Spectroscopy

Introduction:

Spectroscopy is the study of interaction of radiation with matter and imparts information regarding molecular structure (molecular symmetry, bond distances, bond angles),chemistry properties (electronic distribution, bond strength ,intra-inter molecular spectra). Spectra mean radiation and scopy means measurement. "Spectroscopy which deals with the transitions that molecule undergoes between the energy level upon absorption of suitable radiations determined by quantum mechanical selection rule".

Electromagnetic spectrum orderly arrangement of electromagnetic radiations according to their increasing order of wavelength from cosmic ray to radio frequency region. Electromagnetic radiation is radiant energy emitted from any source in the form of heat or light or sound .It consists of both electric and magnetic waves oscillating at right angle to each other.

Molecular Spectroscopy:-

The molecular spectra arise from 3 types of transitions.viz, Rotational ,Vibrational and electronic transition.According to Born-Oppenheimer approximation the energy of the molecule is given by

$E=E_{rot} +E_{vib}+ E_{et} +E_{tran}$

Since the translational energy is not quantized and it is taken as neglibly small so,

$E=E_{rot} +E_{vib}+ E_{et}$

The energy of these are represented as

$E_{et}\gg E_{vib}\gg E_{rot}\gg E_{tran}$

Microwave spectroscopy

If the energy absorbed by the molecules is such that it can cause transition only from one rotational level to another with same vibrational level,the result obtained is called rotational spectrum. These spectra are therefore observed in far infrared region or microwave region (Energy small), The spectra obtained is therefore also called microwave spectra.

Molecule possessing permanent dipole moment show rotational spectrum.

Ex:- HCl –In which Hydrogen carries a permanent net positive charge and Chlorine carries a permanent net negative charge.Homonuclear diatomic molecule such as H_2 ,Cl_2 ,F_2 etc do not possess permanent dipole moment ,so they do not show rotational spectrum .They have a zero dipole ,since there is no such charge separation.All molecule having permanent moment are said to be 'Microwave inactive'.If there is no dipole ,no interaction can take place and the molecule is microwave inactive.

Rotational spectra for rigid diatomic molecule.

Let us consider a diatomic molecule in which m_1 and m_2 are the masses of the two atoms which are joined by a rigid bar(bond) whose length is

$$r_o = r_1 + r_2 \quad \rightarrow 1$$

The molecule rotates end over end about a point C,the center of gravity and it is defined by the equality of the moments about it ,i.e
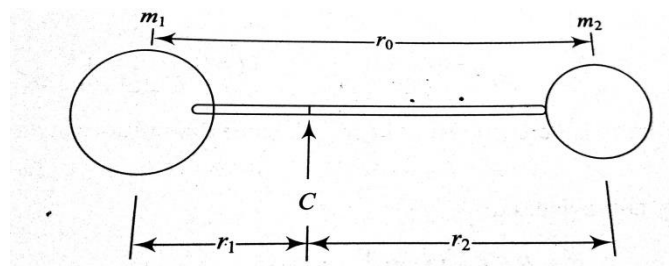
$$m_1 r_1 = m_2 r_2 \quad \rightarrow 2$$

Fig :A rigid diatomic molecule treated as two masses, m_1 ,m_2 joined by the rigid bar of length $r_o = r_1 + r_2$

Moment of inertia (I) of a molecule is defined as

$$I = \pounds_i \, m_i r_i^2 \quad \rightarrow 3$$

r_i is the distance of the ith particle of mass m_i from the centre of gravity .Since we have taken diatomic molecule, whose moment of inertia is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \rightarrow 4$$

Equation 2 ,the above equation take the form.

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

$$= r_1 r_2 (m_1 + m_2) \quad \rightarrow 5$$

However from equation 1 and 2

$$m_1 r_1 = m_2 r_2$$

$$m_1 r_1 = m_2 [r - r_1] \qquad \rightarrow 6 \qquad\qquad m_1 r_1 = m_2 r_0 - m_2 r_1$$

$$m_1 r_1 + m_2 r_1 = m_2 r_0$$

$$r_1 (m_1 + m_2) = m_2 r_0$$

$$r_1 = m_2 r_0 / (m_1 + m_2)$$

Hence,

$$r_1 = m_2 r_0 / (m_1 + m_2) \quad , \quad r_2 = m_1 r_0 / (m_1 + m_2) \qquad \rightarrow 7$$

Substituting the value of 7 in equation 5

$$I = [m_2 r_0 / (m_1 + m_2)] / [m_1 r_0 / (m_1 + m_2)] [(m_1 + m_2)]$$

$$I = [m_1 m_2 / m_1 + m_2] r_0^2$$

$$I = \mu r_0^2 \qquad\qquad \rightarrow 8$$

Where $\mu == [m_1 m_2 / m_1 + m_2]$ and it is known as reduced mass of the system. According to equation 8 moment of inertia is defined in terms of atomic masses and the bond length.

Energy level of rigid rotor:-

By the Schrodinger wave equation it may be shown that rotational energy levels allowed to the rigid diatomic molecule are given by

$E_J = [h^2 / 8\pi^2 I] J (J+1)$ joules, where J=0,1,2…

Angular momentum of a rigid rotor is given by

$$L = IW \rightarrow 1$$

And it is quantized .The expression for angular momentum can be obtained by solving Schrodinger wave equation for a rigid rotor i.e

$$L = \sqrt{J (J + 1)} * h/2\pi \qquad \rightarrow 2 \ J=0,1,2…$$

The energy of rotating molecule is given by

$E_J = (IW)^2 / 2I$

$\quad = L^2 / 2I \qquad \rightarrow 3$

Substituting 2 in 3

$\quad = \sqrt{(J(J+1))}\,^2\, h^2 / 2I(2\pi)^2$

$= J(J+1)\, h^2 / 8\pi^2 I \qquad \rightarrow 4$

This the expression for the energy of different rotational energy levels given by the rotational quantum numbers J=0,1,2...

The energy is expressed in terms of wave number $\bar{\nu}$

$E = hc/\lambda$

$\bar{\nu} = 1/\lambda$

$\bar{\nu} = E_j / hc \qquad\qquad \rightarrow 5$

Substituting 4 in 5

Rotational spectra for rigid diatomic molecule.

$\bar{\nu} = E_j / hc$

$\quad = J(J+1)\, h^2 / 8\pi^2 I\, hc$

$\bar{\nu} = (h / 8\pi^2 I\, c)\, J(J+1)$

Where $(h / 8\pi^2 I c) = \mathbf{B}$ which is a constant called rotational constant.

Therefore $\bar{\nu} = BJ(J+1)$

Selection rule for rigid molecule.

The selection rule for rotational spectrum is obtained by solving Schrodinger wave equation .According to selection rule,only those transitions for which the rotational quantum number changes by one unit are allowed i.e the transitions for which $\Delta J = \pm 1$ are allowed and the other transitions are forbidden .Such a result, it is called selection rule ,and we may formulate it for rigid diatomic rotator as

Selection rule= $\Delta J = \pm 1$

The absorption bands are obtained at

$E_J = \mathbf{B} \, J \, (J + 1)$ where J=0,1,2…

The rotational spectrum of a rigid diatomic molecule consists of a series of lines placed at the wave number 2B,4B,6B… ,from this it is clear that these lines are equally spaced with a difference of 2B.
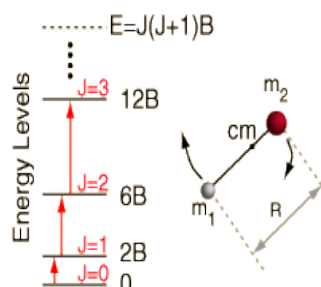

Fig :The allowed rotational energies of a rigid diatomic molecule.

Non Rigid Rotator

According to the rotational spectra of rigid rotator ,internuclear distances could be calculated from microwave spectra.The spectral line of some molecule other than the first,would not show the constant separation 2B ,which was predicted by the equation $\bar{\nu} = \mathbf{B} \, J \, (J + 1)$.The spectrum of HF was observed and value of B and r was calculated.From these value it was clear that the separation between successive lines (B value) decreases steadily with increasing J.The bond length increases with J and we can see that our assumption of a rigid bond is only an approximation,In fact all the bonds are elastic to some extend .A better model ,called the non-rigid rotator ,is representing the rotating system in which the rigid bar is replaced by massless spring.

As J value increases,the molecule rotates faster ,action of centrifugal force increases the internuclear distance thereby decreasing B .This energy level is called centrifugal distortion.So the additional rotational terms of centrifugal distortion is added to energy levels ,in non-rigid rotator

$E_J = hc \, [BJ(J+1) - DJ^2(J+1)^2]$

$D = h^3/32\pi^4 I^2 \, r^2 \, Kc$

When the bond is elastic ,a molecule may have vibrational energy i.e the bond will stretch and compress periodically with fundamental frequency which depend on masses of atoms and elasticity. If the motion is simple harmonic the force constant is given by

$K=4\pi^2 Ш^2 C^2 \mu$

$Ш$= Vibrational frequency (cm^{-1}).Weaker the bond more readily will it distort under centrifugal force.

The quantities r and B vary during a vibration. When these quantities are measured by microwave technique many hundreds of vibration occur during a rotation and hence measured value is an average .Hence

$B=(h/ 8\pi^2 Ic)$

$B= h/ 8\pi^2 c \mu r^2$

$B\alpha(1/r^2)$

Since all other quantities are independent of vibration

Schrodinger wave equation may be setup for a non-rigid molecule ,and the rotational energy level are found to be

$E_J =[h^2 /8\pi^2 I] J (J+1)-[h^4/32\pi^4 I^2 r^2 Kc] J^2 (J+1)^2]$

Or $\varepsilon_j= E_J/hc=BJ(J+1) -DJ^2 (J+1)^2$ cm^{-1}
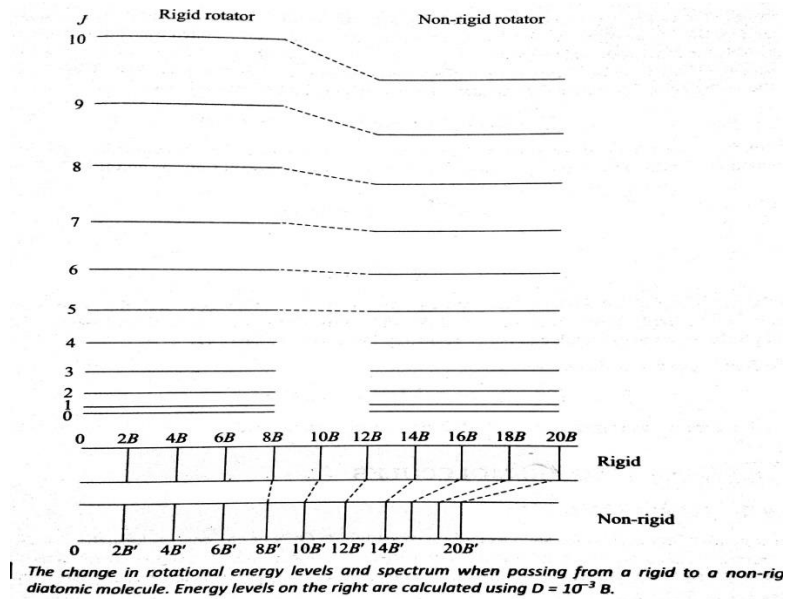
B- Rotational constant and D –Centrifugal distortion constant

$D= h^3/32\pi^4 I^2 r^2 Kc$ cm^{-1}

If the force of field is field is simple anharmonic the expression becomes

$\varepsilon_j= E_J/hc=BJ(J+1)-DJ^2 (J+1)^2 +HJ^3 (J+1)^3+KJ^4 (J+1)^4$ cm^{-1}

H and K are small constant which depend upon the geometry of the molecule.

The change in rotational energy levels and spectrum when passing from a rigid to a non-rig diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3} B$.

There is a lowering when passing from the rigid to non-rigid diatomic molecule.The

Dashed line in the spectra is connecting corresponding energy levels and transition of

Rigid and non-rigid molecules .The selection rule $= \Delta J = \pm 1$.

$E^I = BJ^I(J^I+1)hc - DJ^{I\,2}(J^I+1)^2 hc \rightarrow 1$

$E^{II} = BJ^{II}(J^{II}+1)hc - DJ^{II\,2}(J^{II}+1)^2 hc \rightarrow 2$

$\Delta E = B\{J^I(J^I+1) - J^{II}(J^{II}+1)\}hc - D\{J^{I\,2}(J^I+1)^2 - J^{II\,2}(J^{II}+1)^2\}hc$

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

Effect of isotopic substitution on rotational spectra

 In a diatomic molecule,when one of its atom is replaced by its isotope,the molecule

Will be chemically identical with the original one and the nature of chemical bond

will remain unchanged.There is no change in the internuclear distance on isotopic

substitution as it is practically determined by the electronic structure of the chemical

bond . The element is identical in every aspects except for its atomic mass,hence the

moment of inertia and B value for the molecule.

Ex:- Considering CO ,we see that on going from $^{12}C\,^{16}O$ to $^{13}C\,^{16}O$ there is a mass

 increase and hence a decrease in B value.If we designate ^{13}C molecule with a prime

i.e B^I so that $B>B^I$ .There is a relative lowering of the ^{13}C levels with respect to those of ^{12}C in rotational energy level.Heavier species show smaller separation between the lines $2B^I$ than the lighter.
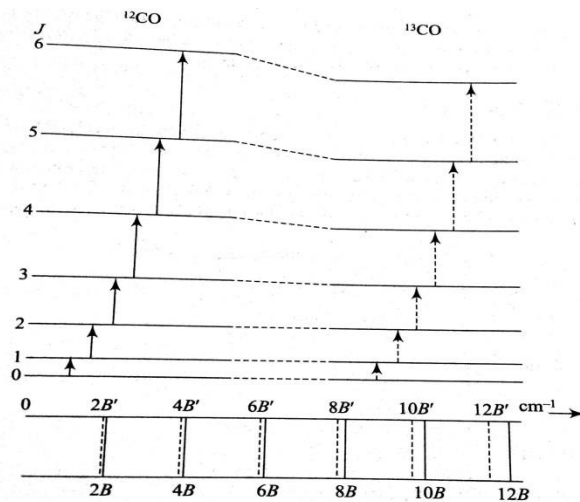
  The first rotational absorption of ^{12}C ^{16}O to be $3.84235cm^{-1}$,while that of ^{13}C ^{16}O was at $3.67337cm^{-1}$;

$B/B^I = h/ 8 \pi^2 Ic * 8 \pi^2 Ic/h$

$= I^I/I = \mu^I/\mu = 1.046$

The mass of oxygen to be 15.994 and that of carbon 12 to be 12.00 .m^I is the atomic weight of carbon 13

$= 15.994 m^I/15.994 + m^I * 12 + 15.994/12 * 15.994$

The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide.

Relative intensity of rotational spectral lines:-

   Intensity of spectral line depends upon the total number of molecules undergoing transition between adjacent levels producing the spectra,As the number of transition increase,the intensity increase,which depends on two factors

1)Relative population of an energy level

Relative intensity of the spectral lines depend upon the relative populations of the energy levels.Since energy level population is given by Boltzmann distribution law,the intensity of the rotational lines is evidently proportional to the Boltzmann distribution of molecules in rotational energy levels i.e

Intensity α $N_J/N_0 = e^{-EJ/KT}$

Where N_J / N_0 =relative population of molecules in levels J

N_J=Number of molecules in J=J level

N_0= Number of molecules in J=0 level

 But

E_J =$\mathbf{B}$ J (J + 1)hc

Therefore Intensity α $e^{-BJ(J+!)/KT}$

It indicates population and hence intensity decreases exponentially with increase in J value.

2)Degenaracy of given energy level

  Existense of two or more states of same energy influence the intensity of spectral lines.As the increase in degenarate state increase,the intensity decreases.Degenarate levels for a particular J value is equal to 2J+1.Thus J value increases ,the number of degenarate energy levels increases.The intensity of rotational spectra is a product of both factor so

Intensity α N_J/N_0 =(2J+1) $e^{-BJ(J+!)/KT \ *hc}$

When the quantity N_J/N_O is plotted against J value for a diatomic molecule at room temperature,following type of graph is obtained.

      The relative population & hence the intensity increases with the increase in J value,reaches a maximum & then decreases.The value of J corresponding to the population maximum is given by

$J_{MAX}=\sqrt{KT/2BhC}$ -1/2

      As the temperature increases,levels with higher J values get more populated.Hence the position of intense line shifts towards higher J value.

Stark effect in microwave spectra

  It is the shifting or splitting of rotational energy levels in the presence of electric field.(E) is known as stark effect .In general one distinguish first and second order stark effects.The first

order stark effect is linear in the applied field,while the second order effect is quadric in the field.It is named after the German Physicist,J stark who was awarded the nobel prize for his discovery of doppler effect in canal rays and splitting of spectral lines in electric fields.The stark effect is responsible for the pressure broadening of spectral lines by charged particles.When the shifted lines appear in absorption ,the effect is called inverse stark effect.It is analog of Zeeman effect where a spectral line is split into several component due to the presence of a magnetic field.The shift of rotational frequency $\Delta \gamma$,for a linear gaseous molecule in the stark effect is given by

$$\Delta \gamma \ \alpha \ (\mu E)^2$$

μ is the electric dipole moment of the molecule .Thus by knowing E and measuring $\Delta \gamma$,μ can be determined.The stark effect is extremely usefull for the determination of dipole moments of gaseous molecules.

Classification of polyatomic molecule based on moment of inertia

1)Linear molecule

   The molecule which are linear in shape ,i.e the molecule in which atoms are arranged in a straight line,such as HCl or Carbon oxysulphide OCS illustrated as,
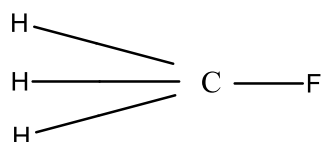
Ex O=C=S ,HCl

The three direction of rotation may be taken as a)about the bond axis b) End over end rotation in the plane of the paper c) End over end rotation at right angle to the plane of the paper.It is self evident that moment of inertia of b and c are same and while (a) it is very small .As an approximation may say that I_A =0,
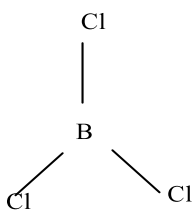
Thus for a linear molecule $I_B = I_C$, I_A =0

2)Symmetric top:-

Let us consider a molecule such as methyl fluoride ,where the 3 hydrogen atoms are bonded tetrahedrally to the carbon as shown below.

There are two division ,they are prolate symmetric top(Elongated in the direction of the line joining the pole)Ex methyl floride($I_B = I_C > I_A$). As in the case of linear molecule ,the end over end rotation in and out of the plane of the paper are still identical and we have $I_B = I_C$ .The moment of inertia about $C-F$ bond axis is now not negligible .However because it involves the rotation of 3 comparitevely massive hydrogen atoms off the axis.Such a molecule which is spinning about the axis can be imagined as top.
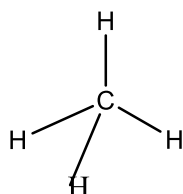
Symmetric top: $I_B = I_C$, $I_A \neq 0$

Another one is oblate symmetric top(Flattened at the poles) An example for this is boron trichloride.In this case $I_B = I_C < I_A$

3)Spherical tops:

When a molecule as all the moment of inertia identical,it is called Spherical top.Pure rotational spectrum does not exist because no permanent dipole moment .Since they have no dipole moment owing to their symmetry ,rotation alone can produce no dipole change and hence no rotational spectrum,so they are microwave inactive.
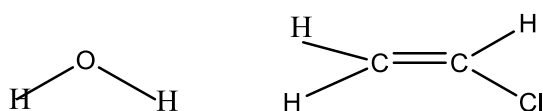
Ex:- Methane. $I_B = I_C = I_A$

4)Asymmetric top :

These molecule,to which majority of the molecule belong,in this case all the three moment of inertia are different.

$I_B \neq I_C \neq I_A$

Ex : water molecule ,vinyl chloride.

Rotational spectra of linear polyatomic molecule(OCS)

Let us consider the triatomic molecule which is linear molecule.Ex OCS ,Chloroacetylene HC≡ CCl ,where the atoms lie on a straight line,these type of molecule gives the simple spectra in the spectrum.For a linear molecule $I_B = I_C$, I_A =0 .the energy levels are given by

ε_j= E_J/hc=BJ(J+1) -DJ^2 (J+1)^2 cm^{-1}

And the spectrum show the 2B separation modified by the distortion constant.

❖ Moment of inertia for end over end rotation of a polyatomic linear molecule is greater than that of diatomic molecule,hence the B value of polyatomic molecule is less and the spectral lines are more closely spaced.The value of B for diatomic molecule is 10cm^{-1} ,for triatomic molecule is 1cm^{-1} and for larger molecule the value of B is less than 1cm^{-1}.

❖ To exhibit a rotational spectrum a molecule must usually posses a dipole moment.OCS will be microwave active while OCO is not.The isotopic substitution does not lead to a dipole moment since the bond length and atomic charges are unaltered by the substitution.Thus isotopic labelled molecule is microwave active.

❖ In non cyclic poly atomic molecule containing N atoms has altogether N-1 individual bond lengths to be determined .Thus in case of triatomic molecule OCS there is the CO distance (r_{CO}) and CS (r_{CS}) ,on the other hand there is only one moment of inertia for end over end rotation of OCS and only this one value can be determined from the spectrum.The isotope shift measurement are of great help in elucidating the bond of polyatomic molecule.In OCS molecule 2 bond length are there,in which one atom is replaced by the isotope,the molecule will have different moment of inertia from this two bond length are determined.

Moment of inertia of linear triatomic molecule.

The molecule of carbon oxysulphide, OCS showing the distances of each atom from the center of gravity.
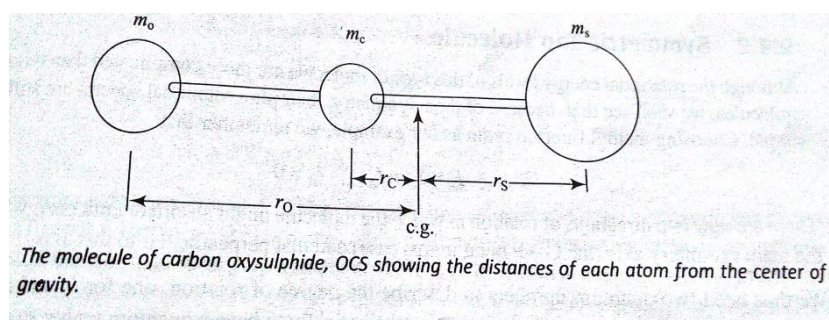
Let us consider the rotation of OCS molecule,where r_0 ,r_C,r_S represent the distances of the atoms from the centre of gravity.Consideration of moment gives

m$_o$ r$_o$ + m$_C$ r$_C$ = m$_S$ r$_S$ →1

The moment of inertia is

$I = m_o r_o^2 + m_C r_C^2 + m_S r_S^2 \rightarrow 2$

And by above fig.

$r_o = r_{CO} + r_C$ and $r_S = r_{CS} - r_C \rightarrow 3$

r_{CO}, r_{CS} these are the bond lengths of molecule.

Substituting 3 in 1

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

$m_o r_{CO} + m_o r_C + m_C r_C = m_S r_{CS} - m_S r_C$

$[m_o + m_C + m_S] r_C = m_S r_{CS} - m_o r_{CO}$

$M r_C = m_S r_{CS} - m_o r_{CO} \rightarrow 4$

M is the total mass of the molecule

Substituting 3 in 2

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

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

$I = m_o r_{CO}^2 + m_o r_C^2 + 2 r_{CO} r_C m_o + m_C r_C^2 + m_S r_{CS}^2 + m_S r_C^2 - 2 r_{CS} r_C m_S$

$I = [m_o + m_C + m_S] r_C^2 + 2 r_C[r_{CO} m_o - r_{CS} m_S] + m_o r_{CO}^2 + m_S r_{CS}^2$

$I = M r_C^2 + 2 r_C[r_{CO} m_o - r_{CS} m_S] + m_o r_{CO}^2 + m_S r_{CS}^2 \rightarrow 5$

Substituting the value of r_C from equation 4 in 5

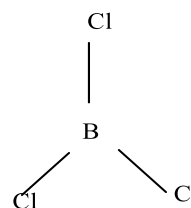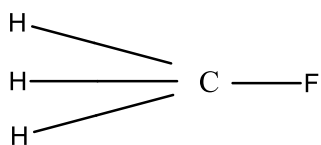$I = m_o r_{CO}^2 + m_S r_{CS}^2 - [m_o r_{CO} + m_S r_{CS}]^2 / M \rightarrow 6$

Now considering isotope molecule , ^{18}OCS we may write m_o' for m_o in 6

$I' = m_o' r_{CO}^2 + m_S r_{CS}^2 - [m_o' r_{CO} - m_S r_{CS}]^2 / M'$

We can now solve for r_{CS} and r_{CO} provided we have extracted the value for I' from the microwave spectrum of the isotope molecule. No need to write r'_{CO}, since we assume that bond length is unaltered by isotopic substitution.

Rotational spectra of polyatomic molecule(CH_3F ,BCl_3)

Let us consider a molecule such as methyl fluoride ,where the 3 hydrogen atoms are bonded tetrahedrally to the carbon as shown below.

There are two division ,they are prolate symmetric top(Elongated in the direction of the line joining the pole)Ex methyl floride($I_B = I_C > I_A$). As in the case of linear molecule ,the end over end rotation in and out of the plane of the paper are still identical and we have $I_B = I_C$ .The moment of inertia about $C-F$ bond axis is now not negligible .However because it involves the rotation of 3 comparitevely massive hydrogen atoms off the axis.Such a molecule which is spinning about the axis can be imagined as top.

Symmetric top:$I_B = I_C$,$I_A \neq 0$

Another one is oblate symmetric top(Flattened at the poles) An example for this is boron trichloride.In this case $I_B = I_C < I_A$

The solution for Schrodinger wave equation for symmetric top molecule gives the following expression for the energy levels of their rotor

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

Where K is the component of J about the unique axis,K represent angular moment about the top axis i.e about C-F and A and B are defined as

$B=(h/ 8 \pi^2 I_B c)$

$A=(h/ 8 \pi^2 I_A c)$

For every value of J ,there are 2J+1 values of K given by

$K=0,\pm 1,\pm 2 \ldots \pm J.$

The selection rule for rotational transition are

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

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