excitation energy of the molecule. A precise determination of Lamb shift of 1s and 2s states is done with the help of multiphoton absorption method. Multiphoton absorption has also been observed on transitions within the electronic ground states of molecules induced by infrared radiations of a CO₂ laser. In short, multi photon absorption can be used for the excitation of high lying molecular levels with radiations having energies lower than one-photon absorption energies.

11.5 Rotational and vibrational spectra of diatomic molecules:

The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the “bond length” r . The rotation with respect to the bond axis is possible only for “classical” objects with large masses.

Multiphoton spectroscopy

Notes

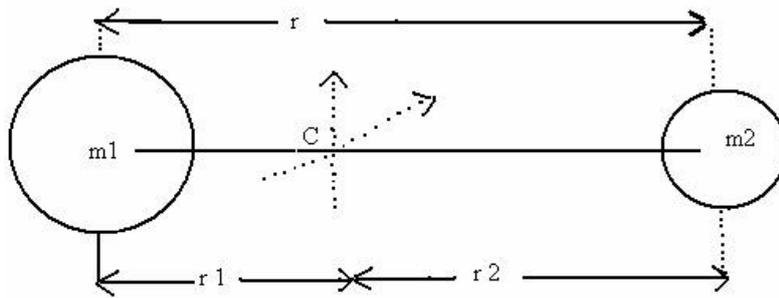


Fig.11.4 A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$. The centre of mass is at C.

For quantum objects, a “rotation” with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2 \quad \dots\dots\dots(11.3)$$

The moment of inertia is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots\dots\dots(11.4)$$

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

$$= r_1 r_2 (m_1 + m_2) \quad \dots\dots\dots(11.5)$$

Since $m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$, $(m_1 + m_2) r_1 = m_2 r$ Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad \dots\dots\dots(11.6)$$

substituting the above equation in (11.5)

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots\dots\dots(11.7)$$

Notes

where μ , the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \dots\dots\dots(11.8)$$

The rotation of a diatomic is equivalent to a “rotation” of a mass μ at a distance of r from the origin C . The kinetic energy of this rotational motion is $K.E=L^2/2I$ where L is the angular momentum, $I\omega$ where ω is the angular (rotational) velocity in radians/sec. The operator for L^2 is the same as the operator L^2 for the angular momentum of hydrogen atom and the solutions of the operator equation $L^2Y_{lm}=l(l+1) Y_{lm}$, where Y_{lm} are the spherical harmonics which have been studied earlier.

The quantized rotational energy levels for this diatomic are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \dots\dots\dots(11.9)$$

The energy difference between two rotational levels is usually expressed in cm^{-1} . The wave number corresponding to a given ΔE is given by

$$\nu = \Delta E/hc \text{ cm}^{-1} \dots\dots\dots(11.10)$$

The energy levels in cm^{-1} are therefore.

$$E_J = B J(J+1) \text{ where } B = \frac{h}{8\pi^2 Ic}$$

The rotational energy levels of a diatomic molecule are shown in Fig.

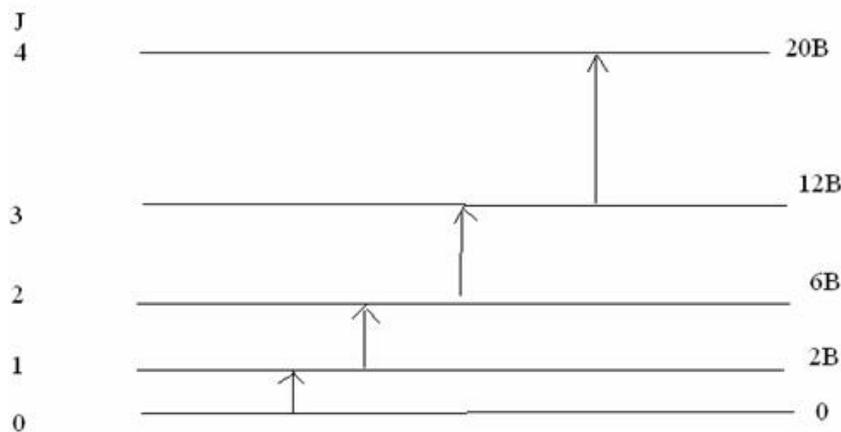


Fig. 11.5 Rotational energy levels of a rigid diatomic molecule and the allowed transitions.

The selection rule for a rotational transition is,

$$\Delta J = \pm 1 \dots\dots\dots(11.11)$$

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ . Molecules such as HCl and CO will show rotational

spectra while H_2 , Cl_2 and CO_2 will not. The rotational spectrum will appear as follows

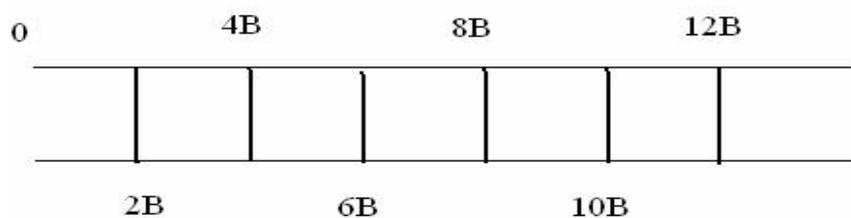


Fig. 11.6 Rotational spectrum of a rigid diatomic. Values of B are in cm^{-1} . Typical values of B in cm^{-1} are 1.92118 (CO), 10.593 (HCl), 20.956 (HF), 1 H_2 (60.864), 2 H_2 (30.442), 1.9987 (N_2).

From the value of B obtained from the rotational spectra, moments of inertia of molecules I , can be calculated. From the value of I , bond length can be deduced.

11.5 Summary

- ❖ Multiphoton processes mean an interaction between radiation and matter accompanied by absorption or emission or both of two or more photons per elementary set.
- ❖ Two-photon absorption is a two-step process in which the transition occurs from the initial state (i) to the first state $|f\rangle$ via a virtual level $|V\rangle$
- ❖ The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the “bond length” r .

11.6 Review questions

1. Write a detail note on multiphoton process.
2. Give the detailed theory on two photon process.
3. What is meant by multiphoton absorption?
4. Describe the rotational and vibrational spectra on diatomic molecule.

11.7 Further Reading

1. Fundamental of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCASH, Tata McGraw Hill Edition.
2. Atomic and Molecular spectroscopy M.C.Gupta, New Age International Publishers.

BLOCK IV: RESONANCE SPECTROSCOPY

UNIT XII NUCLEAR RESONANCE

Content:

- 12.1 Introduction
 - 12.2 Objectives
 - 12.3 Interaction between spin and magnetic field
 - 12.4 Nuclear resonance
 - 12.5 Bloch equations
 - 12.6 Chemical shift
 - 12.7 Dipole –Dipole interaction
 - 12.8 spin lattice interaction
 - 12.9 Summary
 - 12.10 Review questions
 - 12.11 Further readings
-

12.1 Introduction:

It is well known that all electrons and some nuclei possess a property called 'spin'. In atomic spectroscopy, fine structure of spectral lines such as doublet nature of sodium D-line, was explained with the spin of electrons. Nuclear spin was accounted for the hyperfine structure. Any spinning particles with some charges will behave as a tiny magnet with a magnetic moment of its own. The phenomenon of magnetic resonance is due to the interaction of an external magnetic field with the magnetic moment associated with the intrinsic spin of a nucleus or of an electron. Even though the behavior of these particles is almost alike, the experimental approach and the information which can be gained from the results are different. Therefore, the study of magnetic resonance has broadly been classified into two, they are (i) Nuclear Magnetic Resonance (NMR) and (ii) Electron Paramagnetic Resonance (EPR) or Electron spin Resonance (ESR).

12.2 Objectives

In this chapter, Interaction between spin and magnetic field is discussed. Nuclear resonance and Bloch equation are deliberated. Chemical shift, dipole-dipole interaction and spin lattice interaction are discussed

12.3 Magnetic properties of Nuclei:

The particles which make up an atomic nucleus, neutrons and protons, possess a property which is described as spin angular momentum. Nuclear structure is complex since the sub-particles have orbital as well as spin motions which combine together in various ways to give a resultant spin angular momentum of the nucleus, represented by $I\hbar$. This is quantized i.e., only certain values may occur. When a quantum mechanical operator corresponding to the property of spin, operates on nuclear spin wave function, it generates eigen values I which is called the nuclear spin quantum number.

This nuclear spin may be a half integer, or integer or zero depending on the mass number and charge of the nucleus. The following rules may be useful in determining the value of I .

- (1) Nuclei with both charge and mass even have zero spin. Examples:
 ${}^4_2\text{He}$, ${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$, ${}^{32}_{16}\text{S}$ etc.
- (2) Nuclei with both charge and mass odd, have integral spins.
Examples: ${}^2_1\text{H}$, ${}^{14}_7\text{N}$ (spin-1) and ${}^{10}_5\text{B}$ (spin-3), etc.
- (3) Nuclei with odd mass, have half integral spins. Examples:
 ${}^1_1\text{H}$, ${}^{15}_7\text{N}$ (spin=1/2), ${}^{17}_8\text{O}$ (spin=5/2) etc.,

The projection of the spin vector I can have $(2I+1)$ values which are all degenerate in the absence of any external magnetic field. In a magnetic field it splits up into $(2I+1)$ states. If a nucleus has spin, it behaves as a spinning finite spatial distribution of charge and a magnetic moment μ arises which is proportional to the magnitude of the spin, i.e.,

$$\mu = \gamma I \hbar \dots\dots\dots(12.1)$$

The proportionality constant γ is a fundamental nuclear property known as the gyromagnetic ratio, which may take positive or negative value. The equation (12.1) can be alternately expressed as

$$\mu = g_N \mu_N I \dots\dots\dots(12.2)$$

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

$$\mu_N = \frac{e\hbar}{2M} = 5.051 \times 10^{-27} \text{ JT}^{-1} \dots\dots\dots(12.3)$$

e and M are the charge and mass of proton.

12.3.1 Interaction between spin and magnetic field:

Let us consider an isolated nucleus of spin $\frac{1}{2}$ be placed in a steady magnetic induction B_0 . There is an interaction between the magnetic moment μ and the field, and the resulting energy is expressed quantum mechanically as the eigen values of a Hamiltonian operator:

$$H = -\mu B_0 \dots\dots\dots(12.4)$$

Nuclear Resonance

Notes

If the magnetic field is defined in the z-direction, it is necessary to consider the component of the nuclear magnetic moment vector along this direction. Quantum theory required that the z-component of the nuclear spin vector can only take up one of a set of discrete values I , which are the eigen values of the equation

$$I_z \psi_N = I \psi_N \dots\dots\dots(12.5)$$

I_z is spin angular momentum operator and I may only have the values I to $-I$ (i.e., $2I+1$) so that for a spin $\frac{1}{2}$ of a nucleus, its may be $\pm 1/2$.

Equation (12.4) may be written as

$$H = -g_N \mu_N B_0 I_z \dots\dots\dots(12.6)$$

The energy levels of the system are the eigen values of the Schrodinger equation in which the operator H defined by the equation (12.6), operates upon the nuclear spin wave function ψ_N :

$$-g_N \mu_N B_0 I_z \psi_N = E_N \psi_N \dots\dots\dots(12.7)$$

The eigen value E_N becomes simply $-g_N \mu_N B_0 (\pm 1/2)$. Therefore, two energy levels are produced one corresponding to $+1/2$ (lower energy state) and the other to $-1/2$ (upper energy state). This explains the removal of degeneracy due to the application of the magnetic field.

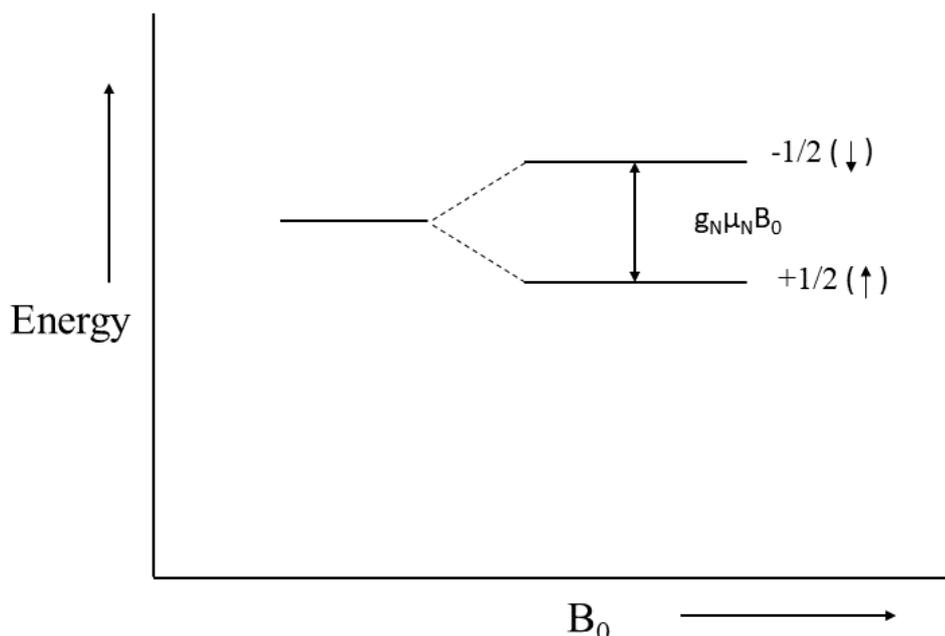


Fig.12.1 The energy of nuclear (spin $\frac{1}{2}$) levels in a magnetic induction B_0

The energy difference between the two levels is $g_N \mu_N B_0$ which correspond to a frequency separation ν is given by

$$\nu = \frac{g_N \mu_N B_0}{h} \dots\dots\dots(12.8)$$

This is so called resonance condition.

The typical external magnetic fields used in NMR experiments are in the range 1 to 5 tesla. Because of the different values of the nuclear g-factor for different nuclei, for a particular value of magnetic induction realizable in the laboratory, the resonant frequency falls in the radio frequency region of the electromagnetic spectrum, in the order of MHz.

The resonance condition defined by the equation (12.8) suggests that the experimental observation of nuclear resonance absorption may be carried out either by fixing ν and varying B_0 until resonance is observed, or by fixing B_0 and varying ν .

The problem of determining the possibility and intensity of transitions involves two factors. The first one is the nature of the formal quantum mechanical selection rules while the second relates to the population of the energy states involved in the transition. For a proton of nuclear spin $\frac{1}{2}$ there is no necessity of selection rule, since there are only two levels and selection becomes meaningless. For magnetic induction realizable in the laboratory, the population of the lower level is found to be more than the upper level and so a net absorption will occur.

When the absorption occurs continuously, we understand that the population in the lower level will gradually diminish with time, while the population of upper level gradually increases, until they become equal, then

Notes

there will be not net absorption. The phenomenon is known as saturation. The process of restoring back the Boltzman's equilibrium is known as relaxation. It is convenient to consider two different relaxation mechanisms characterized by its own time-constant, spin-lattice relaxation, of time constant T1, occurs because there is exchange of energy between the spin states and the surroundings medium, and spin-spin relaxation, of time constant T2, occurs with exchange of energy between different nuclear spins.

12.4 Nuclear resonance:

A particular chemical nucleus is placed in a magnetic field gives rise to a resonance absorption of energy from a beam of radiation, the resonance frequency being characteristic of the nucleus and of the strength of the applied field. Thus r.m.s techniques may be used to detect the presence of particular nuclei in a compound and, since for a given nuclear species the strength of the n.m.r. signal is directly proportional to the number of resonating nuclei, to estimate them quantitatively. However, an n.m.r. spectrometer is an expensive instrument, and there are many simpler and cheaper methods available to detect the presence or absence of a particular atom in a molecule. Two other characteristics of n.m.r spectra which have not so far both mentioned make the technique for more powerful and useful; these are the chemical shift and the coupling constant, which we shall discuss in the following sections.

The vast majority of substances of interest to chemists contain hydrogen atoms and, as the nucleus has one of the strongest resonances, it is not surprising that n.m.r has found the widest application to these substances. When discussing chemical shifts and nuclear coupling it is convenient to use one type of nucleus as an example, although all spinning nuclei show these phenomena, and in what follows we shall consider the spectra of hydrogen-containing sub-states only.

12.5 Block equation:

It is known that torque is equal to rate of change of angular momentum. If the magnetic field causes the angular momentum to change with respect to time, then the torque exerted on the magnetic moment by the applied field will be

$$\frac{d}{dt}(I\eta) = T^l \dots\dots\dots(12.9)$$

From simple electromagnetic theory we know

$$T^l = \mu \times B \dots\dots\dots(12.10)$$

Add and comparing (12.9) and (12.10) we have

$$\frac{d}{dt}(I\eta) = \mu \times B \dots\dots\dots(12.11)$$

Referring equ.(12.1) we can write (12.11) as

$$\frac{d}{dt}\left(\frac{\mu}{\gamma}\right) = \mu \times B$$

(or)

$$\frac{d\mu}{dt} = \gamma (\mu \times B) \dots\dots\dots(12.12)$$

If M is the vector sum of the individual μ 's, $\sum_i \mu_i$, we can write

$$\frac{dM}{dt} = \gamma M \times B \dots\dots\dots(12.13)$$

If the applied magnetic field B is along z-direction $B=B_0 \bar{k}$ where \bar{k} is the unit vector along z-axis, under thermal equilibrium the magnetization will be only along the z-axis.

$$M_x=0, M_y=0, M_z =0 \dots\dots\dots(12.14)$$

If N_2 and N_1 are the population per unit volume of the upper and lower levels

$$M_z = (N_1 - N_2)\mu = N\mu \dots\dots\dots(12.15)$$

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \dots\dots\dots(12.16)$$

This is, if an unmagnetized specimen is placed in a magnetic field $B_0 \bar{k}$ at $t=0$, the magnetization will increase from initial value of $M_z=0$ to the final equilibrium magnetization value of M_0 at a rate governed by equation (12.16), Here T_1 is the simple spin lattice relaxation time.

With this additional interaction, the equation (12.14) may be written as

$$\frac{dM_z}{dt} = \gamma (M \times B) + \frac{M_0 - M_z}{T_1} \dots\dots\dots(12.17)$$

This indicates that the magnetization vector besides processing about the magnetic field, will relax to the equilibrium value M_0 .

In a static magnetic field $B_0 \bar{k}$, the x and y components of magnetization will be zero. Therefore M_x and M_y components will be decaying to zero, giving the x and y components of M as,

$$\frac{dM_x}{dt} = \gamma (M \times B) - \frac{M_x}{T_2} \dots\dots\dots(12.18)$$

$$\frac{dM_y}{dt} = \gamma (M \times B) - \frac{M_y}{T_2} \dots\dots\dots(12.19)$$

Where T_2 is the spin-spin relaxation

On expanding the vector product $(M \times B)$, we have

Notes

$$\frac{dM_x}{dt} = \gamma (M_y B_z - M_z B_y) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma (M_z B_x - M_x B_z) - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma (M_x B_y - M_y B_x) - \frac{M_z - M_0}{T_1} \dots\dots\dots(12.20)$$

Our interest in NMR experiment is the study of combined effect of resonating r.f magnetic field and the static field. The magnetic vector of the radio frequency B_1 is equivalent to an induction rotating in the xy plane with an angular frequency ω rad s^{-1} .

The components of B_1 can be easily deduced as,

$$B_x = B_1 \cos \omega t, B_y = -B_1 \sin \omega t, B_z = B_0 \dots\dots\dots(12.21)$$

Substituting the values of B_x , B_y and B_z in (12.20), we have

$$\frac{dM_x}{dt} = \gamma (M_y B_0 + M_z B_1 \sin \omega t) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma (M_z B_1 \cos \omega t + M_x B_0) - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = -\gamma (M_x B_1 \sin \omega t + M_y B_1 \cos \omega t) - \frac{M_z - M_0}{T_1} \dots\dots\dots(12.22)$$

This set of equations is called Bloch equations. Since T_1 is the time constant for the decay of the component of magnetization along the z-axis (Parallel to B_0) it is called the longitudinal relaxation time; T_2 describes the decay of magnetization in the xy-plane and is therefore transverse relaxation time.

12.6 Chemical shift:

The precise value of the Larmor frequency for a given nucleus depends upon its electronic environment i.e., upon the chemical properties of the atom in which it is present. Thus, all ^1H nuclei do not have precisely the same Larmor frequency, and different compounds have absorption signals at different frequencies for a given applied field. For example, water, benzene and cyclohexane each show a single resonance at a different frequency. This phenomenon is called chemical shift and is particularly important because chemically different nuclei in the same molecule also have different chemical shifts; ethanol for example, shows three distinct ^1H absorption signals of relative intensities 1;2;3 ((OH), CH_2 , CH_3).

In our theoretical discussions, we have considered only the behavior of an isolated nucleus in an applied field. Such a situation is not the reality since all nuclei are associated with electron electrons in atoms and molecules. When placed in a magnetic field the surrounding electron cloud tends to circulate in such a direction as to produce a field opposing that applied. That is, the nucleus finds itself in an effective field less than the actual applied

field. In other words, the nucleus can be said to be shielded from the applied field by diamagnetic electronic circulation.

$$B_{\text{eff}} = B_{\text{applied}} - B_{\text{induced}} \dots\dots\dots(12.23)$$

Since, the induced field is directly proportional to the applied field.

$$B_{\text{induced}} = \sigma B_{\text{applied}}$$

Where σ is a dimensionless constant called screening constant or shielding parameter.

$$B_{\text{eff}} = B_0 (1 - \sigma) \dots\dots\dots(12.24)$$

It is conventional to measure chemical shift in frequency units (Hz). The situation of a shielded spin $\frac{1}{2}$ nucleus is depicted in the fig. (12.2)

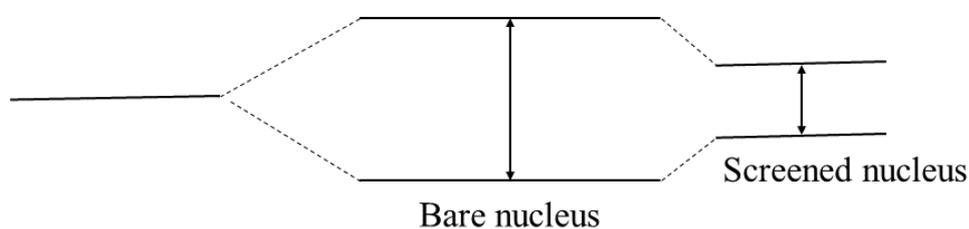


Fig.12.2 Bare and screened, spin $\frac{1}{2}$ nucleus in a magnetic field B_0

The shift of the resonance line of a given compound from that of a standard reference is measured as the chemical shift (δ) of the compound. Let B_r and B_x be the magnitude fields at which resonance occurs for the reference and the given sample compound. Then,

$$B_r = B_0(1 - \sigma_r), B_s = B_0(1 - \sigma_s) \dots\dots\dots(12.25)$$

$$\delta = \frac{B_r - B_s}{B_0} = \sigma_s - \sigma_r \dots\dots\dots(12.26)$$

The chemical shifts however, are reported in terms of dimensionless parameter, parts per million or p.p.m., which is field independent.

$$\delta = \frac{B_r - B_s}{B_0} \times 10^6 \text{ ppm} \dots\dots\dots(12.27)$$

(or)

$$\delta = \frac{\nu_s - \nu_r}{\nu_0} \times 10^6 \text{ ppm} \dots\dots\dots(12.28)$$

Equation (12.27) is the chemical shift in terms of field while (12.28) is in terms of frequency.

In general, trimethyl silane (TMS) is used as reference since it gives its resonance at a very high field. It is chemically inert and contains 12 protons of the same type.

Notes

A different scale used by chemists in measuring the chemical shift is τ scale. Where,

$$\tau = 10.00 - \delta \dots\dots\dots(12.29)$$

From the definition it is obvious that the τ value for TMS is 10.

For same nucleus, if the resonance is observed at two different absorption positions, then it indicates that the two nuclei are in different chemical surroundings. For example, the spectrum of methanol CH_2OH consists of two absorptions lines at two different fields figure (12.3). The OH nucleus resonates first and CH_3 nuclei absorbing at a higher field. This is due to the reason that the oxygen is a much better electron acceptor than carbon therefore, the field experienced by the hydrogen nucleus in O-H bonds is greater than that at the same nucleus in the environment of carbon (C-H bond).

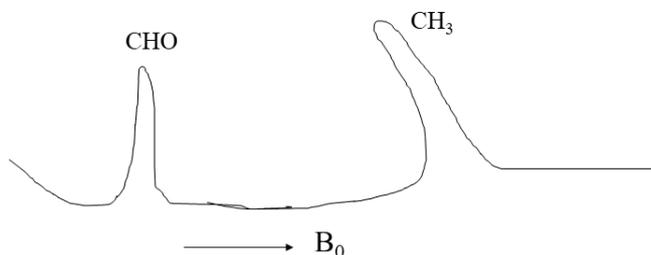


Fig.12.3 NMR spectrum of CH_3CHO

Combining detailed knowledge of chemical shift positions with the fact that the area of each resonance in the spectrum is proportional to the number hydrogen nuclei contributing to that resonance, we understand that NMR is an excellent technique for both quantitative and qualitative group analysis in organic chemistry.

12.7 Dipole-Dipole Interaction:

In a crystalline solid the nuclei are located in a quite restricted environment, their change in position being only the slight motion associated with vibration of the lattice or molecules. Translation and rotation of the molecules are highly contained. In the presence of an externally applied magnetic field, the nuclear dipoles will be thermally distributed among their allowed M_f values. Magnetic dipole interaction. The net effect of this interaction is to produce at any given dipole an additional magnetic field, termed the local magnetic field, which is superimposed on the applied field. Depending on the crystalline environment of a particular nucleus, this effect can both broaden and split the observed resonance. The order of magnitude of this broadening is many times larger than the splitting observed in liquid systems.

For a set of N magnetic moments located in a rigid lattice, the Hamiltonian for the system is given by

$$H = \sum_{i=1}^N \mu_i \cdot B + \sum_{i=0}^n \left[\frac{\mu_i \mu_j}{r^3} - \frac{3(\mu_i r_{ij})(\mu_j r_{ij})}{r^5} \right] \dots \dots \dots (12.30)$$

Where the first term gives the magnetic energy levels... $g_N B_N I B_z$ and the second is the chemical potential for a set of N magnetic dipoles.

12.8 Spin-lattice interaction:

Consider applying a 180° pulse initially to the spin system. Fig.12.4 (a) and (b) show that this will reverse the direction of M, and will leave the spin system in an unstable state since more spins point against the field than with it. As excited nuclei give up their energy (i.e relax) M will become smaller, pass through zero, then grow upwards until it reaches the equilibrium value once more-an exponential change which is illustrated in 'Fig.12.4 (c). Remembering that the relaxation time is the time required for $1/e=0.37$ of the original excitation energy to be dissipated. We can indicate this time on the curve.

Two points are important here. Firstly, the excess spin energy is given up by the nuclei to their surroundings, and so the time involved is the spin-lattice relaxation time, and we can see that the alternative name, for this, the longitudinal relaxation time, is because M relaxes along the main field axis. Secondly, all the changes in M sketched in fig. are confined to the z axis and so will produce no signal in the receiver coil along y.

We know that we can induce signal emission, however, by applying a subsequent 90° pulse to the system after some delay time τ , as shown (here not visible) thus reaching the situation discussed earlier. M will spiral up to equilibrium, emitting a decaying signal, but the initial intensity of the signal, immediately after the 90° pulse, will be directly proportional to the magnitude of M at the time of that pulse. If we lengthen τ , M will have grown more before being tipped into the xy plane, and a more intense signal will result. Shorten τ a little, and the signal will be weaker because M has not grown so much. Indeed, make τ much shorter, so that M is still pointing in the 'wrong' direction when it is tipped in to the xy plane, and the signal will be negative, i.e., it will be an out-of-phase signal which, on Fourier transformation, will give a negative spectrum peak rather than a positive one. In order to measure spin-lattice relaxation, then, we must carry out several 180° - τ - 90° experiments with different values of the delay time τ between the pulses, and then plot the intensity of the signal, observed immediately after the 90° pulse, against τ will be of the order of seconds.

Of course the relaxation of M into its final equilibrium position and magnitude continues after we have observed the initial stage. We are not interested to this, however-indeed we saw in the previous section that subsequent relaxation is also affected by field inhomogeneities and spin-spin relaxation. We can best think of the 90° pulse as 'freezing' the spin-lattice

Notes

relaxation of M at various times after reversal so that we can measure how far relaxation has progressed each time.

Naturally the computer attached to the spectrometer is used to control the whole process of measurement. It times the original 180° pulse, selects increasing τ values, times the 90° pulse, and collects and measures the signal intensity. From these data it can readily calculate and report a value for T_1 directly, and there is again strictly no reason to Fourier Transform the signal and produce frequency spectra. It has become conventional, however, to do the final step and to display the resulting spectra in a particularly graphic form giving a pseudo three-dimensional picture showing the frequency of lines in the spectrum and the relationship of their intensities to the delay time τ . Typically the computer plots a set of 'stacked' spectra in the form of Fig. 12.5, where each spectrum is offset vertically and to the right by an amount proportional to the delay time. Such a picture shows very pleasingly the initial negative signal from the peak, its diminishment through zero, and subsequent growth to a maximum. On the figure we have joined the peak maxima with a dashed line to show the exponential change in height. Comparison of this figure, viewed sideways, with Fig. 12.4 (c) shows the very precise correspondence between the magnitude and direction of M and its n.m.r. signal. An approximate value for the spin-lattice relaxation time, T_1 can be found very simply from such a display-in fact T_1 is about 1.5 times, the time taken for the peak to decay to zero intensity. In this particular (hypothetical example, the signals become zero at about 7 sec, so the relaxation time is 1.5×7 or about 10 sec.

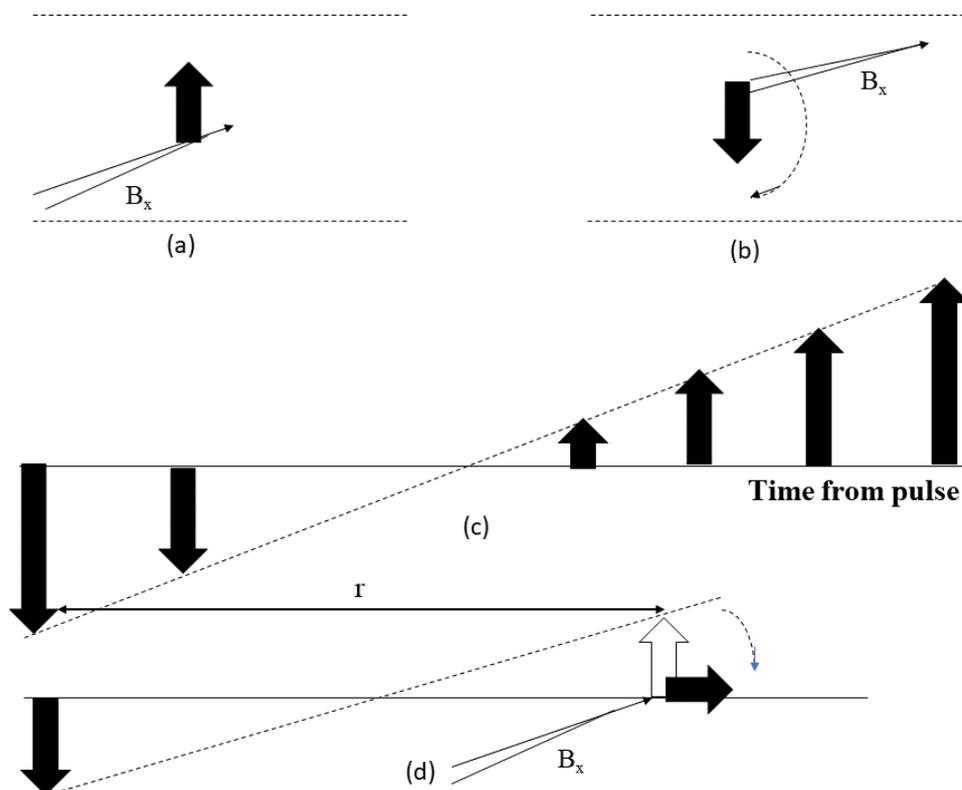


Fig.12.4 180° - γ - 90° pulse sequence and its effect on M

In summary, then, T_1 measurements are relatively easy and usually fairly fast. Some half a dozen 180° - τ - 90° experiments, each lasting a few seconds or a minute, can establish T_1 with good accuracy. Small errors in pulse timings are not significant, nor are field irregularities. Complicated spectra, containing several resonances, are not more difficult to tackle than simple ones. Small wonder, then, that T_1 measurements are increasingly being used to assist in spectral assignments and structure determination by n.m.r.

12.9 Summary

- ❖ The particles which make up an atomic nucleus, neutrons and protons, possess a property which is described as spin angular momentum.
- ❖ A particular chemical nucleus is placed in a magnetic field gives rise to a resonance absorption of energy from a beam of radiation, the resonance frequency being characteristic of the nucleus and of the strength of the applied field.
- ❖ The precise value of the Larmor frequency for a given nucleus depends upon its electronic environment i.e., upon the chemical properties of the atom in which it is present.

12.10 Review questions

1. Obtain the Bloch equations.
2. Define chemical shift? Distinguish between δ and τ chemical shifts.
3. Discuss in detail about the nuclear resonance.
4. Define dipole-dipole interaction.
5. Describe in detail about the spin-lattice interaction.

12.11 Further Reading

1. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCash. Fourth edition, Tata McGraw Hill Education pvt.Ltd.
2. Atomic and Molecular spectroscopy M.C.Gupta, New Age International publishers.

UNIT XIII ESR AND NQR SPECTROSCOPY

Content:

13.1 Introduction

13.2 Objectives

13.3 ESR

13.4 Its application

13.5 NQR (principle only) spectroscopy

13.6 Summary

13.7 Review questions

13.8 Further Readings

13.1 Introduction:

Electron spin resonance is a spectroscopic technique confirmed to the study of those species having one or more unpaired electrons. Substances with unpaired electrons may either arise naturally or be produced artificially. Natural is in the case of molecules NO, O₂ and NO₂ and the ions of transition metals and their complexes. These substances are stable and easily studied by ESR. Unstable paramagnetic materials, usually called free radicals or radical ions, may be formed either as intermediates in a chemical reaction or by irradiation of a normal molecules with uv or X-ray radiation or with beam of nuclear particles.

Nuclear Quadrupole Resonance is a branch of radio frequency spectroscopy which is closely related to NMR. All Nuclei with a spin ≥ 1 possess an electrical quadrupole moment, which arises because the nuclei are not spherical. Such nuclei are shaped either like a symmetrical egg or like a tangerine. Even if the charge density within the nucleus is constant, the distorted shape gives rise to a charge distribution which is non-spherical; the electric quadrupole moment is a measure of departure from sphericity, being positive for egg shaped and negative for tangerine-shaped nuclei. For spherical nuclei (i.e spin $\frac{1}{2}$ or 0).

13.2 Objectives

In this chapter, ESR and NQR and its applications are discussed.

13.3 Electron spin Resonance (ESR)

The origin of ESR spectroscopy lies in the spin of the electron and its associated magnetic moment. These magnetic moments are aligned at random in the absence of a field. When placed in a magnetic field, they are aligned

according to the applied magnetic field. The magnetic dipoles may arise from both spin and orbital angular momenta. In the majority of cases the magnetic dipole arises spin angular momentum only.

Principle:

The energy E of a magnetic dipole of moment μ in the presence of magnetic induction B is given by

$$E = -\mu \cdot B \dots\dots\dots(13.1)$$

If the system has only spin magnetic moment then the component of it along the direction of an applied magnetic induction is

$$\mu = -g\mu_B M_s \dots\dots\dots(13.2)$$

Where g is a dimension less proportionality constant, referred to as g -factor, μ_B is the Bohr magnetron ($=eh/4\pi m_e$ where e and m_e are the charge and mass of the electron respectively) and M_s is the electron spin quantum number. Combining Equation (13.1) and (13.2), we have

$$E = g\mu_B M_s B \dots\dots\dots(13.3)$$

The electron spin quantum number has two allowed values $+1/2$ and $-1/2$ and consequently there are two energy states:

$$\begin{aligned} E_1 &= +1/2 g\mu_B B \\ E_2 &= -1/2 g\mu_B B \dots\dots\dots(13.4) \end{aligned}$$

The difference in energy between these two states is $g\mu_B B$ and the application of e.m.radiation of a suitable frequency γ will induce transition between the two states when the energy of the radiation is equal to ΔE i.e., when

$$h\gamma = g\mu_B B \dots\dots\dots(13.5)$$

It is the transition between these two energy states which is studied by ESR.

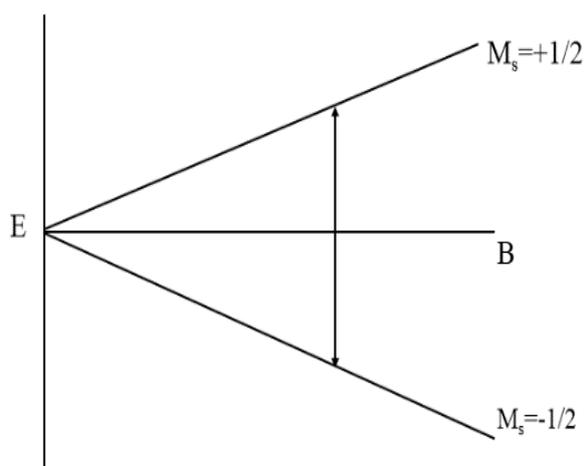


Fig.13.1 Zeeman splitting of unpaired electron

Notes

13.4 Applications of ESR:

Interaction of the unpaired electron with the magnetic moments of the nuclei within its orbital gives rise to two additional terms, the nuclear-electron spin coupling and the Fermi contact term. The splitting of the spectra observed due to this is called hyperfine structure. This hyperfine structure makes the ESR a very interesting one. The nuclear electron coupling is a direct dipole-dipole interaction between the electron and the nuclear magnetic moments. As this interaction depends upon the angle between the magnetic field and the line joining the two dipoles, it is directional and is referred to as the anisotropic interaction. Its magnitude decreases rapidly ($\propto r^{-3}$) as the distance between the dipole increases. For a system such as an organic free-radical in solution, the orientation of the radical with respect to the magnetic field changes rapidly and the interaction averages to zero.

Energy levels for a radical with $S=1/2$ and $I=1/2$

Consider the simplest possible free radical, the hydrogen atom, which has one unpaired electron ($S=1/2$) and one proton ($I=1/2$). There are therefore two orientations of the nuclear magnetic moment for each orientation of the electron magnetic moment, leading to four energy levels as indicated in Fig. Already we have seen the selection rule for an ESR transition as $\Delta M_s = \pm 1$. Since the total angular momentum must remain unchanged, a second selection rule applies when interaction with nuclear magnetic moments are present i.e $\Delta M_I = 0$.

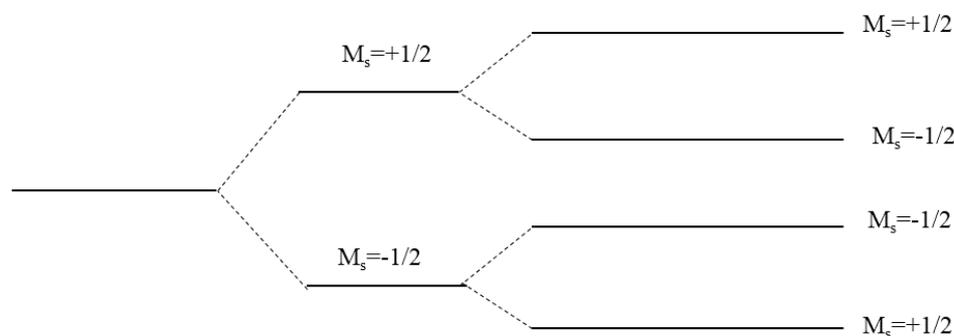


Fig.13.2 Energy levels for a radical with $S=1/2$ and $I=1/2$

For the hydrogen atom two transitions are therefore allowed and are observed. The spacing between the two absorptions corresponding to these two transitions is termed the hyperfine splitting constant (a). The fields at which the absorption occurs are therefore,

$$B = B' \pm a/2 \dots\dots\dots(13.6)$$

Where 'B' is the field where the absorption would occur if $a=0$. Since the populations of the two states are almost equal, the two absorptions will be of equal intensity. The spectrum of the hydrogen atom therefore consists of two equally intense absorptions.

Similarly the interaction of an unpaired electron in a free radical with two equivalent protons, three equivalent protons and four equivalent protons may also be deduced. It is observed that their spectrum consists of 3 lines with relative intensities 1:2:1, 4 lines with intensities 1:3:3:1 and 5 lines with intensities 1:4:6:4:1 respectively. Therefore these information may be summarized as two rules.

- i) In equivalent protons give (n+1) equally spaced absorptions in the ESR spectrum;
- ii) The relative intensities of these absorptions will be proportional to the coefficients of a binomial expansion of order n.

The interaction of unpaired electrons with two magnetically non-equivalent protons can also be studied using E.S.R.spectrum.

13.4.1 E.S.R. Spectra in solutions:

The investigations of ESR spectra of free radicals in solution are very useful for getting details of electron distribution and structure of the radical. We shall consider the typical case of the methyl radical $^{120}\text{CH}_3$ in solution. It belongs to the type of an electron interacting with three equivalent protons, since the nuclear spin of carbon is zero. So for interaction of unpaired electron with 3 equivalent protons we expect four equally spaced lines with relative intensities 1:3:3:1. This spectrum observed is as shown in the Fig.13.3



Fig.13.3 ESR spectrum of methyl radical $^{120}\text{CH}_3$

Since the observed spectrum is symmetrical, the proton hyperfine coupling constant is isotropic and the unpaired electron density is distributed equally among the protons in the system. The measurement cannot give the electron density on the carbon atom as its nuclear spin is zero. However, the electron density on carbon can be investigated by studying the ESR of the radical $^{130}\text{CH}_3$.

Similarly using ESR spectra Benzene anion, and p-nitrobenzoate Dianion can also be studied.

Notes

13.5 NQR:

In both NMR and NQR involve the coupling of radio frequency radiation with a nuclear magnetic moment to bring about transitions between nuclear orientations of different energies. In the case of nuclear magnetic resonance, the energy levels are governed by the interaction of the nuclear magnetic dipole moment with an externally applied magnetic induction, whereas in nuclear electric quadrupole moment with the electric field gradient produced at the nucleus by the charge distribution to the environment.

With nucleus magnetic resonance the transition frequencies are proportional to the applied magnetic induction, so transition between the magnetic levels are possible using a fixed frequency oscillator while sweeping the magnetic field. With NQR the electric induction gradient is a fixed property of the molecule or crystal, So, a variable frequency detection system must be used. The range of nuclear quadrupole interactions is such that transition frequencies can occur anywhere between 100 KHz and 1GHz.

Principle:

A quadrupole nucleus will have different nuclear orientations caused by the interaction between the nuclear quadrupole moment of a nucleus and the electric field gradient, giving rise to a set of quantized energy levels. Nuclear quadrupole resonance spectroscopy deals with transition between these quantized energy levels when electromagnetic radiation of proper frequency is allowed to interact with the system. Though the origin of the levels are electrical in nature, the transitions are of magnetic type possessed by the quadrupole nuclei and if an oscillating magnetic induction is applied from a coil round the sample, coupling occur between the magnetic moment of the nucleus and the magnetic component of the radiation.

13.5.1 Application of NQR

The main uses of nuclear quadrupole resonance spectroscopy are listed below.

- 1) Information about chemical bonding in the solid state
- 2) Molecular structure information
- 3) Characterization of molecular or ionic species (i.e., as a finger print technique)
- 4) Test for electronic wave-functions used in calculating theoretical coupling constants.
- 5) Crystallographic and molecular symmetry information
- 6) Determination of phase transitions
- 7) Solid state molecular motion studies.

13.6 Summary

- ❖ The origin of ESR spectroscopy lies in the spin of the electron and its associated magnetic moment.
- ❖ The investigations of ESR spectra of free radicals in solution are very useful for getting details of electron distribution and structure of the radical.
- ❖ NQR involve the coupling of radio frequency radiation with a nuclear magnetic moment to bring about transitions between nuclear orientations of different energies.

13.7 Review questions

1. Give the theory on E.S.R spectra on solution.
2. Discuss the principle and applications of NQR.
3. Explain some applications of ESR.

13.8 Further Reading

1. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCash. Fourth edition, Tata McGraw Hill Education pvt.Ltd.
2. Atomic and Molecular Spectroscopy-M.C.Gupta, New Age International Publishers.

UNIT XIV MOSSBAUER SPECTROSCOPY

Content:

- 14.1 Introduction
- 14.2 Objectives
- 14.3 Mossbauer spectroscopy
- 14.4 Molecular structure
- 14.5 Crystal symmetry and molecular structures.
- 14.6 Electronic structure
- 14.7 Applications
- 14.8 Summary
- 14.9 Review questions
- 14.10 Further Reading

14.1 Introduction:

Mossbauer spectroscopy named after its discoverer who received a Nobel prize in 1961 for his work, is concerned with transitions between energy levels within the nuclei of atoms. About a third of the known elements, principally the heavier ones, when formed by the radioactive decay of an isotope of the same or a different element, are initially produced in an excited nuclear state, after a very short delay, of the order of microseconds, the excited nucleus reverts to the ground state and emits energy of a very high frequency, usually in the γ -ray region of the spectrum. It is the study of this γ -ray emission and subsequent reabsorption which constitutes Mossbauer of γ -ray spectroscopy.

14.2 Objectives

In this chapter, Mossbauer spectroscopy and its application are discussed. Electronic structure and Molecular structure are deliberated. Crystal symmetry and molecular structure is discussed.

14.3 Mossbauer spectroscopy:

Both NMR and NQR are concerned with the ground-state properties of the nucleus. However there is another kind of spectroscopy that deals with both the excited as well as the ground-state properties.

Most modes of radioactive decay produce a daughter nucleus in a highly excited state, which then decays to the ground state by emitting a series of γ -ray photons. AS analogues to the atomic resonant fluorescence, a γ -ray emitted during a nuclear transition from an excited state to the ground state

should be capable of exciting second ground state nucleus of the same isotope, thereby giving rise to nuclear resonant absorption and fluorescence. Unfortunately, the high energy and momentum of the photon cause the nucleus to have a high recoil energy, and momentum of the photon cause the nucleus to have a high recoil energy, and reduce the probability of detecting this resonant absorption to almost negligible proportion. This problem was solved and solution was found by R.L. Mossbauer in 1958. Under appropriate experimental condition in the solid state it is possible to produce recoilless emission and absorption events, so that resonant absorption and fluorescence can be detected quite easily. This new branch of spectroscopy was popularly referred to as Mossbauer spectroscopy or nuclear gamma resonance (NGR).

14.3.1 Recoilers emission and absorption:

Nuclear resonance absorption is expected to occur when gamma radiation emitted in a transition from E_i to E_f is reabsorbed by another nucleus of the same kind so as to have a transition from E_f to E_i (Fig.14.1)



Fig.14.1 Nuclear Resonant Absorption

In practice this resonant absorption is not possible, because the emitted photon is with a high energy and consequence of which the nucleus emitting it gets a recoil. If the wavelength of the radiation is λ , then the momentum is given by

$$P = \frac{h}{\lambda} \dots\dots\dots(14.1)$$

Conservation of linear momentum requires that the nucleus recoil with an equal momentum in the opposite direction. The corresponding recoil Kinetic energy R of the nucleus is given by,

$$R = \frac{p^2}{2M} \dots\dots\dots(14.2)$$

Where M is the mass of the recoiling nucleus.

Therefore, the energy of the emitted γ -ray will not be equal to E_0 the energy above the ground state, but will be less than, as given by

$$E = E_0 - R \dots\dots\dots(14.3)$$

According to the equation (14.3), the centre of emitted spectral line will be shifted from the expected position E_0 by R.

Notes

Similarly, during the process of resonant absorption by another nucleus of the same kind, the nucleus will have momentum and energy so, the energy for the absorber will be given by,

$$E = E_0 + \frac{p^2}{2M} = E_0 + R \dots\dots\dots(14.4)$$

Thus, the emission and the absorption lines will be centered $2R$ apart (Fig.14.2)

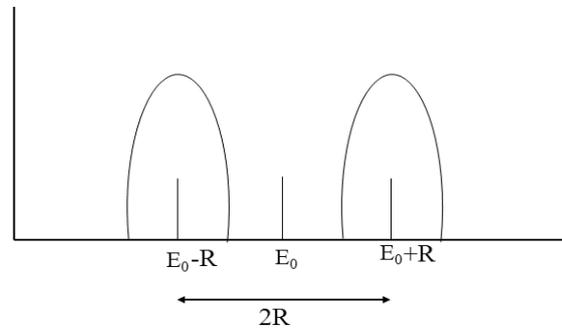


Fig.14.2 Emission and Absorption lines with recoil energy

In order to have resonant absorption, the line width of the spectral line (Full width at half-maximum)

$$\Gamma \geq R \dots\dots\dots(14.5)$$

If the above condition is satisfied, then the two curves would overlap (Fig.14.3) and one would observe resonant absorption. Greater the overlap greater is the absorption.

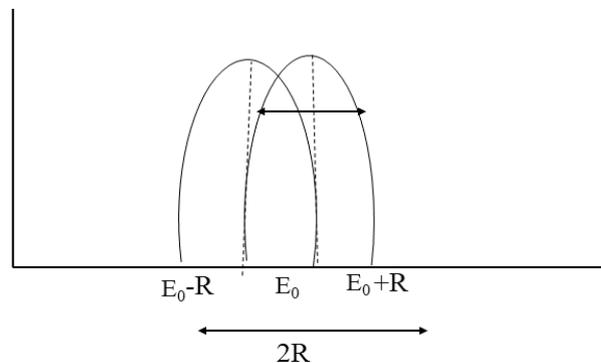


Fig. 14.3 Overlap of emission and absorption lines

A moment of the source and absorber relative to the other with velocity v will alter the effective value of the energy seen by the absorber by a Doppler shift of energy equal to $\frac{v}{c} E_0 = 2R$. In this way the loss of energy due to recoil is made up, and the resonance is satisfied.

This would have a very limited usefulness if it were not for the fact that the energy of the nucleus is slightly influenced by its chemical environment.

The Hamiltonian describing the energy of the nucleus may be written as,

$$H = H_0 + E_0 + M_1 + E_2 \dots\dots\dots(14.6)$$

When H_0 contains all terms other than the hyperfine interactions with the environment, E_0 is the coulombic interaction with the electron which alters separation of the ground excited states of the nucleus, and thus can cause a shift of the resonance line. It is therefore known as chemical isomer shift. The M_1 term refers to an interaction of the nucleus spin with a magnetic field and the resultant multiplex line structure known as magnetic hyperfine splitting. The E_2 term describes the interaction of the nuclear quadrupole moment with the local electric field gradient produced by the surrounding charge distribution. This also results in the line splitting and is known as an electric quadrupole interaction.

14.4 Molecular Structure:

Mossbauer spectroscopy is most useful in which molecular configuration can be determined. Determination of molecular geometry is decided by circumstance, which can be understood from the following example, The ^{129}I spectrum of $[\text{IF}_6]^+$ $[\text{AsF}_6]^-$ is a single line, there by confirming that the $[\text{IF}_6]^+$ cation has a regular octahedral geometry (cubic geometry); in contrast, the $[\text{IF}_6]^-$ anion in CsIF_6 shows a large quadrupole splitting because the additional line-pair of electrons is stereo chemically active and results in a distorted 7-coordinate geometry.

Another good example from iodine chemistry concerns, the geometry of the compound $\text{I}_2\text{Cl}_4\text{Br}_2$, which is derived from the planar bridged structure of I_2Cl_6 . Accordingly, there are six possible structures (a)-(f) as shown in fig. The ^{129}I spectrum shows are not identical. This elimination structures (b), (c) and (d). From the quadrupole coupling constants, it was observed that one iodine in $\text{I}_2\text{Cl}_4\text{Br}_2$ has geometry similar to that in I_2Cl_6 , eliminating the structures (e) and (f) and establishing structures (a) as the correct one Similar success has been achieved in establishing the structures of $\text{Fe}_3(\text{CO})_{12}$ also.

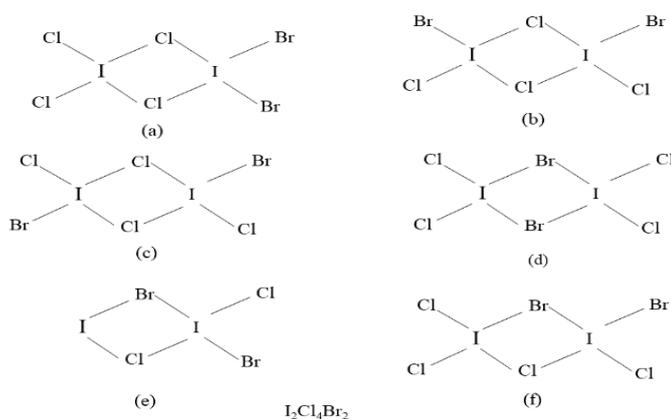


Fig.14.4 Possible structures of $\text{I}_2\text{Cl}_4\text{Br}_2$

14.5 Crystal symmetry and magnetic structure:

We have already seen that the presence of magnetic hyperfine interaction causes line splitting and this magnetic field could be intrinsic as well. The analysis of the spectra sometimes reveals information regarding the crystal symmetry and intrinsic magnetic field.

Mossbauer spectroscopy is an excellent method of studying magnetically ordered materials. Below the ferro magnetic and anti ferro magnetic ordering temperature, the Mossbauer resonance is split by a magnetic hyperfine interaction. The value of the magnetic field increases with decreasing temperature until it reaches a saturation value at 0K. An appropriate thumb rule for ^{57}Fe is that the value at 0K is about 11T per unpaired electron.

An excellent example of this is given by the compound LiFe_2F_6 in which the Mossbauer spectrum determines not only the relative orientation of the spin-axis and the electric field gradient tensor, but also allows a complete assignment of the magnetic structure. This compound is anti-ferro magnetically ordered below 10^5 K. Above this temperature, the Mossbauer spectrum is comparatively simple with two quadrupole doublets of equal area which are characteristic of high-spin Fe^{2+} and high-spin Fe^{3+} . The formulation is thus $\text{LiFe}^{2+}\text{Fe}^{3+}\text{F}_6$. From the Mossbauer spectrum of LiFe_2F_6 at 4.2K, it was shown that the compound must have an ordered cation arrangement and the magnetic ordering can also be alone. Thus, the Mossbauer spectrum leads to a very detailed knowledge of the magnetic and crystal structure of this compound.

14.6 Electronic structure:

The isomer shift is a direct function of the s-electron density at the nucleus, the Mossbauer effect is of great interest to chemist. Changes in shielding of s-electron by p, d, f-electrons produce secondary effects also. Removal or addition of a valence electron (a change in the oxidation state), may change the s-electron density at the nucleus shift, we can get relative s-electron density and from that we can estimate of bond character of atoms chemically bonded to the Mossbauer nucleus.

14.7 Applications:

The most useful features of the Mossbauer effect is the sharpness of the γ -ray emission (line width $\approx 10^{-13}$ as compared to 10^{-8} for NMR and 10^{-4} for IR). The width is purely due to nuclear levels and no phonon-excitation is involved. A fractional line width ($\frac{\delta\nu}{\nu}$) of 10^{-13} implies that the energy of the γ -ray emitted is measurable to an accuracy of 1 part in 10^{13} . Such an accuracy in measurement is not achievable even with lasers. Thus, γ -ray provides us the

most stable and accurately defined electromagnetic radiation source for use in experiments. Some of the important applications of the Mossbauer effect are as follows:

1. Isomer shift or chemical shifts in the Mossbauer spectra reflects difference in the s-electron density around the emitter and absorber nuclei.
2. When the absorber atom is in a reasonably symmetrical environment a single line is observed in the Mossbauer spectrum. When the environment is asymmetrical a feeble internal electric field operates giving rise to a quadrupole splitting. This is used in structure determination.
3. Biochemical Applications: Since the Mossbauer effect produces a powerful probe of the chemical state and the environment of iron atoms, it can be applied to the study of proteins and enzymes.

14.8 Summary

- ❖ Mossbauer spectroscopy is most useful in which molecular configuration can be determined.
- ❖ The presence of magnetic hyperfine interaction causes line splitting and this magnetic field could be intrinsic as well.
- ❖ The isomer shift is a direct function of the s-electron density at the nucleus, the Mossbauer effect is of great interest to chemist.
- ❖ The presence of magnetic hyperfine interaction causes line splitting and this magnetic field could be intrinsic as well.

14.9 Review questions

1. With theory explain the principle of Mossbauer spectroscopy.
2. Explain with example how molecular structure can be identified with the help of Mossbauer spectroscopy.
3. Discuss about the Recoillers emission and absorption.

14.10 Further Reading

1. Fundamentals of Molecular spectroscopy- Colin N.Banwell and Elaine M.McCash, Tata McGraw Hill Edition.
2. Molecular spectroscopy- Suresh Chandran, Narosa Pub.Pvt.Ltd.

**Distance Education- CBCS- (2018-19 Academic
year onwards)**

M.Sc (PHYSICS) Degree Examination

Question paper pattern (ESE)

MOLECULAR SPECTROSCOPY 34531

Time: 3 hours

Maximum: 75 Marks

PART- A (10×2=20 Marks)

Answer all questions

1. Give an account of sp hybrids
2. What is directed bonds?
3. Define Stark effect.
4. Define mutual exclusion principle.
5. Explain Franck-Condon principle
6. What is meant by hyper Raman effect?
7. Write a note on Anti-stoke's Raman scattering.
8. Define Chemical shift.
9. Explain the principle of ESR.
10. Define Mossbauer spectroscopy.

PART-B (5×5=25 Marks)

Answer all questions choosing either (a) or (b)

11. a. Discuss the effect of isotopic substitution on rotational spectrum
(OR)
b. Give a theory on Sp² hybridization.
12. a. Give a brief account on Quadrupole hyperfine interaction
(OR)
b. Discuss the rotational energy of a diatomic molecule.
13. a. Give an account of vibrational Raman spectra.
(OR)
b. What is dissociation energy? Arrive an expression for the maximum number of vibrational levels below the dissociation limit.
14. a. Explain the principle of stimulated Raman scattering.
(OR)
b. Describe the techniques of observing the Coherent Anti-Stoke's Raman scattering.
15. a) Obtain the Block equation.
(OR)
b) Discuss the principle and applications of NQR.

PART-C (3×10=30 Marks)

**MODEL
QUESTIONS**

Answer any THREE questions:

16. Give the Heitler London theory for hydrogen molecule.
17. Find the molecular structure using IR and Raman spectrometer.
18. Explain the vibrational spectra of diatomic molecule.
19. What is dissociation energy? Arrive an expression for the maximum number of vibrational levels below the dissociation limit.
20. Describe an experimental arrangement for studying Mossbauer spectrum.