Spectroscopic Techniques for Pharmaceutical
and
Biopharmaceutical Industries
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Lecture-08
Rotational, Rotational Raman Spectroscopy Theory and Application-II

In the last lecture, we have seen the theory and principle behind Rotational Spectroscopy. In this lecture we will discuss in brief the principle of Rotational Spectroscopy, then we will go to Rotational Raman Spectroscopy and also we will discuss application of Rotational and Rotational Raman Spectroscopy.

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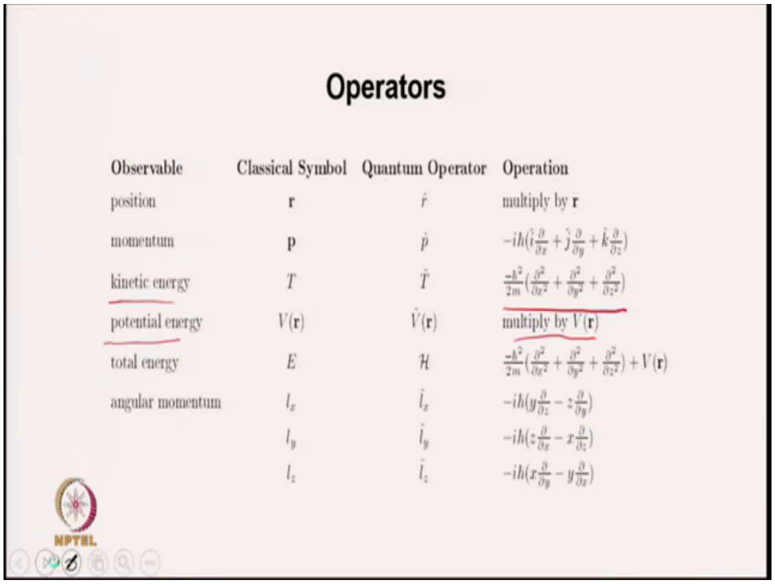

Operators

Observable	Classical Symbol	Quantum Operator	Operation
position	$\mathbf{r}$	$\hat{r}$	multiply by $\mathbf{r}$
momentum	$\mathbf{p}$	$\hat{p}$	$-i\hbar(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z})$
kinetic energy	T	$\hat{T}$	$\frac{-\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$
potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $V(\mathbf{r})$
total energy	E	$\mathcal{H}$	$\frac{-\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})+V(\mathbf{r})$
angular momentum	l_x	$\hat{l}_x$	$-i\hbar(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y})$
	l_y	$\hat{l}_y$	$-i\hbar(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z})$
	l_z	$\hat{l}_z$	$-i\hbar(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x})$

The last class we discussed about operators, there are 2 different operators, Kinetic Energy Operator and Potential Energy Operator. These 2 are use to calculate your energy of the different rotational levels just to summarize kinetic energy operator is your this double differential and potential energy is your simply U multiply by Vr. If you do that on a wave function, rotational wave function and you can get the energy of different rotational levels.

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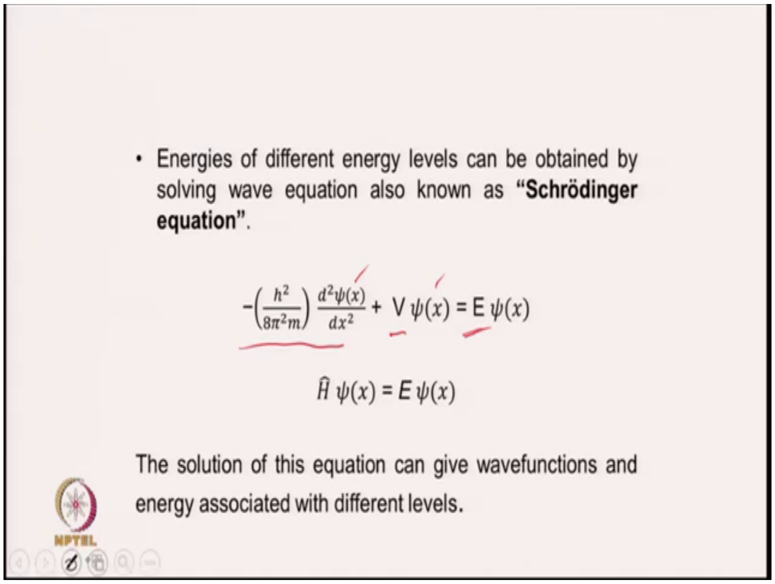

- Energies of different energy levels can be obtained by solving wave equation also known as **"Schrödinger equation"**.

$$-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi(x)}{dx^2} + V\,\psi(x) = E\,\psi(x)$$

$$\hat{H}\,\psi(x) = E\,\psi(x)$$

The solution of this equation can give wavefunctions and energy associated with different levels.

So, energies of different energy level can be obtained by solving wave equation which is known as Schrödinger Equations. So, this is your kinetic energy operator, this is potential energy operator, when they are applied on the wave function, what you can get is energy of the rotational levels. So, solution of this equation can give you wave function and energy associated with different levels.

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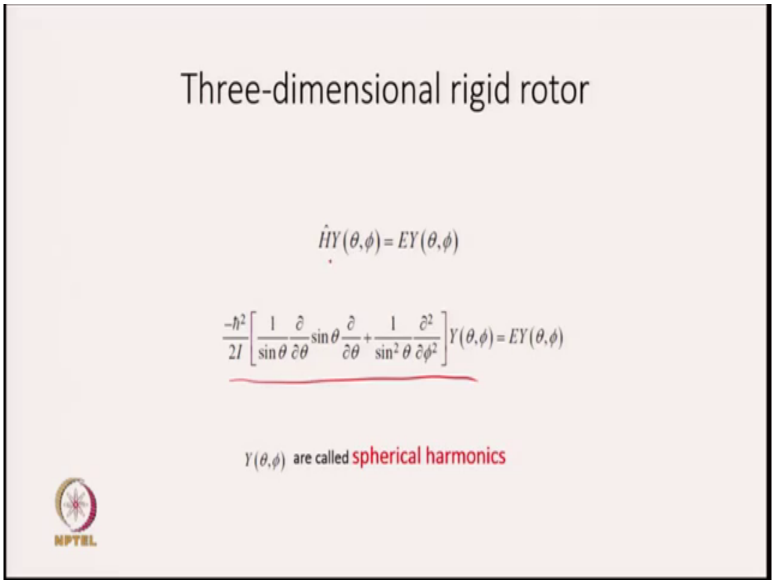

Three-dimensional rigid rotor

$$\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$$

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = EY(\theta,\phi)$$

$Y(\theta,\phi)$ are called spherical harmonics

For 3 dimensional rigid rotor your Hamiltonian will be given by this equation. Since this is a rigid rotor and so, R is constant and it means that your wave function is a function of theta and phi and that is called a Spherical Harmonics and when you apply Hamiltonian on a Spherical Harmonics you can get the energy of 3 dimensional rigid rotor.

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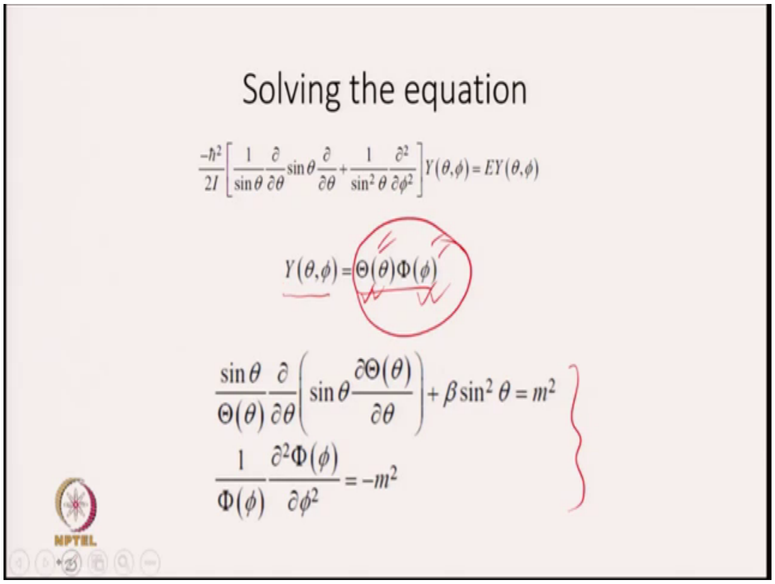

Solving the equation

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi)=EY(\theta,\phi)$$

$$\underline{Y(\theta,\phi)}=\Theta(\theta)\Phi(\phi)$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2$$

The way we solve this equation is first we we divide this wave function as a multiple of 2 functions, 1 is a function of theta and other is function of phi. And when you do that, you will get this 2 equation and solution of this will give you your, this, function of theta and the function of phi. When you multiply these 2, you will get the Spherical Harmonics.

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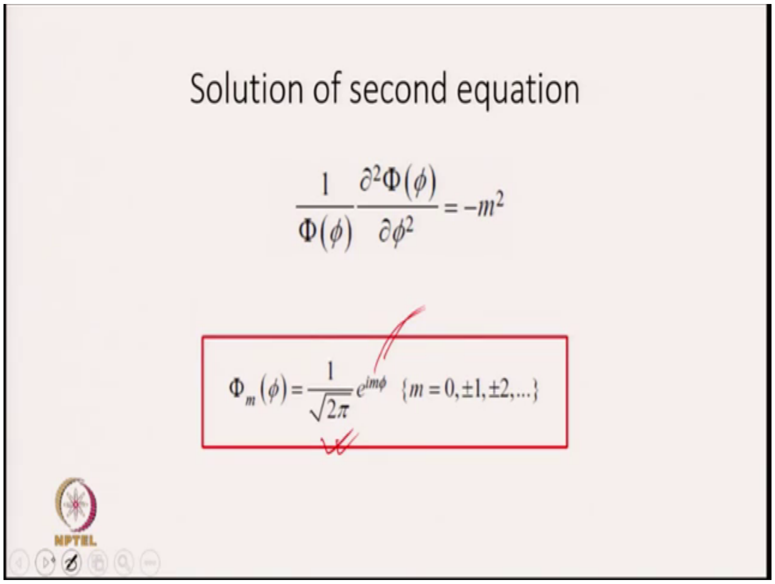

Solution of second equation

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2$$

$$\boxed{\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}\quad\{m=0,\pm1,\pm2,\ldots\}}$$

So, solution of the second equation which we discussed last time is your, this, 1 by root 2 pi exponential i m phi and so, you can see that there is 1 quantum number required that is called m, where m can take only integer values and m is equal to 0 plus minus 1 plus minus 2.

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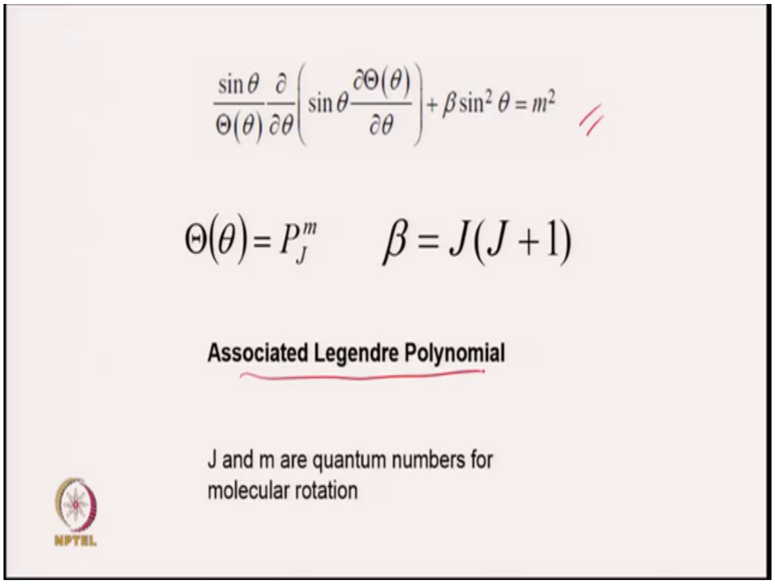

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\Theta(\theta)=P_J^m \qquad \beta=J(J+1)$$

Associated Legendre Polynomial

J and m are quantum numbers for molecular rotation

Second wave function which is a function of theta can be obtained by solving this differential equation and the solution is given by the Associated Legendre Polynomial. So, now, we derive phi part of the wave function and theta part of a function. So, Spherical Harmonics is basically multiple of these 2 wave functions and the value of these are given for different value of your L and m, or J and m.

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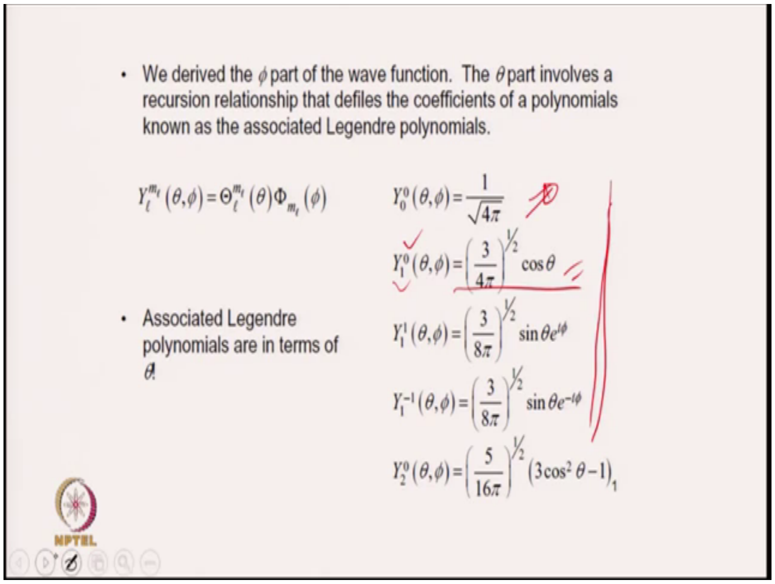

- We derived the ϕ part of the wave function. The θ part involves a recursion relationship that defiles the coefficients of a polynomials known as the associated Legendre polynomials.

$$Y_\ell^{m_\ell}(\theta,\phi)=\Theta_\ell^{m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

- Associated Legendre polynomials are in terms of θ

$$Y_0^0(\theta,\phi)=\frac{1}{\sqrt{4\pi}}$$

$$Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_1^1(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}$$

$$Y_1^{-1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$$

$$Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$$

So, if J is equal to 0, m is equal to 0, then you have a Spherical Harmonics as the value is equal to 1 by root 4 pi and similarly when J is equal to 1, your m is equal to 0, then you will get this function. So, in some situation, this is independent of theta for a particle value of J and m some time it is function of theta and sometimes it is function of theta and phi.

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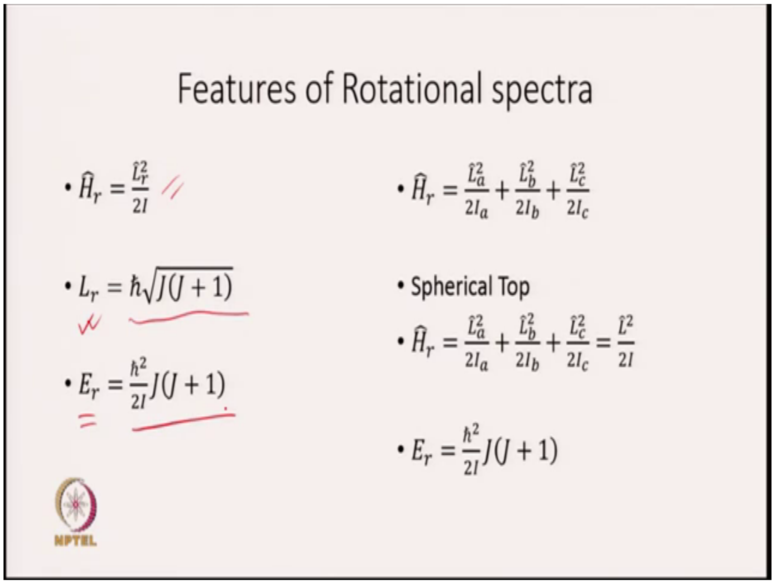

Features of Rotational spectra

- $\hat{H}_r=\frac{\hat{L}_r^2}{2I}$
- $L_r=\hbar\sqrt{J(J+1)}$
- $E_r=\frac{\hbar^2}{2I}J(J+1)$
- $\hat{H}_r=\frac{\hat{L}_a^2}{2I_a}+\frac{\hat{L}_b^2}{2I_b}+\frac{\hat{L}_c^2}{2I_c}$
- Spherical Top
- $\hat{H}_r=\frac{\hat{L}_a^2}{2I_a}+\frac{\hat{L}_b^2}{2I_b}+\frac{\hat{L}_c^2}{2I_c}=\frac{\hat{L}^2}{2I}$
- $E_r=\frac{\hbar^2}{2I}J(J+1)$

So, once you know wave function, we also know what will be the Hamiltonian, Hamiltonian is generally given in terms of momentum operator, momentum operator square divided by 2 I and momentum when you apply this operator on wave function you can get momentum value and that is h bar under root J, J plus 1. And energies obtained when you apply Hamiltonian to the wave function and that is equal to h bar square by 2I J J plus 1.

So, this is for your diatomic molecule, but for different other kind of molecule, we can similarly obtain your linear momentum and momentum and energy. Hamiltonian can be expressed in this formula, where you have, you see in this molecule your Ia, Ib and Ic is different. And so, you have a formula where Hamiltonian in axis A, Hamiltonian in axis B and Hamiltonian in axis C. So, your Hamiltonian will be sum of these 3 part for a spherical top.

Since Ia is equal to Ib is equal to Ic, your Hamiltonian can be just given by operator L square divided by 2I and Er is simply h bar square by 2I J J plus 1. For prowled symmetric top Ia is less than Ib and Ic; Ib and Ic is equal.

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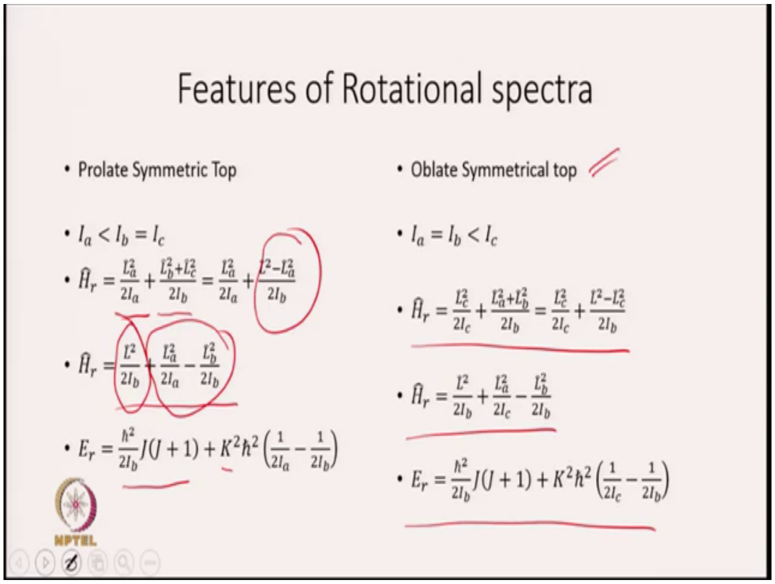

Features of Rotational spectra

- Prolate Symmetric Top
- $I_a < I_b = I_c$
- $\hat{H}_r = \frac{L_a^2}{2I_a} + \frac{L_b^2+L_c^2}{2I_b} = \frac{L_a^2}{2I_a} + \frac{L^2-L_a^2}{2I_b}$
- $\hat{H}_r = \frac{L^2}{2I_b} + \frac{L_a^2}{2I_a} - \frac{L_b^2}{2I_b}$
- $E_r = \frac{\hbar^2}{2I_b}J(J+1) + K^2\hbar^2\left(\frac{1}{2I_a} - \frac{1}{2I_b}\right)$

- Oblate Symmetrical top
- $I_a = I_b < I_c$
- $\hat{H}_r = \frac{L_c^2}{2I_c} + \frac{L_a^2+L_b^2}{2I_b} = \frac{L_c^2}{2I_c} + \frac{L^2-L_c^2}{2I_b}$
- $\hat{H}_r = \frac{L^2}{2I_b} + \frac{L_a^2}{2I_c} - \frac{L_b^2}{2I_b}$
- $E_r = \frac{\hbar^2}{2I_b}J(J+1) + K^2\hbar^2\left(\frac{1}{2I_c} - \frac{1}{2I_b}\right)$

So, Hamiltonian can be written like this operator La square divided by 2 Ia and then Lb square plus Lc square divided by 2Ib. So, here your moment of inertia along B axis and C axis is equal. And this can be written as La square minus La square.

So, La square is basically your operator La square plus Lb square plus Lc square. So, Lb Square plus Lc Square will be equal to La square minus La square. And that is what is done here. And then Hamiltonian can be written like this and this value, we already know, this h bar square by 2Ib J J plus 1 and then your, for these 2 terms, we can write another quantum number k. So, this is equal to k square, h bar square, 1 by 2 Ia minus 1 by 2 Ib.

Similarly, we can obtain energy for Oblate Symmetrical Top. In this kind of molecule Ia is equal to Ib. But this is less than Ic. So, Ic is greater than Ia and Ib. So, similarly, we can calculate Hamiltonian and once we know Hamiltonian, then we can get the energy term and that is simply h bar square by 2 Ib J J plus 1 plus k square h bar square into 1 by 2 Ic minus 1 by 2 Ib. It is similar to what we obtain for Prolate Symmetric Top. So, this is all about what we discussed last time.

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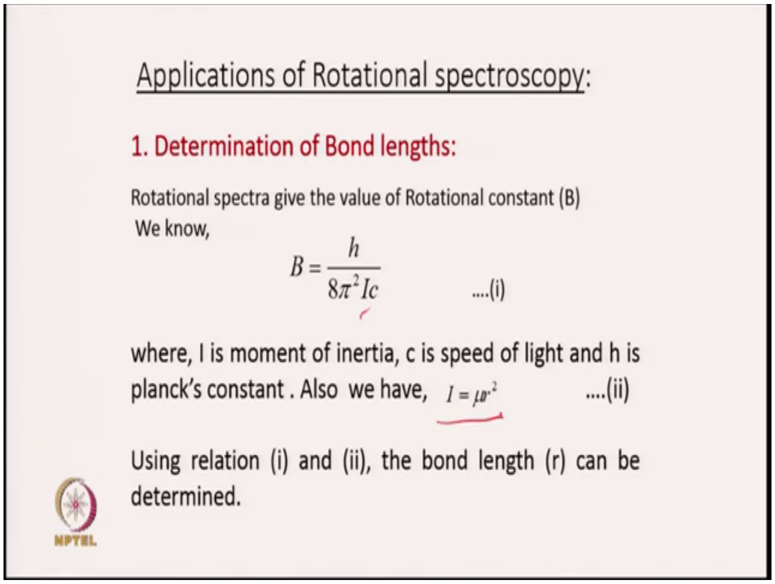

Applications of Rotational spectroscopy:

1. Determination of Bond lengths:

Rotational spectra give the value of Rotational constant (B)
We know,

$$B = \frac{h}{8\pi^2 Ic} \qquad \text{....(i)}$$

where, I is moment of inertia, c is speed of light and h is planck's constant . Also we have, $I = \mu r^2$ ....(ii)

Using relation (i) and (ii), the bond length (r) can be determined.

Now, we will go to application part, application of Rotational Spectroscopy. So, 1 of the most important application of Rotational Spectroscopy is determination of bond length. From the Rotational Spectra we can measure B and we know that B is inversely proportional to I. B is your rotational constant and it is inversely proportional to I, I is moment of inertia.

And I is given by reduce mass multiplied by R square, where R is your bond length. These 2 relations, we can calculate a bond length.

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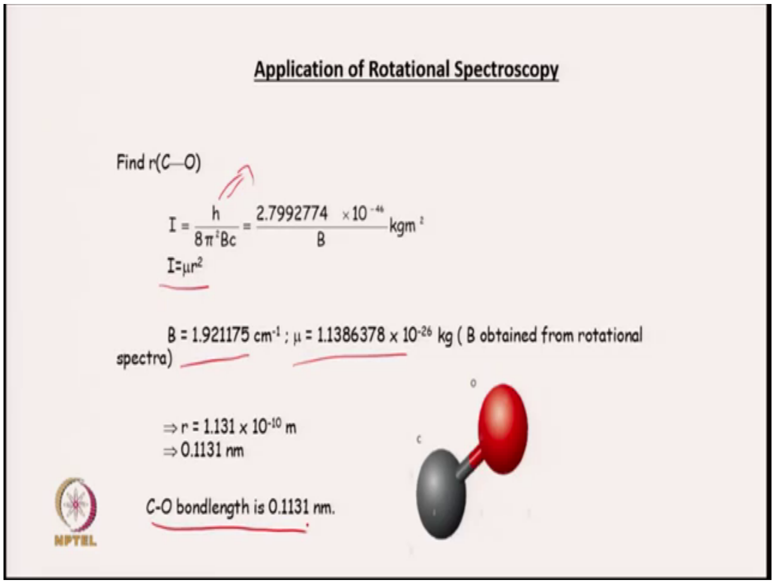

Application of Rotational Spectroscopy

Find r(C—O)

$$I = \frac{h}{8\pi^2 Bc} = \frac{2.7992774 \times 10^{-46}}{B} kgm^2$$

$I=\mu r^2$

$B = 1.921175\ cm^{-1}$; $\mu = 1.1386378 \times 10^{-26}$ kg (B obtained from rotational spectra)

$\Rightarrow r = 1.131 \times 10^{-10}$ m

$\Rightarrow$ 0.1131 nm

C-O bondlength is 0.1131 nm.

So, for example, if we take CO molecule, we can calculate CO bond length, if we can obtain Rotational Spectra of this molecule. From the Rotational Spectra what was observed that B is equal to 1.921175 centimeter inverse and by putting this into equation I is equal to h by 8 pi Square Bc, we can obtain your value of I and from I we can calculate your R since nu is equal to your 1.1386378 into 10 to power minus 26 kg.

So, if you can measure rotational constant from Rotational Spectroscopy, you can calculate moment of inertia and since moment of inertia is related to bond length, bond length can be calculated and that is what we have done in this example. From this CO bond length is calculated to be 0.1131 nanometer.

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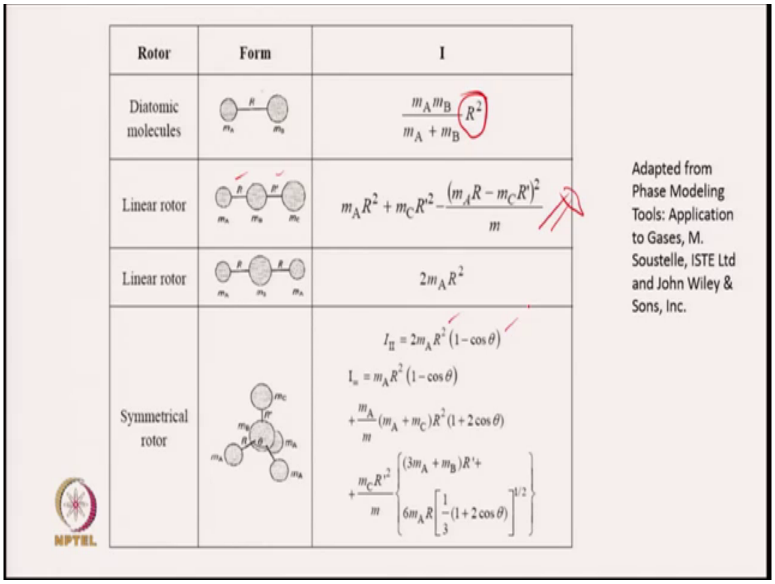

Rotor	Form	I
Diatomic molecules	R m_A m_B	$\frac{m_A m_B}{m_A + m_B} R^2$
Linear rotor	R R' m_A m_B m_C	$m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$
Linear rotor	R R m_A m_B m_A	$2 m_A R^2$
Symmetrical rotor	m_C R' m_B R θ m_A m_A m_A	$I_{\parallel} = 2m_A R^2 (1 - \cos\theta)$ $I_{\perp} = m_A R^2 (1 - \cos\theta)$ $+ \frac{m_A}{m}(m_A + m_C) R^2 (1 + 2\cos\theta)$ $+ \frac{m_C R'^2}{m} \left\{ \begin{matrix} (3m_A + m_B) R' + \\ 6m_A R \left[\frac{1}{3}(1 + 2\cos\theta) \right]^{1/2} \end{matrix} \right\}$

Adapted from Phase Modeling Tools: Application to Gases, M. Soustelle, ISTE Ltd and John Wiley & Sons, Inc.

Now, this is for diatomic molecule, but for other kind of molecule the I is not a simple function of R it is a function of 2 different distance or 1 distance and angle and this, this is basically given. Here diatomic molecule, you can see this is only function of R, but for linear molecule, which has 2 different distances R and R dash.

So, distance between atom A and B is R and atom B and C is R dash, then your moment of inertia can be written like this mA R square plus mC R square plus this whole term. Now, you can see that apart from mass this moment of inertia is a function of R and R dash. So, from simple 1 rotational constant you cannot calculate your bond length. Similarly, for symmetric rotor of this type, you can see that is a function of R and theta, R and theta.

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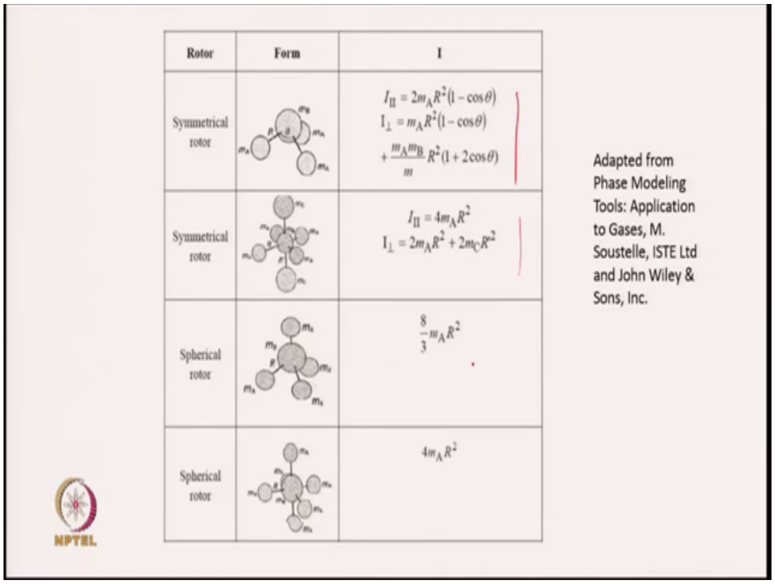

Rotor	Form	I
Symmetrical rotor		$I_{II} = 2m_A R^2(1-\cos\theta)$ $I_\perp = m_A R^2(1-\cos\theta)$ $+\frac{m_A m_B}{m} R^2(1+2\cos\theta)$
Symmetrical rotor		$I_{II} = 4m_A R^2$ $I_\perp = 2m_A R^2 + 2m_C R^2$
Spherical rotor		$\frac{8}{3} m_A R^2$
Spherical rotor		$4m_A R^2$

Adapted from Phase Modeling Tools: Application to Gases, M. Soustelle, ISTE Ltd and John Wiley & Sons, Inc.

And similarly, you can have a different kind of rotors and for different kind of rotors moment of inertia will be different and these are the equation which is given here again you see I perpendicular and I parallel can be given. So, if there is more than 1 variable on which moment of inertia depends then what will you do?

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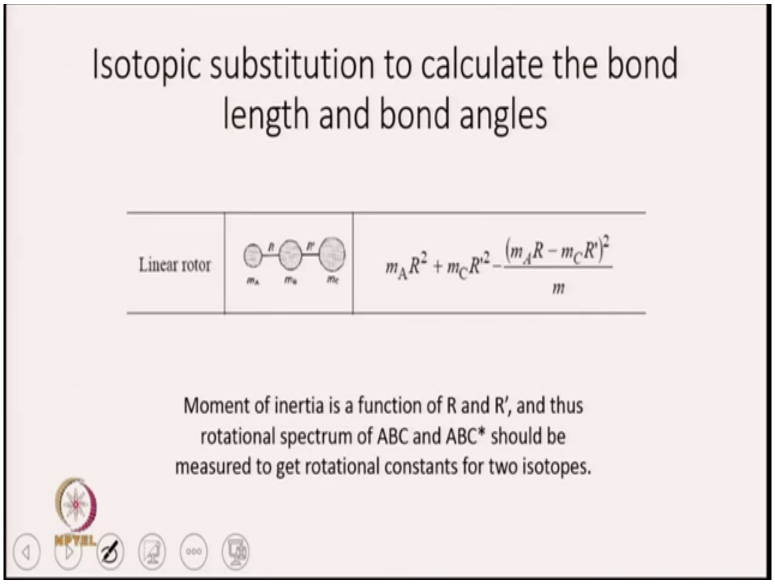

Isotopic substitution to calculate the bond length and bond angles

Linear rotor		$m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$

Moment of inertia is a function of R and R′, and thus rotational spectrum of ABC and ABC* should be measured to get rotational constants for two isotopes.

1 thing which is done is to do Isotopic Substitution and good thing is once you do that and see the Rotational Spectra of that isotope, isotopic molecule, then not only you can get bond length, you can also calculate bond angle. For example, for this linear rotor, I just told you that moment of inertia is function of R and R dash.

So, 1 of the way to get R and R dash is to obtain rotational a spectrum of molecules, suppose ABC and ABC star, C star is basically isotope of C everything is same R and R dash is same, mC differs and you know what is the mC. Then you have a 2 rotational constant and your moment of inertia is variable of 2 functions. So, you have a 2 constants and 2 functions, 2 unknowns and so you can calculate R and R dash.

And similarly, if your moment of inertia is a function of RN theta you can get RN theta by isotopic substitution.

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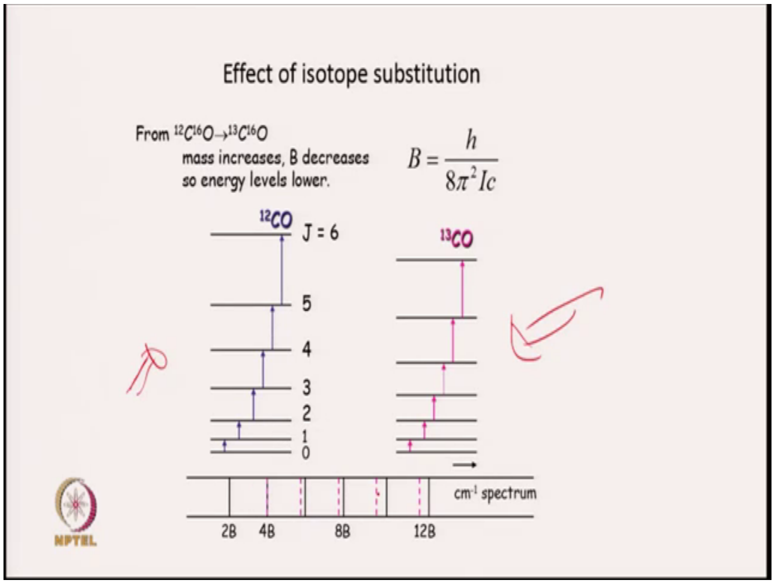

Effect of isotope substitution

From $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$
mass increases, B decreases
so energy levels lower.

$$B = \frac{h}{8\pi^2 Ic}$$

So, next we will discuss what is the Effect of Isotope of Substitution. For example, if we go from 12 Carbon 16 Oxygen to 13 Carbon and 16 Oxygen, so, here we are going from 1 isotope 12C to 13C. So, we know that B is inversely proportional to I and since I increases when you go from 12C, 16O to 13C, 16O, and so, B is going to decrease and once B is going to decrease and then you can see that the difference between different energy level is also going to decrease.

So, this is your rotational energy level of 12CO and this is your rotational energy level of 16CO and you can see that here energy difference is greater and here energy difference is small. And so, your peak or spectra of this isotope 13CO will come at a smaller B value, smaller B value. So, you can see the shift is towards left hand side.

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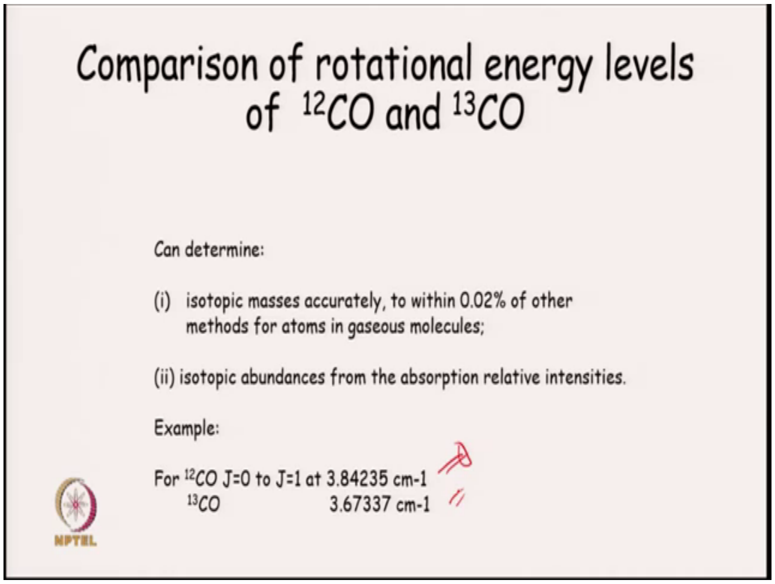

Comparison of rotational energy levels of ^{12}CO and ^{13}CO

Can determine:

(i) isotopic masses accurately, to within 0.02% of other methods for atoms in gaseous molecules;

(ii) isotopic abundances from the absorption relative intensities.

Example:

For ^{12}CO J=0 to J=1 at 3.84235 cm-1
^{13}CO 3.67337 cm-1

So, apart from giving the value of R and R dash or R and theta, the isotopic substitution can also help us in 2 different things. 1 is to calculate isotopic mass accurately within 0.02 percent of other methods. And then second is isotopic abundance from the absorption relative intensity. So, just we calculated from the Rotational Spectra what people saw is 12 for 12CO, your rotational constant is 3.84325 centimeter inverse and from 13CO it is this value. Now, this can be used to calculate accurate mass of your 13C.

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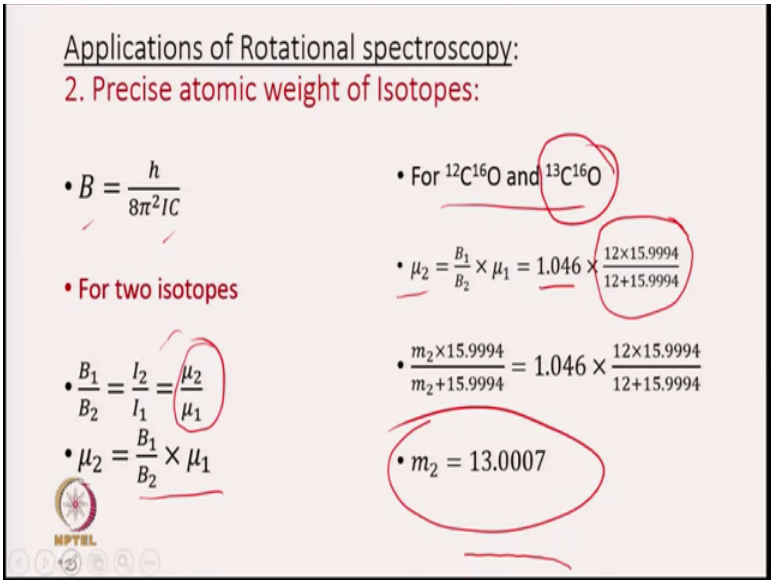

Applications of Rotational spectroscopy:

2. Precise atomic weight of Isotopes:

- $B = \frac{h}{8\pi^2 IC}$
- For two isotopes
- $\frac{B_1}{B_2} = \frac{I_2}{I_1} = \frac{\mu_2}{\mu_1}$
- $\mu_2 = \frac{B_1}{B_2} \times \mu_1$

- For $^{12}C^{16}O$ and $^{13}C^{16}O$
- $\mu_2 = \frac{B_1}{B_2} \times \mu_1 = 1.046 \times \frac{12\times15.9994}{12+15.9994}$
- $\frac{m_2\times15.9994}{m_2+15.9994} = 1.046 \times \frac{12\times15.9994}{12+15.9994}$
- $m_2 = 13.0007$

So, the second application of Rotational Spectroscopy is to get Precise atomic weight of isotopes. B value we know that it is inversely proportional to I. So, if you take 2 isotopes for example 12C and 13C, then your B 1 by B 2 will be going to I 2 by I1 and since I is mu R square and if we assume that bond length does not change, if I change; 12C by 13C in CO then you can simply write it is I2 by I1 is equal to mu 2 by mu 1. B is basically inversely proportional to reduced mass. So, reduced mass of the second component can be calculated by simply B 1 by B 2 into mu 1. So, if I take the example of 12C 16O and 13C 16O, so, mu 2 means reduced mass of 13C 16O, will be given by B1 by B2 into mu 1.

We already know (1) B1 by B2 is 1.046. This is obtained from rotational spectroscopy; rotational spectra of 12C 16O and 13C 16O. So, this is 1.046 and then this is your mu of 12C 16O, reduced mass of 12C 16O and if you put in this equation, you can get accurate mass of 13C, you can get accurate mass of 13C and that is 13.0007.

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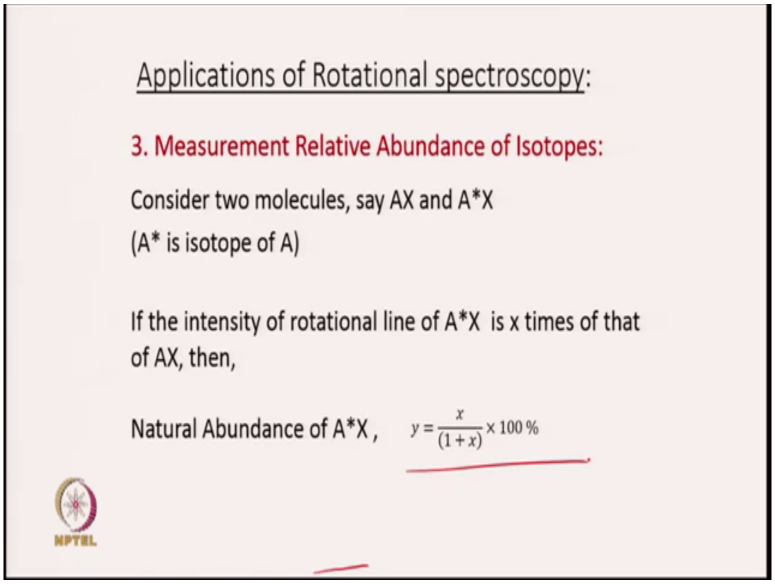

Applications of Rotational spectroscopy:

3. Measurement Relative Abundance of Isotopes:

Consider two molecules, say AX and A*X
(A* is isotope of A)

If the intensity of rotational line of A*X is x times of that of AX, then,

Natural Abundance of A*X, $y = \frac{x}{(1+x)} \times 100\,\%$

Then, the next application is again this is related to isotope effect that you can also measure relative abundance of isotopes. So, suppose there are 2 molecule in a sample AX and A star X where, A star is your isotope of A and if we see the spectra of this sample and what we found out that intensity of rotational line of A star X is X times that of AX, then we can calculate natural abundance of A star X and that is given by this equation, y is equal to x divided by 1 plus x into 100 percent.

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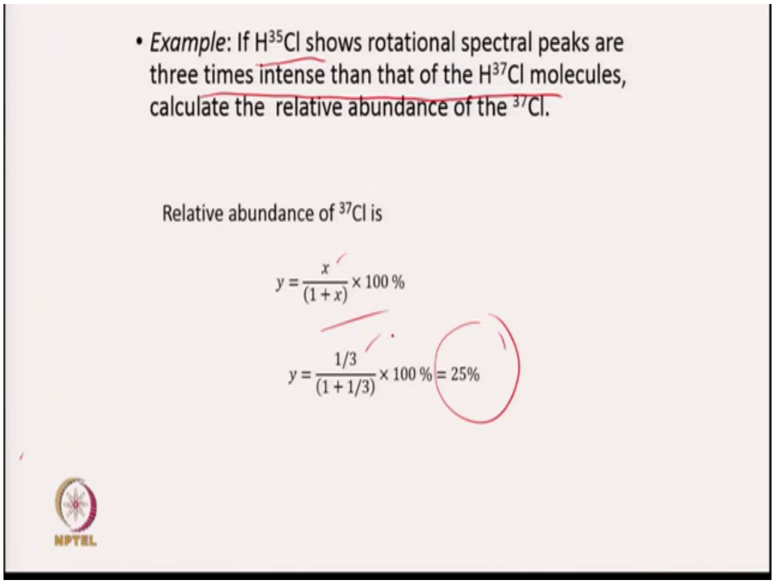

- *Example*: If H^{35}Cl shows rotational spectral peaks are three times intense than that of the H^{37}Cl molecules, calculate the relative abundance of the ^{37}Cl.

Relative abundance of ^{37}Cl is

$$y = \frac{x}{(1+x)} \times 100\,\%$$

$$y = \frac{1/3}{(1+1/3)} \times 100\,\% = \boxed{25\%}$$

So, now, we will see how to calculate relative abundance of certain isotope in a molecule by looking at the rotational a spectrum of the molecule. So, in the given example, it is given that H35Cl. So, hydrochloric acid where chlorine is, chlorine is in the isotope form 35Cl. It shows rotational spectrum peak which is 3 time intense, 3 times intense than the H37Cl molecule. So, now, we have to calculate what is the relative abundance of 37Cl in the molecule. So, relative abundance of 37Cl can be calculated by using this method, where x is the intensity of molecule with the isotope with respect to the H35Cl, with respect to H35Cl.

So, y will be given by x divided by 1 plus x into 100 percent and since it is given that H35Cl has 3 times more intense peak than H37Cl. What does that mean is H37Cl intensity, peak intensity is 1 third of H35Cl peak intensity and so, x is equal to 1 by 3 and if you put x is equal to 1 by 3, what you are going to get is 25 percent. So, just by looking at the intensity of, intensity of different peaks in the rotational spectrum, we can calculate relative abundance of the isotope of the isotope. There are other application of Rotational Spectroscopy.

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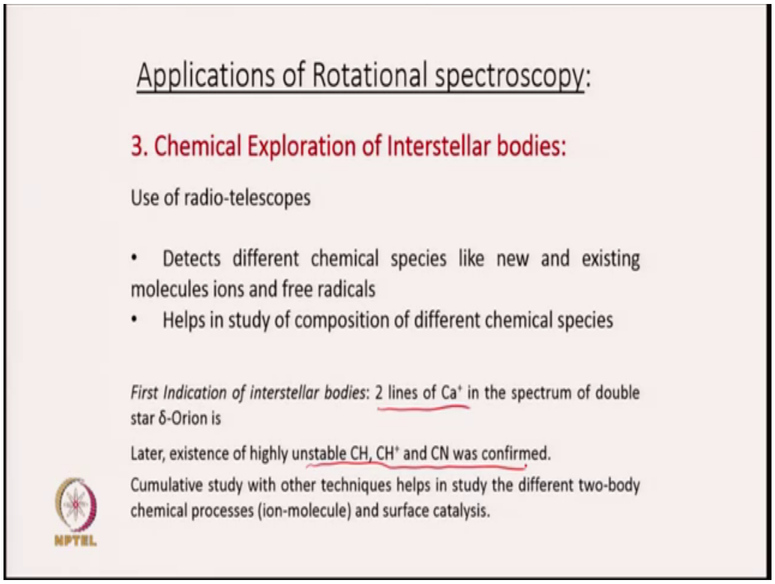

Applications of Rotational spectroscopy:

3. Chemical Exploration of Interstellar bodies:

Use of radio-telescopes

- Detects different chemical species like new and existing molecules ions and free radicals
- Helps in study of composition of different chemical species

First Indication of interstellar bodies: 2 lines of Ca^+ in the spectrum of double star δ-Orion is

Later, existence of highly unstable CH, CH^+ and CN was confirmed.

Cumulative study with other techniques helps in study the different two-body chemical processes (ion-molecule) and surface catalysis.

Rotational Spectroscopy is quite often used for chemical exploration of interstellar bodies. And for that radio telescopes are used. They detect different chemical species like new and existing molecules and free radicals and then they also help us in a study of composition of different chemical species. So, first indication of interstellar body comes by looking at calcium 2 plus lines in a spectrum of double star delta Orion, ok.

And later existence of highly unstable species was confirmed using Rotational Spectroscopy. It has also been seen that few molecules are discovered in the interstellar bodies, which were not seen in the experimental methods, but when you find out, ok, this molecule can exist then people went back to lab and try to confirm those molecules and they were able to see those molecules. So, cumulative studies with other techniques were also used to find out different chemical processes in interstellar bodies.

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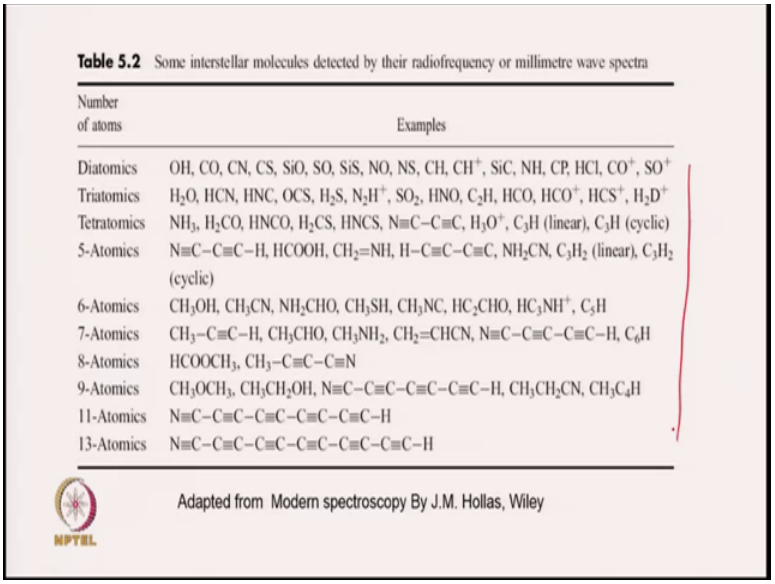


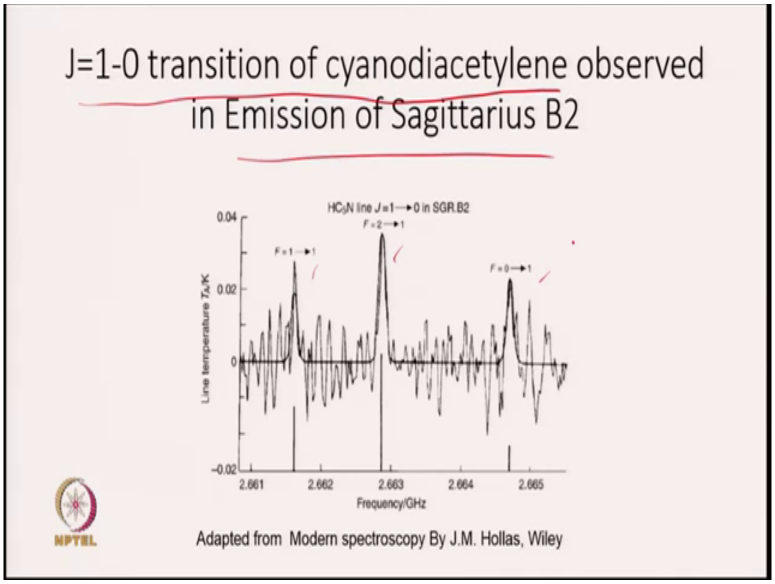
Table 5.2 Some interstellar molecules detected by their radiofrequency or millimetre wave spectra

Number of atoms	Examples
Diatomics	OH, CO, CN, CS, SiO, SO, SiS, NO, NS, CH, CH^+, SiC, NH, CP, HCl, CO^+, SO^+
Triatomics	H_2O, HCN, HNC, OCS, H_2S, N_2H^+, SO_2, HNO, C_2H, HCO, HCO^+, HCS^+, H_2D^+
Tetratomics	NH_3, H_2CO, $HNCO$, H_2CS, $HNCS$, $N\equiv C-C\equiv C$, H_3O^+, C_3H (linear), C_3H (cyclic)
5-Atomics	$N\equiv C-C\equiv C-H$, $HCOOH$, $CH_2=NH$, $H-C\equiv C-C\equiv C$, NH_2CN, C_3H_2 (linear), C_3H_2 (cyclic)
6-Atomics	CH_3OH, CH_3CN, NH_2CHO, CH_3SH, CH_3NC, HC_2CHO, HC_3NH^+, C_5H
7-Atomics	$CH_3-C\equiv C-H$, CH_3CHO, CH_3NH_2, $CH_2=CHCN$, $N\equiv C-C\equiv C-C\equiv C-H$, C_6H
8-Atomics	$HCOOCH_3$, $CH_3-C\equiv C-C\equiv N$
9-Atomics	CH_3OCH_3, CH_3CH_2OH, $N\equiv C-C\equiv C-C\equiv C-C\equiv C-H$, CH_3CH_2CN, CH_3C_4H
11-Atomics	$N\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-H$
13-Atomics	$N\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-H$

Adapted from Modern spectroscopy By J.M. Hollas, Wiley

So, this is different kind of molecule which has been detected by radio frequency or Rotational Spectroscopy. So, there are whole lot of molecule which was found in the interstellar bodies, it is from diatomic to 13 atomic molecules and the list is given here and that is taken from modern spectroscopy book by Hollas.

(Refer Slide Time: 22:22)



J=1-0 transition of cyanodiacetylene observed in Emission of Sagittarius B2

Adapted from Modern spectroscopy By J.M. Hollas, Wiley

There are other planets or stars has been studied for their chemical composition and this is cyanodiacetylene. This was found to be in the emission of your Sagittarius B2 and these are your spectral lines corresponding to 1-0 transition. And that is how it was found out that in emission, there is presence of cyanodiacetylene.

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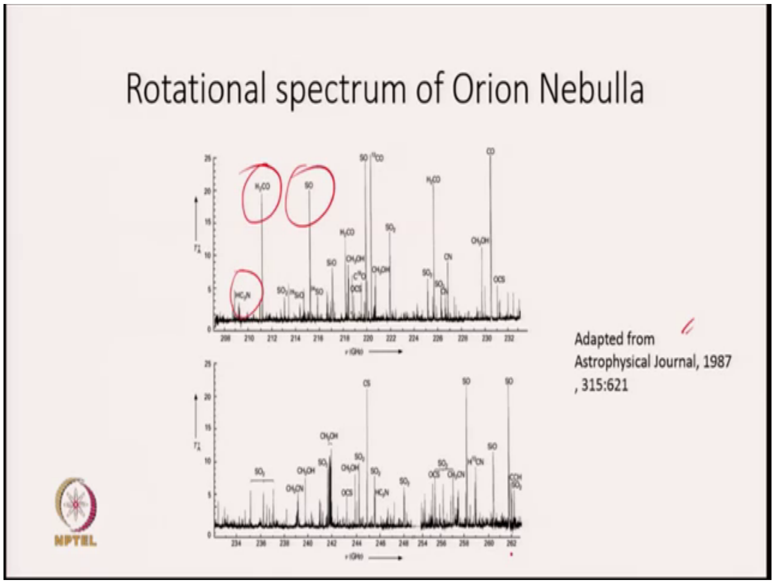

Rotational spectrum of Orion Nebula

Adapted from Astrophysical Journal, 1987 , 315:621

Similarly, Rotational Spectrum of Orion Nebulla has also been carried out and this is adapted from Astrophysical Journal and here you can see that there are different kind of molecules like HC3N, H2CO, SO.

So, you see this is from 208 to 232 gigahertz and then 234 to 262 gigahertz. So many molecules can be seen in the rotational spectrum of Orion Nebulla.

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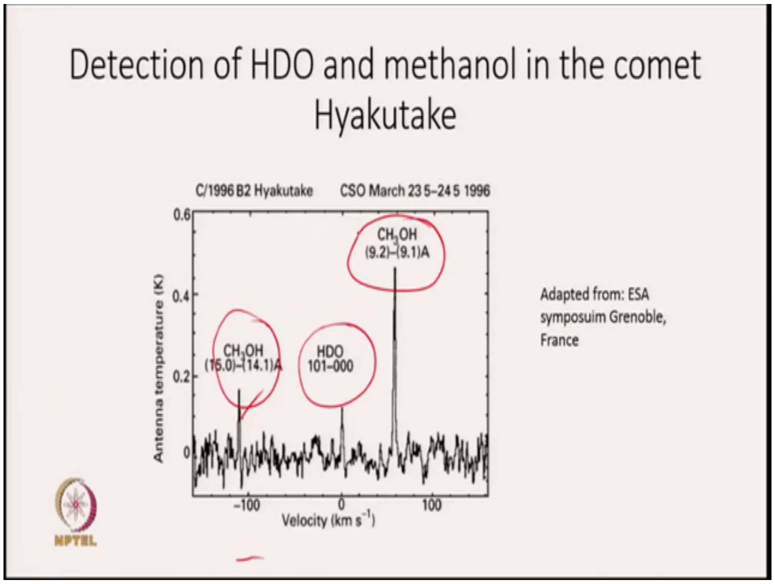

Detection of HDO and methanol in the comet Hyakutake

Adapted from: ESA symposuim Grenoble, France

Similarly, HDO and methanol is detected these molecules are detected in the comet Hyakutake and you can see this is the methanol this peak is corresponds to methanol. This peak corresponds to HDO and this again peak correspond to methanol. So, different kind of species contribute to different kind of planets, comets, stars. Rotational spectroscopy is 1 of the very important tool to know the composition of these emissions.

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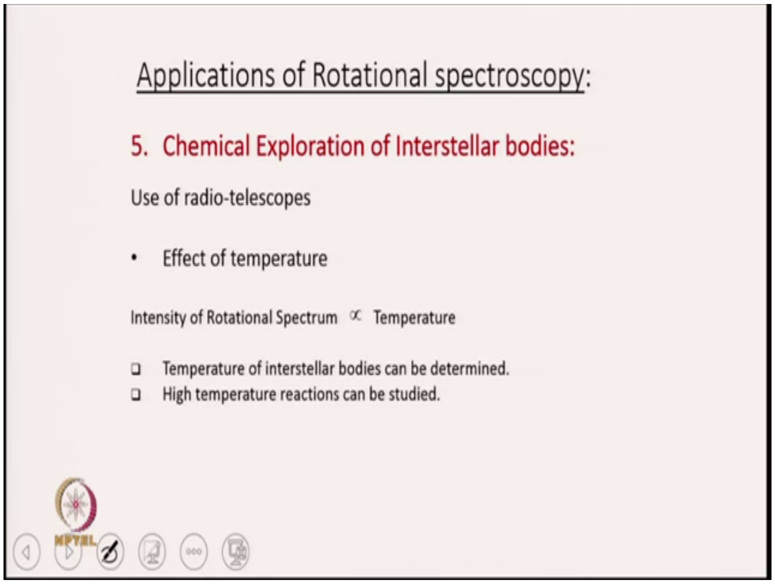

Applications of Rotational spectroscopy:

5. Chemical Exploration of Interstellar bodies:

Use of radio-telescopes

- Effect of temperature

Intensity of Rotational Spectrum ∝ Temperature

☐ Temperature of interstellar bodies can be determined.
☐ High temperature reactions can be studied.

It has been used for determination of temperature. So, intensity of rotational a spectrum is proportional to temperature if you remember that intensity is related to number of atoms in ground state and excited state and Boltzmann distribution depends on temperature. So, intensity of rotational a spectrum also depends on temperature. So, temperature of interstellar bodies can also be determined using rotational spectroscopy, high temperature reaction can also be studied.

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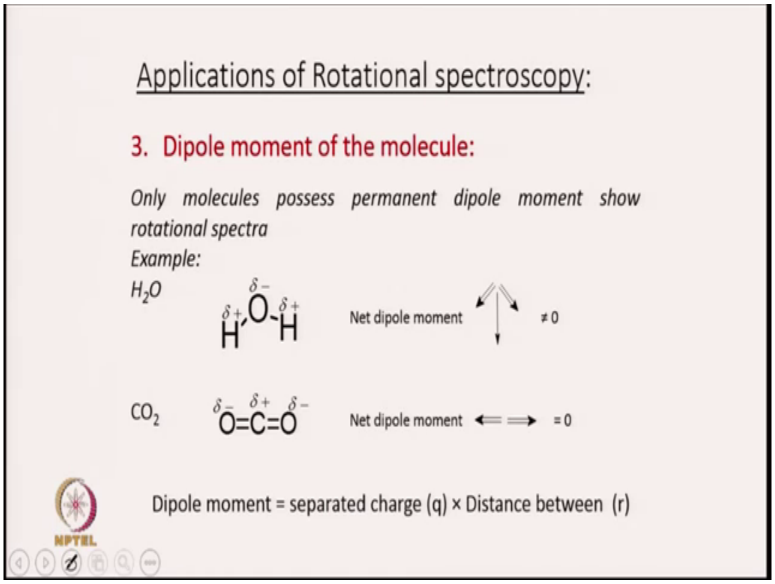

Applications of Rotational spectroscopy:

3. Dipole moment of the molecule:

Only molecules possess permanent dipole moment show rotational spectra

Example:

H_2O Net dipole moment $\neq 0$

CO_2 Net dipole moment $= 0$

Dipole moment = separated charge (q) × Distance between (r)

Now, next application of Rotational Spectroscopy is in obtaining dipole moment of the molecule and we already know from the Gross Selection Rule of Rotational Spectroscopy that only molecule that posses permanent dipole moment will show Rotational Spectra. Dipole moment is separated charge into distance. So, the dipole moment can also be calculated by rotors now.

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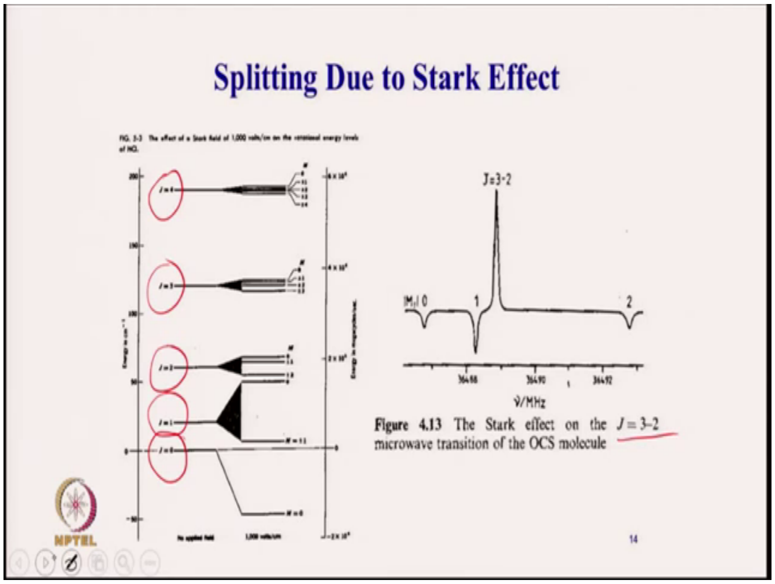

Splitting Due to Stark Effect

FIG. 3-3 The effect of a Stark field of 1,000 volts/cm on the rotational energy levels of HCl.

Figure 4.13 The Stark effect on the $J = 3–2$ microwave transition of the OCS molecule

What we do is generally we see the effect of a Stark, effect of electrical field on the rotational spectroscopy and that is related to dipole moment. And that is known as Stark Effect. If you remember that you know rotational levels are degenerate and degeneracy is given by 2j plus 1. But, this degenerate levels degeneracy is lifted in presence of electrical field which is known as Stark Effect and this levels, so, J is equal to 0, J is equal to 1, J is equal to 2, 3, 4, they split into J plus 1 level.

So, for example, if J is equal to 2, then it will split in 3 levels. If J is equal to 3 then it will be split into 4 levels and this is your Stark Effect on J is equal to 3 to 2 your rotational spectrum of OCS molecule.

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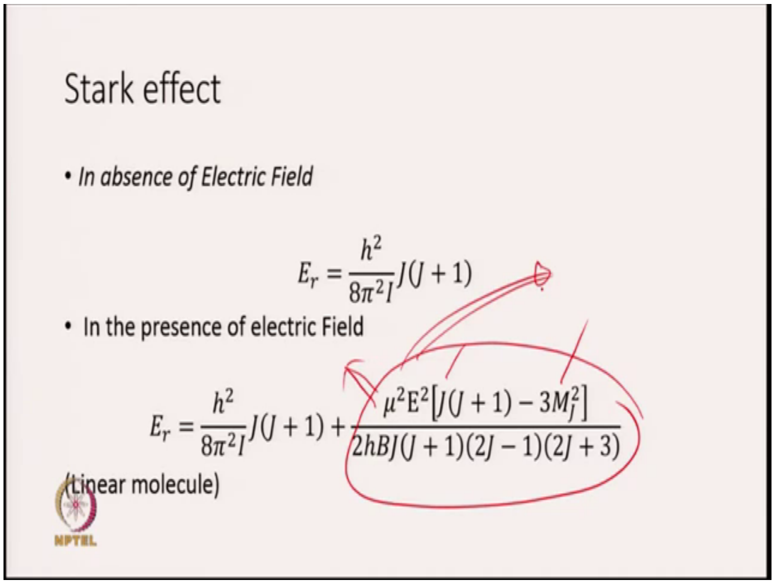

Stark effect

- *In absence of Electric Field*

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

- In the presence of electric Field

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) + \frac{\mu^2 E^2 [J(J+1) - 3M_J^2]}{2hBJ(J+1)(2J-1)(2J+3)}$$

(Linear molecule)

And this splitting is dependent on dipole moment okay. So, in absence of electric field, we know that energy is given by h square by 8 pi Square I J J plus 1, but influence of electric field particularly for linear molecule, there is 1 more terms here comes.

So, in absence of electrical field your energy is not dependent on m, but in presence of electrical field energy is dependent on not only J it will also be dependent on m and here mu is your dipole moment, mu is your dipole moment. E is electrical field. So, by studying Stark Effect, we can obtain the value of (())(27:04). So, this is the way dipole moment is calculated.

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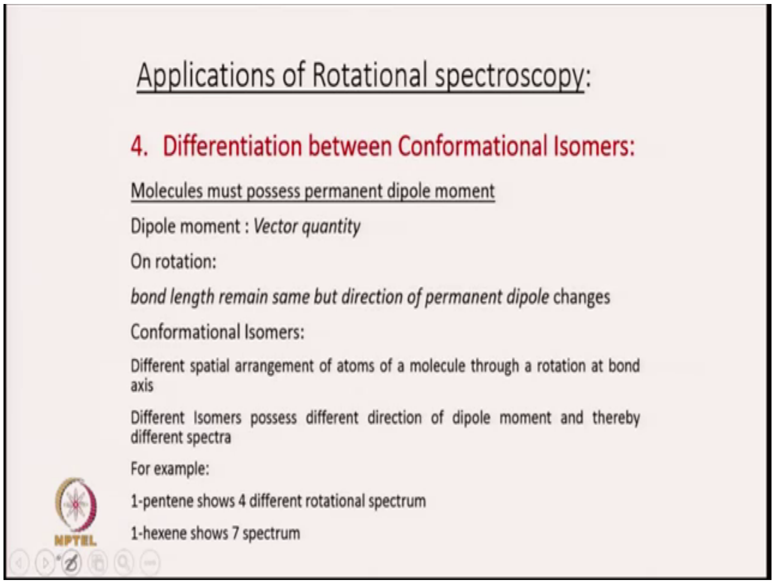

Applications of Rotational spectroscopy:

4. Differentiation between Conformational Isomers:

Molecules must possess permanent dipole moment

Dipole moment : *Vector quantity*

On rotation:

bond length remain same but direction of permanent dipole changes

Conformational Isomers:

Different spatial arrangement of atoms of a molecule through a rotation at bond axis

Different Isomers possess different direction of dipole moment and thereby different spectra

For example:

1-pentene shows 4 different rotational spectrum

1-hexene shows 7 spectrum

There are other application, Differentiation between Conformational Isomers and conformational isomers will have different dipole moment if they are polar. And on rotation bond length will remain same but direction of permanent dipole moment changes. So, everything is same. Only thing is your dipole moment is different. And, so, we can know from the Rotational Spectroscopy which conformational isomer exists.

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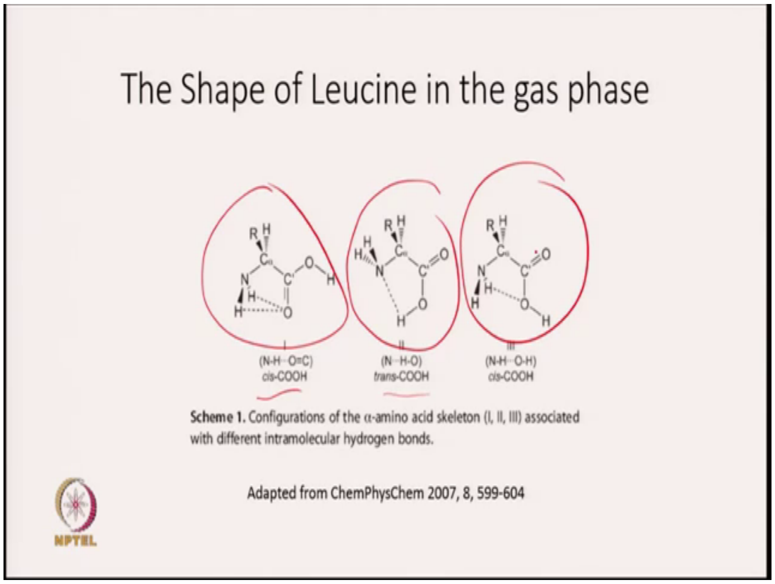

The Shape of Leucine in the gas phase

Scheme 1. Configurations of the α-amino acid skeleton (I, II, III) associated with different intramolecular hydrogen bonds.

Adapted from ChemPhysChem 2007, 8, 599-604

So, I will discuss 1 paper, Shape of Leucine has been seen in the gas phase. So, this is your skeleton of alpha amino acids and based on different intramolecular hydrogen bond 3 conformation has been considered, 3 conformation has been considered 1, 2 and 3, this is called sis COOH, trance COOH and this sis COOH, but you can see here that this H like here, here this H this 2 H and then here H is like this. But, now here, there is a flipping. So, this 3 different kind of amino acid skeleton you can think of with different intramolecular bonds.

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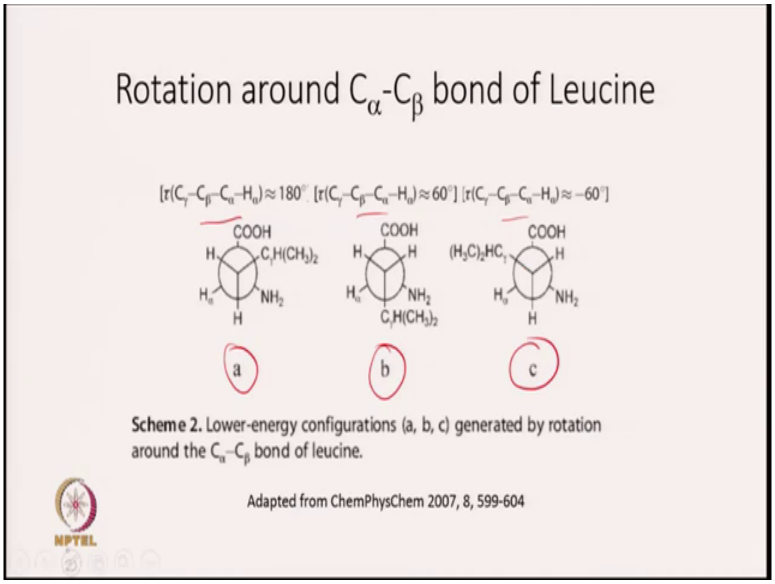

Rotation around C_α-C_β bond of Leucine

$[\tau(C_\gamma-C_\beta-C_\alpha-H_\alpha)\approx 180^\circ]$ $[\tau(C_\gamma-C_\beta-C_\alpha-H_\alpha)\approx 60^\circ]$ $[\tau(C_\gamma-C_\beta-C_\alpha-H_\alpha)\approx -60^\circ]$

Scheme 2. Lower-energy configurations (a, b, c) generated by rotation around the C_α–C_β bond of leucine.

Adapted from ChemPhysChem 2007, 8, 599-604

Now, we can again think of each of this 1, 2, 3 isomer can exist as a, b and c depending on rotation about C alpha and C beta bond, C alpha and C beta bond. So, you see, C alpha, C beta bond. This is C alpha, C beta, C alpha, this is C alpha we had and this is your C beta the upper bond is C beta, lower bond is C alpha and this is C gamma.

So, here can see the angle is 180 degree. In this again you will see this is C alpha, C beta is the upper bond and C gamma here this angle is your 60 degree. And here your C alpha which is below the plane C beta is up the plane and your C gamma here, this is your minus 60 degree. So, this 3 conformation you can think of, these are lower energy configuration and they are generated by rotation around C alpha, C beta bond. Similarly, C beta and gamma.

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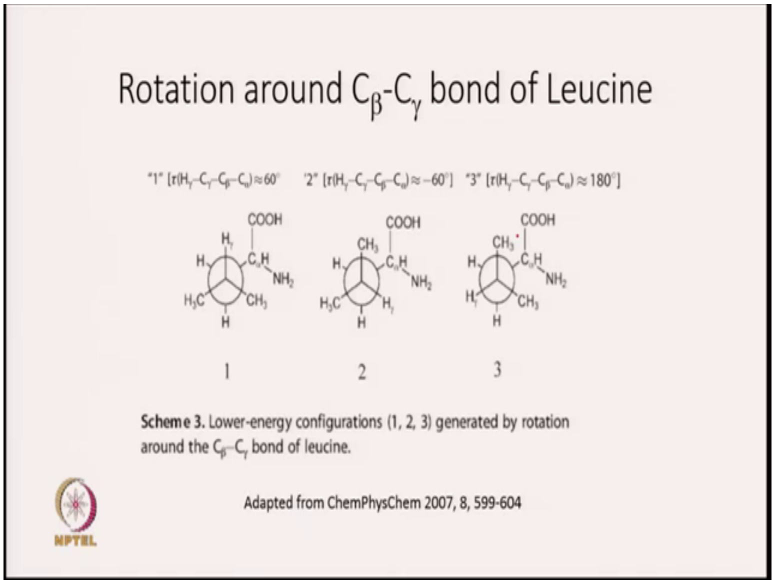

Rotation around C_β-C_γ bond of Leucine

"1" [$\tau(H_\gamma-C_\gamma-C_\beta-C_\alpha) \approx 60°$] "2" [$\tau(H_\gamma-C_\gamma-C_\beta-C_\alpha) \approx -60°$] "3" [$\tau(H_\gamma-C_\gamma-C_\beta-C_\alpha) \approx 180°$]

1 2 3

Scheme 3. Lower-energy configurations (1, 2, 3) generated by rotation around the C_β–C_γ bond of leucine.

Adapted from ChemPhysChem 2007, 8, 599-604

So, again, there will be 3 different angles 60 degree, minus 60 degree, 180 degree. So, you have C gamma. So, you see this is the H gamma and this is C gamma and then below 1 will be C beta and this is C alpha this angle is 60 degree. Similarly, minus 60 degree and 180 degree. So, these are low energy configuration generated by the rotation around the C beta, C gamma bond of Leucine. So, in effect, there will be 3 into 3 into 3, 27 different kind of conformation which you can think of which, which are lower energy configurations.

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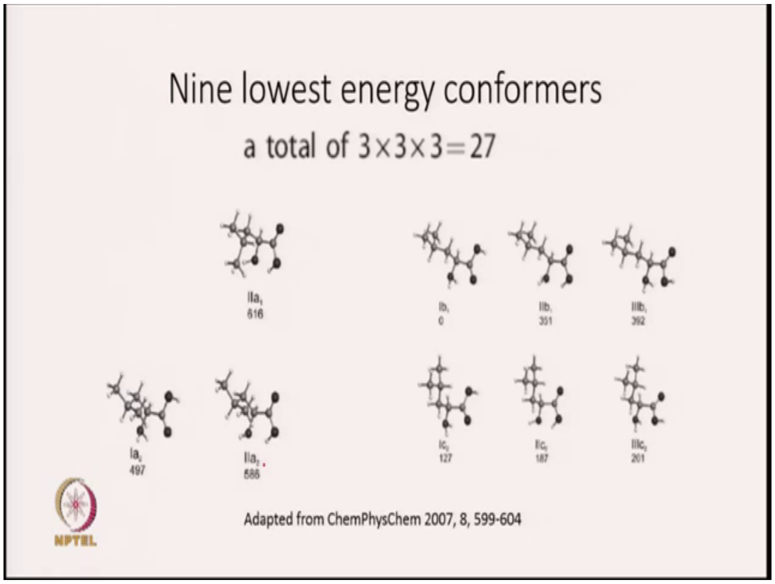

Nine lowest energy conformers

a total of 3×3×3=27

Adapted from ChemPhysChem 2007, 8, 599-604

So, total of 27 conformation and then they did (())(30:26) calculation and they find out that out of this 27 your 9 is the lowest in energy conformation and they have given the name 2 a 1, 2 1 v similarly, so 2 is your based on hydrogen bonding, the A is based on rotation around C alpha, C beta bond and this 1 and this is 2 is based on your rotation around C beta, C gamma bond.

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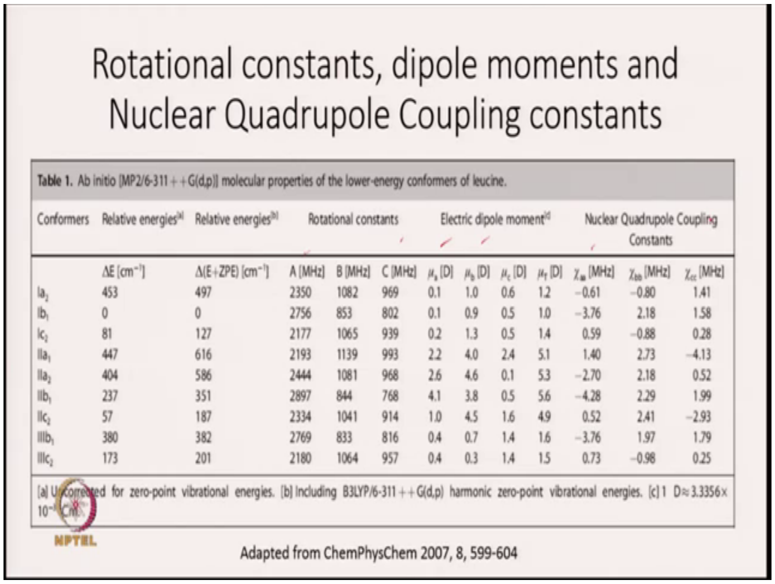

Rotational constants, dipole moments and Nuclear Quadrupole Coupling constants

Table 1. Ab initio [MP2/6-311++G(d,p)] molecular properties of the lower-energy conformers of leucine.

Conformers	Relative energies[a]	Relative energies[b]	Rotational constants			Electric dipole moment[c]				Nuclear Quadrupole Coupling Constants		
	ΔE [cm^{-1}]	Δ(E+ZPE) [cm^{-1}]	A [MHz]	B [MHz]	C [MHz]	μ_a [D]	μ_b [D]	μ_c [D]	μ_T [D]	χ_{aa} [MHz]	χ_{bb} [MHz]	χ_{cc} [MHz]
Ia$_2$	453	497	2350	1082	969	0.1	1.0	0.6	1.2	−0.61	−0.80	1.41
Ib$_1$	0	0	2756	853	802	0.1	0.9	0.5	1.0	−3.76	2.18	1.58
Ic$_2$	81	127	2177	1065	939	0.2	1.3	0.5	1.4	0.59	−0.88	0.28
IIa$_1$	447	616	2193	1139	993	2.2	4.0	2.4	5.1	1.40	2.73	−4.13
IIa$_2$	404	586	2444	1081	968	2.6	4.6	0.1	5.3	−2.70	2.18	0.52
IIb$_1$	237	351	2897	844	768	4.1	3.8	0.5	5.6	−4.28	2.29	1.99
IIc$_2$	57	187	2334	1041	914	1.0	4.5	1.6	4.9	0.52	2.41	−2.93
IIIb$_1$	380	382	2769	833	816	0.4	0.7	1.4	1.6	−3.76	1.97	1.79
IIIc$_2$	173	201	2180	1064	957	0.4	0.3	1.4	1.5	0.73	−0.98	0.25

[a] Uncorrected for zero-point vibrational energies. [b] Including B3LYP/6-311++G(d,p) harmonic zero-point vibrational energies. [c] 1 D≈3.3356×10$^{-[illegible]}$ Cm.

Adapted from ChemPhysChem 2007, 8, 599-604

This 9 lowest energy conformations, they calculated your rotational spectra, they calculated rotational constant and these are the different rotational constant and A, B, C,they calculated electric dipole moment, they calculated nuclear dipole moment. So, these are all theoretical calculations.

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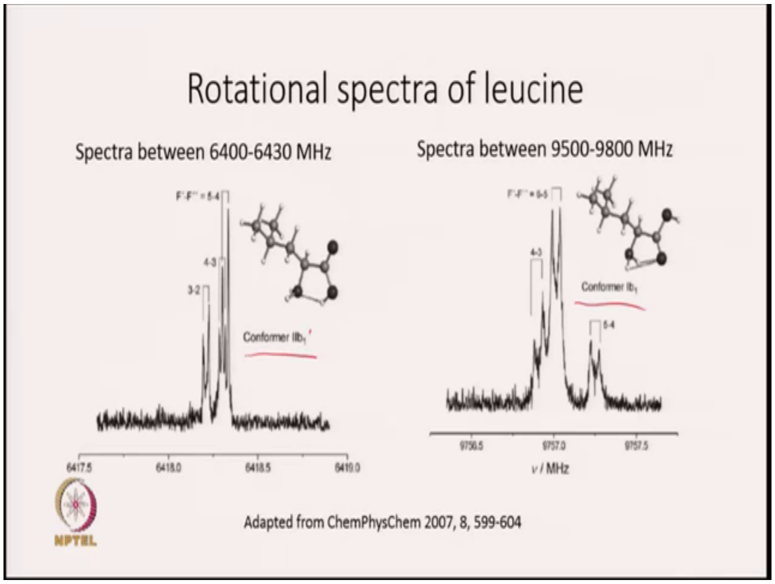

Rotational spectra of leucine

Spectra between 6400-6430 MHz

Spectra between 9500-9800 MHz

Adapted from ChemPhysChem 2007, 8, 599-604

So, they obtained the Rotational Spectra of Leucine and what they are able to find out, there are only 2 conformation they can find only 2 conformation, which is basically your populating the leucine in the sample and that is called 2 B 1, that is 2 B 1 and this is your 1 B 1.

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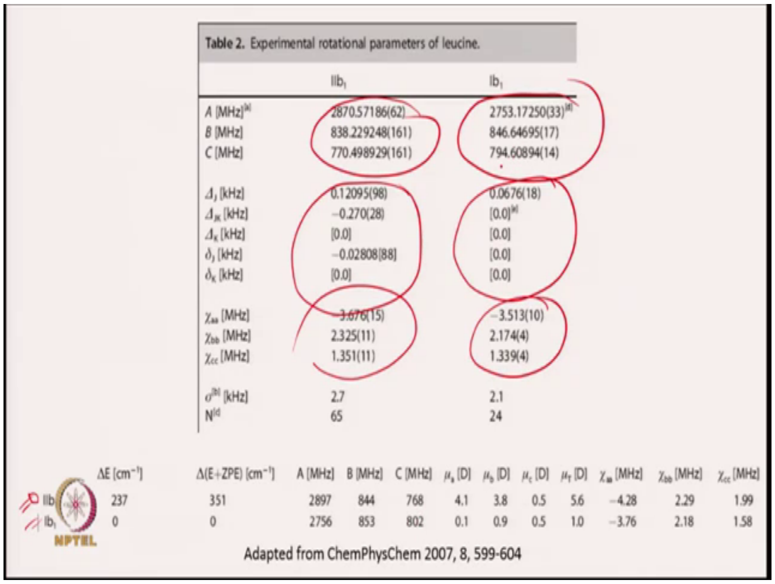

Table 2. Experimental rotational parameters of leucine.

	IIb_1	Ib_1
A [MHz][a]	2870.57186(62)	2753.17250(33)[a]
B [MHz]	838.229248(161)	846.64695(17)
C [MHz]	770.498929(161)	794.60894(14)
Δ_J [kHz]	0.12095(98)	0.0676(18)
Δ_{JK} [kHz]	−0.270(28)	[0.0][a]
Δ_K [kHz]	[0.0]	[0.0]
δ_J [kHz]	−0.02808(88)	[0.0]
δ_K [kHz]	[0.0]	[0.0]
χ_{aa} [MHz]	−3.676(15)	−3.513(10)
χ_{bb} [MHz]	2.325(11)	2.174(4)
χ_{cc} [MHz]	1.351(11)	1.339(4)
σ[b] [kHz]	2.7	2.1
N[c]	65	24

	ΔE [cm⁻¹]	Δ(E+ZPE) [cm⁻¹]	A [MHz]	B [MHz]	C [MHz]	μ_a [D]	μ_b [D]	μ_c [D]	μ_T [D]	χ_{aa} [MHz]	χ_{bb} [MHz]	χ_{cc} [MHz]
IIb	237	351	2897	844	768	4.1	3.8	0.5	5.6	−4.28	2.29	1.99
Ib_1	0	0	2756	853	802	0.1	0.9	0.5	1.0	−3.76	2.18	1.58

Adapted from ChemPhysChem 2007, 8, 599-604

And you can see here that for this 2 B 1 these are the values which has been obtained by Rotational Spectroscopy 1 B 1 these are the value for rotational constant, these are the values for dipole moment and this is value for the clear quadruple splitting, these are the values for; and this is the 1 which they obtained from the theoretical modeling and you can see that A value 2008 97 and you see 2 870 844 838 768 770 and for 1 B 1, 2756, A, B value is 853 and C value is, 802.

On, so, now, by matching experimental with the theoretical calculation and they are able to predict that Leucine exist in 2 different form, 1 is 2 B 1 and another is 1 B 1. Conformation can be differentiated by obtaining your rotational spectrum.

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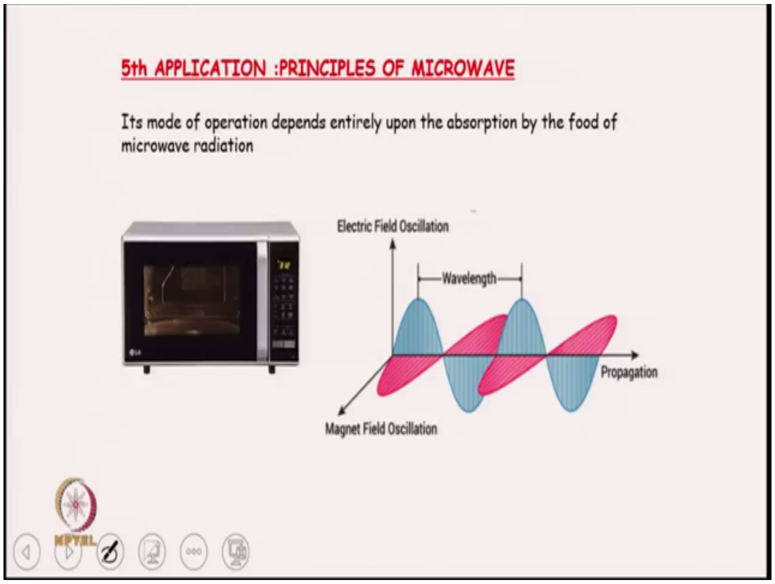

5th APPLICATION :PRINCIPLES OF MICROWAVE

Its mode of operation depends entirely upon the absorption by the food of microwave radiation

Another application is which is well known application is microwave, ok. Its mode of operation depends entirely upon the absorption by the food of micro wave radiation.

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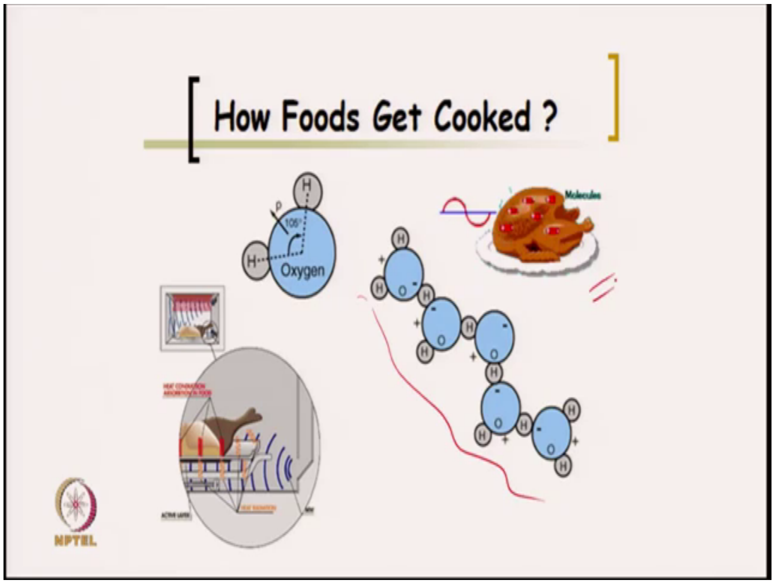

How Foods Get Cooked ?

So, how food gets cooked is like this. Microwave Radiation is absorbed by water molecules. So, these are the water molecules and they basically absorb microwave radiation and what they do is when it is trying to come to ground state they do is by non-radiative emission. What does that mean is, it releases heat and then it comes back to ground state. This heat is used to cook food, is used to cook food.

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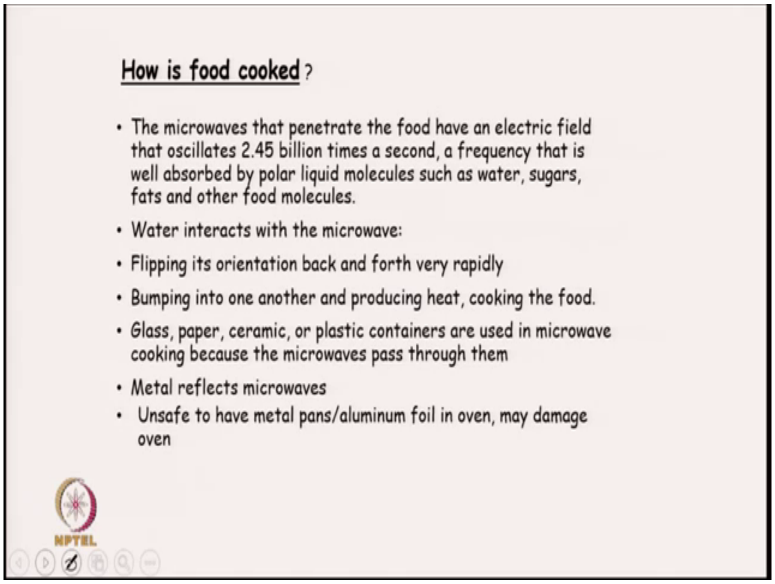

How is food cooked ?

- The microwaves that penetrate the food have an electric field that oscillates 2.45 billion times a second, a frequency that is well absorbed by polar liquid molecules such as water, sugars, fats and other food molecules.
- Water interacts with the microwave:
- Flipping its orientation back and forth very rapidly
- Bumping into one another and producing heat, cooking the food.
- Glass, paper, ceramic, or plastic containers are used in microwave cooking because the microwaves pass through them
- Metal reflects microwaves
- Unsafe to have metal pans/aluminum foil in oven, may damage oven

So, the microwave, that penetrate the food have an electrical field that oscillate, 2.45 billion times a second a frequency that is well absorbed by polar liquid molecules such as water, sugars, fats and other molecules.

This water interacts with microwave. They go from your ground state to higher excited state, they flip their orientation, they rotate very rapidly, they bump into 1 another and also, they produce heat, which is used for cooking the food. Glass, paper, ceramic or plastic containers are used in microwave cooking, because the microwave passed through them, but metal reflects microwaves and that is why it is not safe to use metal pans or aluminum foils in oven may went damage your microwave, ok.

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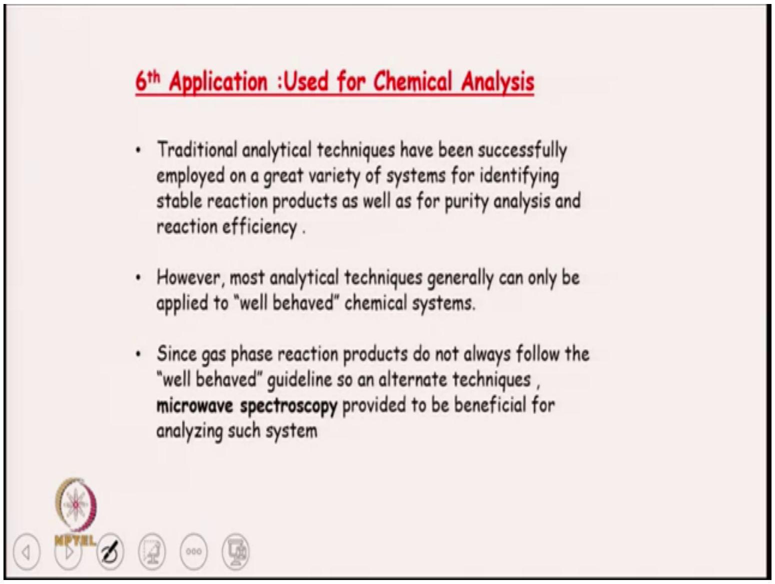

6th Application :Used for Chemical Analysis

- Traditional analytical techniques have been successfully employed on a great variety of systems for identifying stable reaction products as well as for purity analysis and reaction efficiency .
- However, most analytical techniques generally can only be applied to "well behaved" chemical systems.
- Since gas phase reaction products do not always follow the "well behaved" guideline so an alternate techniques , **microwave spectroscopy** provided to be beneficial for analyzing such system

Next application you used for chemical analysis. So, these methods are quite used to know the different chemicals. Only disadvantage is molecules must be in gaseous form or it can be converted into gaseous form then only you can study that. This gas phase reactions is, Rotational Spectroscopy is particularly important for gas phase reactions, because they do not follow well behaved guidelines. So, microwave spectroscopy is particularly use for this kind of studies.

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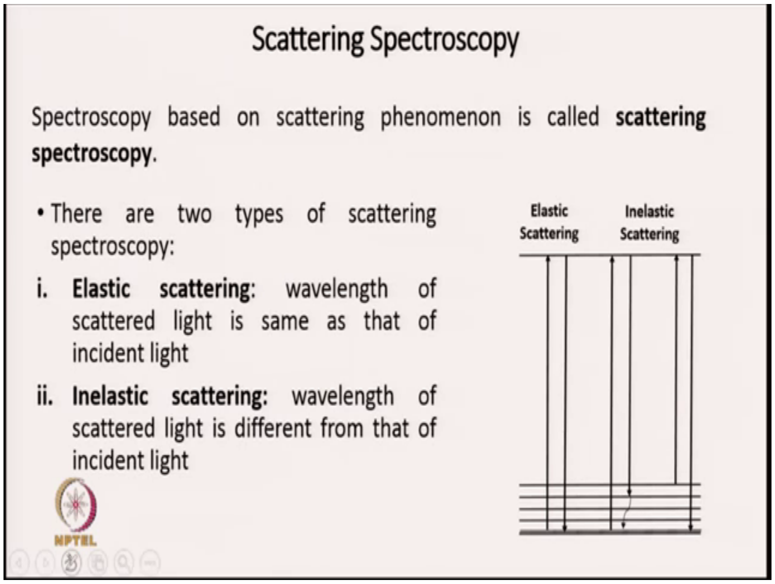

Scattering Spectroscopy

Spectroscopy based on scattering phenomenon is called **scattering spectroscopy**.

- There are two types of scattering spectroscopy:

i. **Elastic scattering**: wavelength of scattered light is same as that of incident light

ii. **Inelastic scattering:** wavelength of scattered light is different from that of incident light

Now, the next thing which we are going to discuss is Scattering Spectroscopy. These are particularly important if you want to calculate energy of rotational level for nonpolar molecule. These are basically based on a scattering phenomena and scattering can be of 2 types, 1 is Elastic Scattering where, wavelength of a scattered light is seen as that of incident light and the second is the Inelastic Scattering, where wavelength of a scattered light is different from that of incident light.

So, this is your elastic scattering. So, you can see this is energy gap is seen for both your incident light and a scattered light and so, lambda is going to be seen for the scattered light and incident light, but in Inelastic Scattering energy gap is going to be different for the emission and your scattered light. And in this case, your lambda is going to be higher for scattered light in comparison to lambda of your incident light. But, in the next case here it is going to be different.

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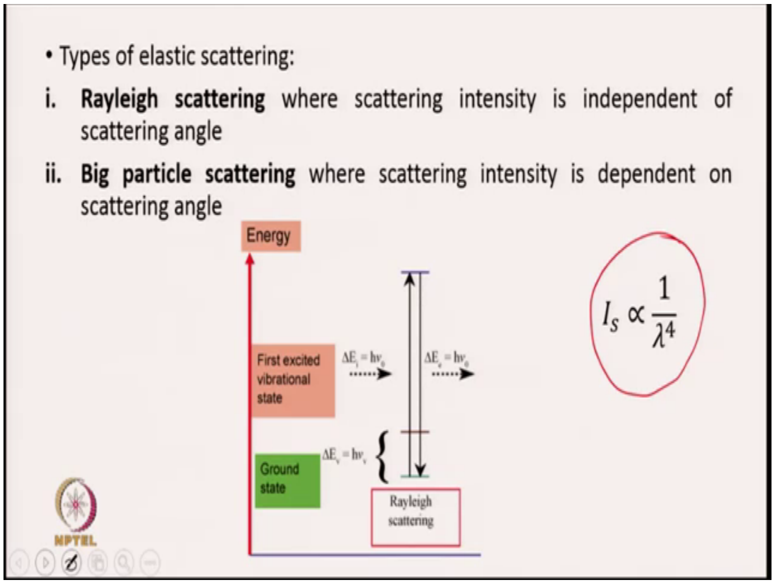

- Types of elastic scattering:

i. **Rayleigh scattering** where scattering intensity is independent of scattering angle

ii. **Big particle scattering** where scattering intensity is dependent on scattering angle

Again elastic scattering can be of 2 type. One is Rayleigh Scattering whereas scattering intensity is independent of scattering angle, independent of scattering angle and in this case your intensity is proportional to 1 by lambda 4, intensity is proportional to 1 by lambda 4. So, R inversely proportional to lambda 4. Whereas, Big Particle Scattering, where a scattering is dependent on a scattering angle. So, in Rayleigh Scattering your angle, your scattering only depends on wavelength but in Big Particle Scattering, your scattering intensity is dependent on both lambda and your scattering angle.

So, this is your ground state and there is a first excited vibrational levels. So, here is the incident if light is incident, it goes to higher excited level and then you see. This is your Rayleigh Scattering. So, lambda of incident ray is similar to lambda of your scattered light.

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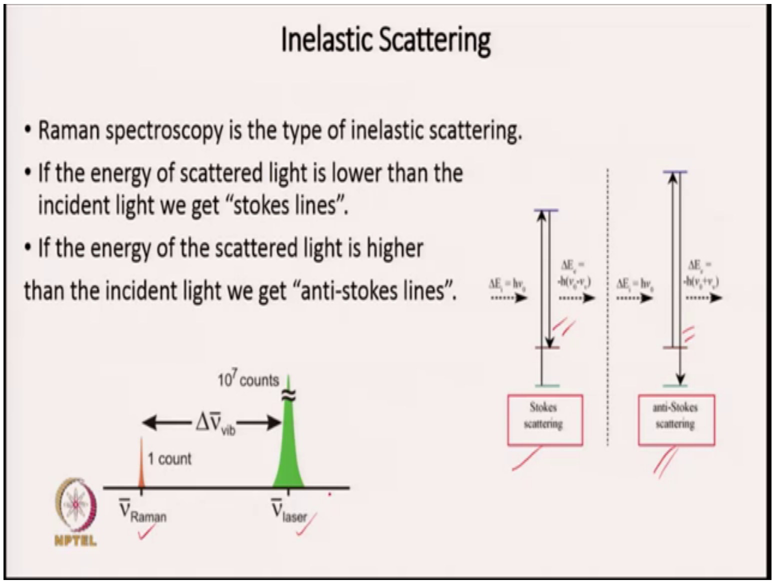

Inelastic Scattering

- Raman spectroscopy is the type of inelastic scattering.
- If the energy of scattered light is lower than the incident light we get "stokes lines".
- If the energy of the scattered light is higher than the incident light we get "anti-stokes lines".

In Inelastic Scattering, most important one is Raman Spectroscopy, it is a type of inelastic scattering. So, if the energy of a scattered light is lower than incident light, we get "Stokes Lines". So, there are 2 different kind of Raman Spectroscopy one is your Stokes Scattering, 2 different kind of a scattering in the Raman Spectroscopy, 1 is Stokes Scattering and another is Anti-Stokes Scattering. So, in Anti-Stokes Scattering, your lambda is going to be lower whereas, in a Stokes Scattering, your lambda is going to be higher. So, what we generally calculate is what is the difference between your peak and your for laser peak.

So, if energy of scattered light is lower than that of incident light, we get a Stokes Line, if the energy of scattered light is higher than incident light, we get Anti-Stokes Line.

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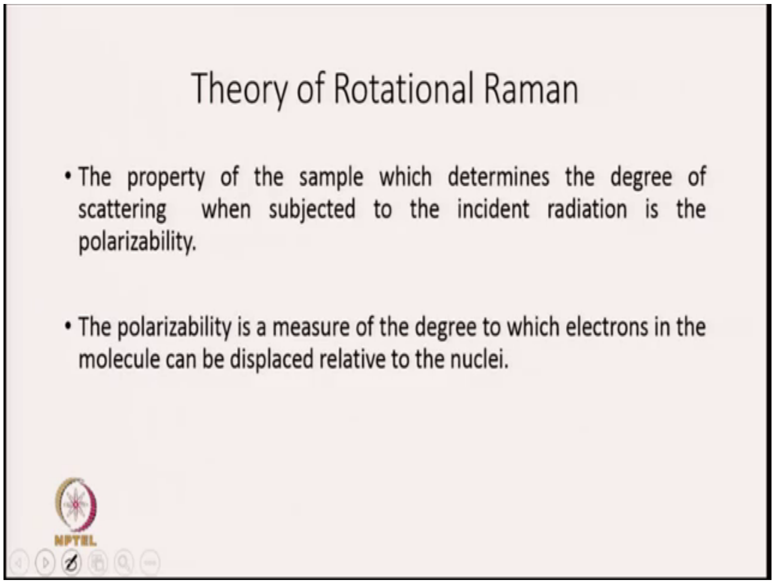

Theory of Rotational Raman

- The property of the sample which determines the degree of scattering when subjected to the incident radiation is the polarizability.
- The polarizability is a measure of the degree to which electrons in the molecule can be displaced relative to the nuclei.

So, this is Theory of Rotational Ramen, it is basically property of the sample, which determines scattering is polarizability. So, the factor on which scattering depends is polarizability of the molecule, not the dipole moment as we seen for Rotational Spectroscopy.

So, what is polarizability, it is a measure of the degree to which electrons in the molecule can be displaced related to the nuclei.

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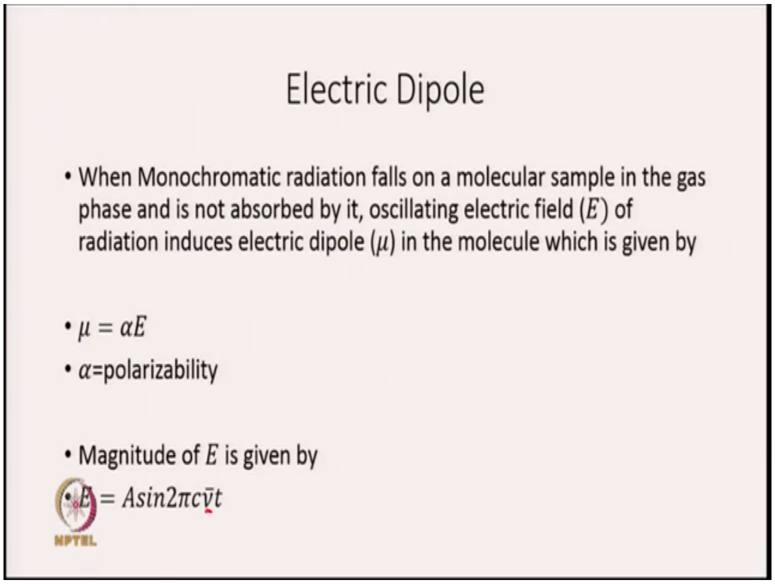

Electric Dipole

- When Monochromatic radiation falls on a molecular sample in the gas phase and is not absorbed by it, oscillating electric field (E) of radiation induces electric dipole (μ) in the molecule which is given by
- $\mu = \alpha E$
- α=polarizability
- Magnitude of E is given by
- $E = Asin2\pi c\bar{\nu}t$

So, when monochromatic radiations falls on molecular sample in the gas phase and not absorb then your scattering can happen and oscillating electric field of radiation induces electric dipole in the molecule and this electric dipole mu is given by alpha into E, E is your oscillating electric field and alpha is polarizability. If suppose magnitude of E is given by this formula A sin 2 pi c nu bar into t, ok. So, this is your frequency. This is a frequency of incident radiation.

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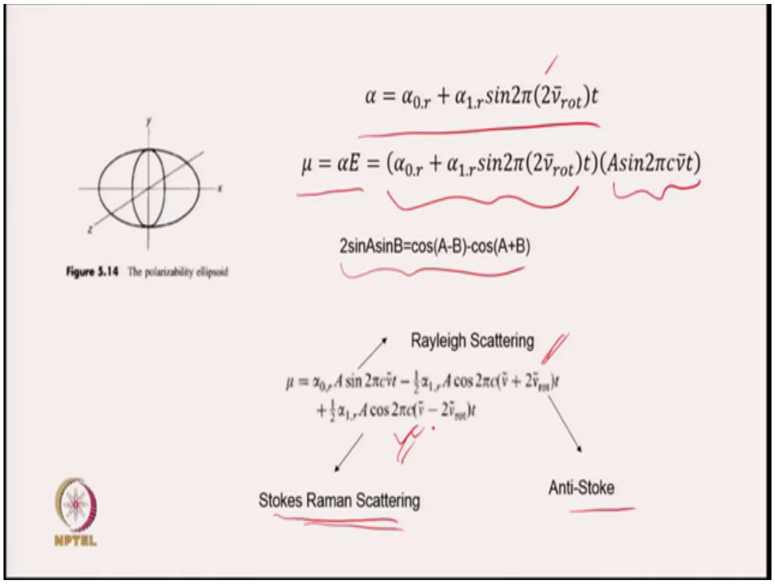

Figure 5.14 The polarizability ellipsoid

$$\alpha = \alpha_{0.r} + \alpha_{1.r} sin2\pi(2\bar{v}_{rot})t$$

$$\mu = \alpha E = (\alpha_{0.r} + \alpha_{1.r} sin2\pi(2\bar{v}_{rot})t)(Asin2\pi c\bar{v}t)$$

2sinAsinB=cos(A-B)-cos(A+B)

Rayleigh Scattering

$$\mu = \alpha_{0,r} A \sin 2\pi c\tilde{v}t - \tfrac{1}{2}\alpha_{1,r} A \cos 2\pi c(\tilde{v} + 2\tilde{v}_{rot})t + \tfrac{1}{2}\alpha_{1,r} A \cos 2\pi c(\tilde{v} - 2\tilde{v}_{rot})t$$

Stokes Raman Scattering

Anti-Stoke

Now, once it falls, it interacts with electric field interacts with polarizability, polarizability will be given by this formula, alpha is equal to alpha 0 R plus alpha 1 R sin 2 pi 2 nu rotational into t. Now, this 2 factor comes because of during rotation polarizability becomes sin twice, polarizability becomes sin twice in 360 degree rotation.

And so, you can calculate mu. So, alpha is this value and your this is E there is a multiplication of the 2 sin terms and we know that from 2 sin A into sin B is equal to cos A minus B minus cos A plus B and that gives you 3 different terms if you multiply this alpha into E will get first term, the second term you can see this a nu bar plus 2 nu bar rotation, ok. So, here your frequency is increasing and then this is third term is nu bar minus 2 nu bar rotation.

So, first term is Rayleigh Scattering, second term is your Anti-Stokes Line and the last term correspond to Stokes Raman Scattering. So, you see cos A minus B minus cos A plus B. So, this is your cos A plus B and this is your cos A minus B, cos A minus B.

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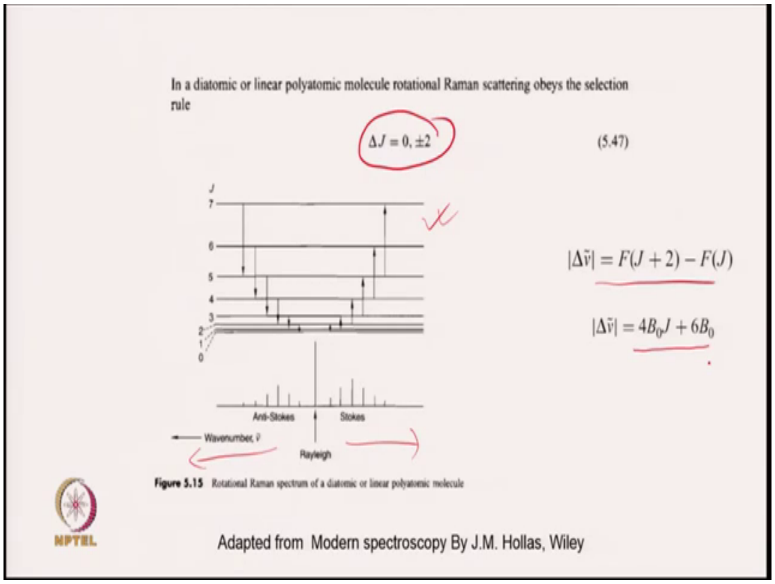

In a diatomic or linear polyatomic molecule rotational Raman scattering obeys the selection rule

$$\Delta J = 0, \pm 2 \qquad (5.47)$$

$$|\Delta\tilde{\nu}| = F(J+2) - F(J)$$

$$|\Delta\tilde{\nu}| = 4B_0 J + 6B_0$$

Figure 5.15 Rotational Raman spectrum of a diatomic or linear polyatomic molecule

Adapted from Modern spectroscopy By J.M. Hollas, Wiley

So, this is your typical Rotational Spectra in this diatomic or linear polyatomic molecule your gross selection rule for Rotational Raman Scattering is delta J is equal to 0 plus minus 2 and this is wave number.

So, this side is your Anti-Stokes Line, this side is a Stock Line. So, in your Anti Stokes delta J is equal to your minus, minus 2 where, for Stokes delta J is equal to plus 2 and delta nu bar means difference between this side or this side is given by F, J plus 2 minus FJ and delta nu bar is 4 B 0 J, plus 6 B 0. So, it will depend on Anti-Stokes then it will be towards this side and your for Stokes it will be towards right hand side.

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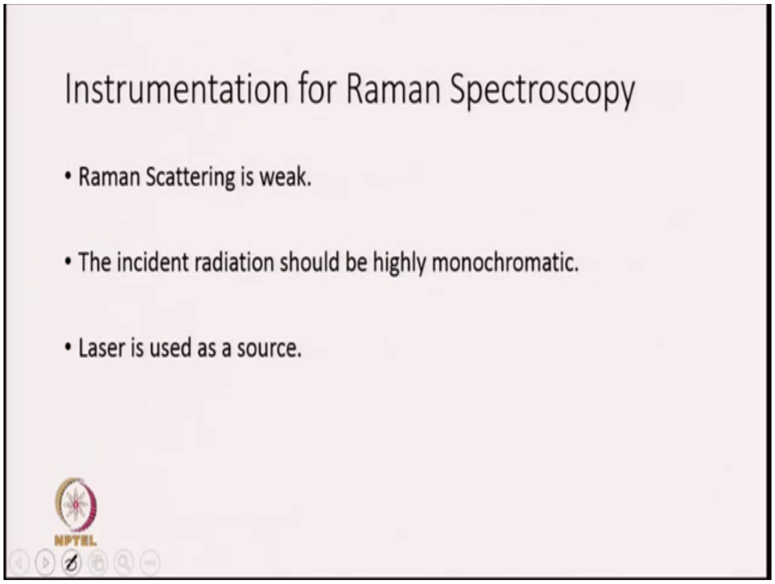

Instrumentation for Raman Spectroscopy

- Raman Scattering is weak.
- The incident radiation should be highly monochromatic.
- Laser is used as a source.

So, instrumentation of Raman Spectroscopy it is very important. Raman (Spectro) Scattering is very weak phenomena. So, incident radiation should be highly monochromatic and that is why laser is used as a source.

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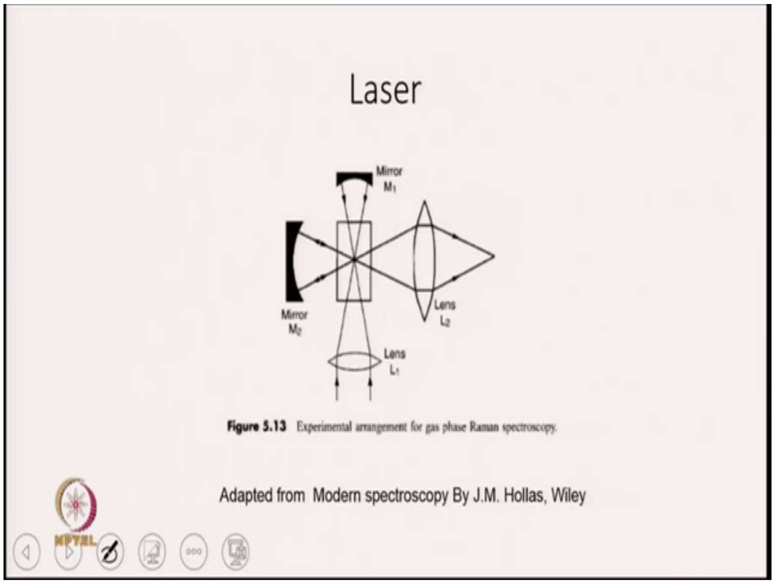

Laser

Figure 5.13 Experimental arrangement for gas phase Raman spectroscopy.

Adapted from Modern spectroscopy By J.M. Hollas, Wiley

So, this is your typical experimental setup for Raman Spectroscopy, different lenses are used to focus, focus incident ray back to the sample.

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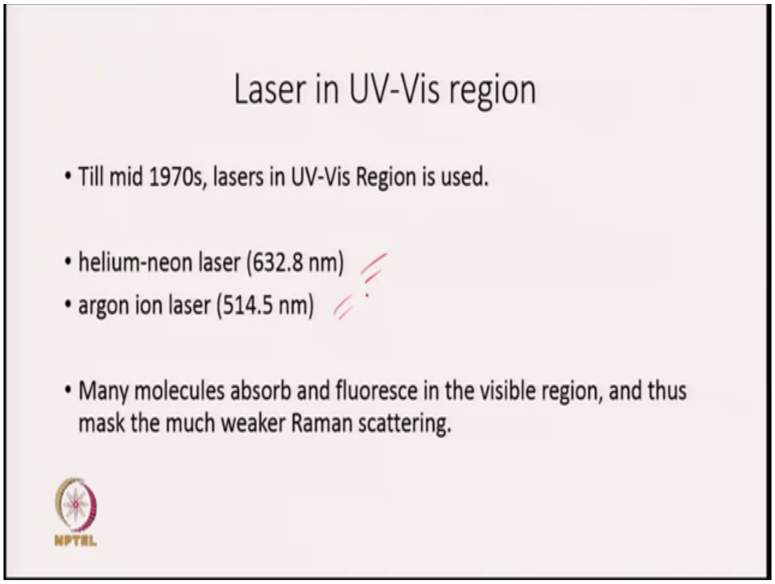

Laser in UV-Vis region

- Till mid 1970s, lasers in UV-Vis Region is used.
- helium-neon laser (632.8 nm)
- argon ion laser (514.5 nm)
- Many molecules absorb and fluoresce in the visible region, and thus mask the much weaker Raman scattering.

And initially lasers are used in UV-Vis region. The most commonly used was helium neon laser, which has wavelength of 632.8 nanometer and then argon ion laser which has wavelength of 514.5 nanometer. But problem with this kind of lasers are that many molecules absorb and fluoresce in visible region and the fluorescence will mask the much weaker Raman Scattering.

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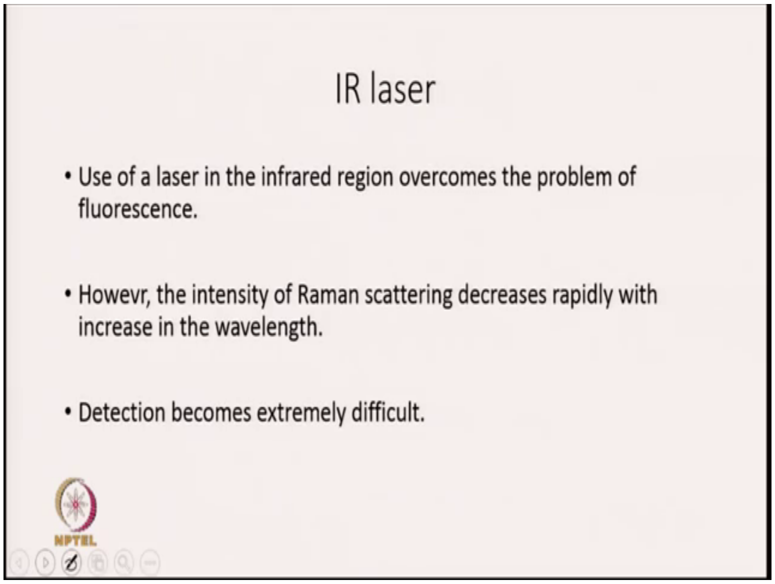

IR laser

- Use of a laser in the infrared region overcomes the problem of fluorescence.
- Howevr, the intensity of Raman scattering decreases rapidly with increase in the wavelength.
- Detection becomes extremely difficult.

So, next came is IR lasers, good thing is that you can avoid the problem of fluorescence, but bad thing is since we know that scattering is basically proportional to 1 by lambda 4, so, it is basically decreases Raman Scattering decreases rapidly with increase in the wavelength and so, detection becomes extremely difficult, since, signal to noise ratio is very low.

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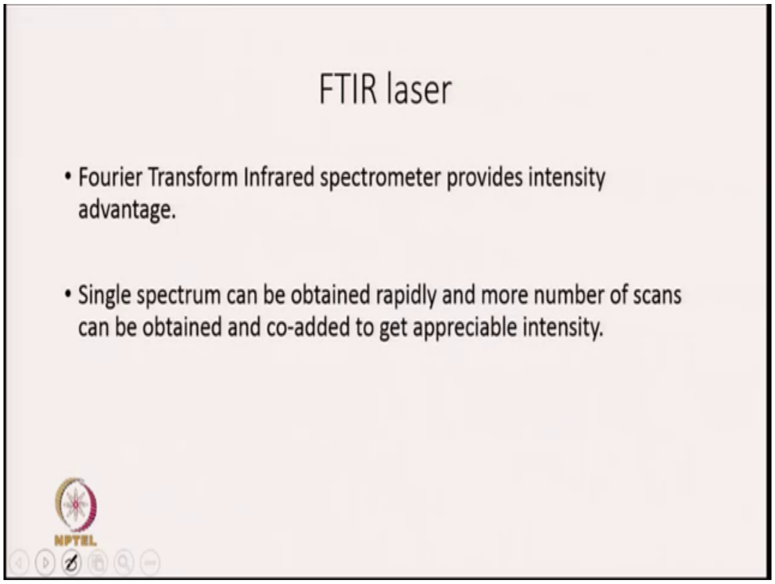

FTIR laser

- Fourier Transform Infrared spectrometer provides intensity advantage.
- Single spectrum can be obtained rapidly and more number of scans can be obtained and co-added to get appreciable intensity.

To avoid this problem, people have started using FTIR laser, again FTIR, FTIR is generally used for the low sensitive technique. And here again, it can provide intensity advantage. A single spectrum can be obtained rapidly and you can take more number of scan and then you can add up to get appreciable intensity.

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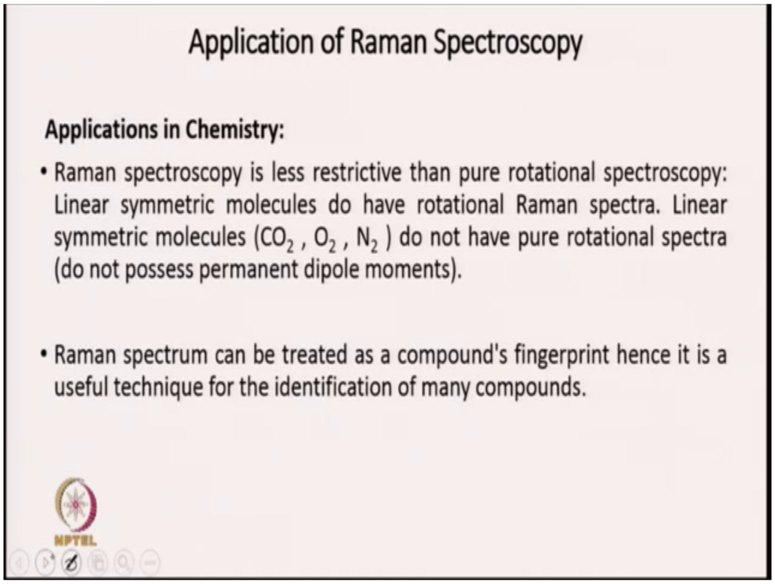

Application of Raman Spectroscopy

Applications in Chemistry:

- Raman spectroscopy is less restrictive than pure rotational spectroscopy: Linear symmetric molecules do have rotational Raman spectra. Linear symmetric molecules (CO_2 , O_2 , N_2) do not have pure rotational spectra (do not possess permanent dipole moments).
- Raman spectrum can be treated as a compound's fingerprint hence it is a useful technique for the identification of many compounds.

Application Raman Spectroscopy, Raman Spectroscopy is less restrictive than pure Rotational Spectroscopy, since here, you do not have to think about whether it is a polar molecule or not. Linear symmetric molecule does not show rotational spectra but linear symmetric molecules shows Rotational Raman Spectra. Raman Spectra can be used as a compound fingerprint hence it is useful technique for identification of many compounds.

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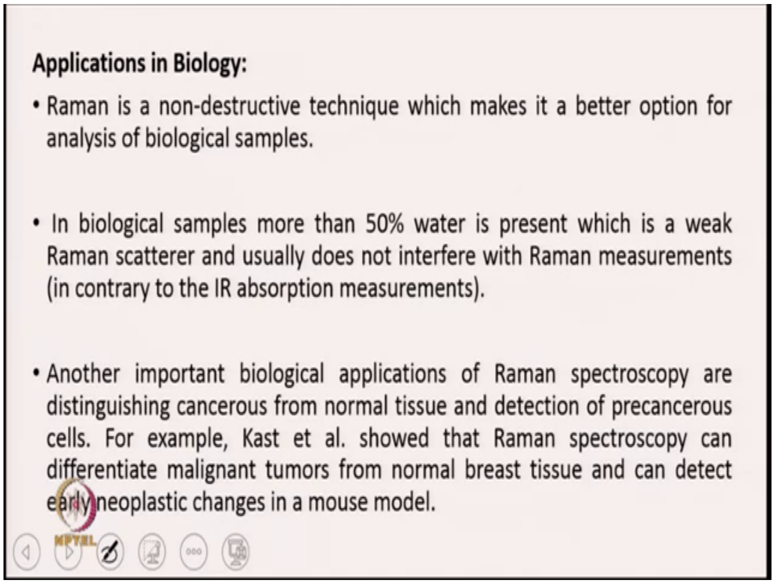

Applications in Biology:

- Raman is a non-destructive technique which makes it a better option for analysis of biological samples.
- In biological samples more than 50% water is present which is a weak Raman scatterer and usually does not interfere with Raman measurements (in contrary to the IR absorption measurements).
- Another important biological applications of Raman spectroscopy are distinguishing cancerous from normal tissue and detection of precancerous cells. For example, Kast et al. showed that Raman spectroscopy can differentiate malignant tumors from normal breast tissue and can detect early neoplastic changes in a mouse model.

This is a non-destructive technique, which makes it a better option for analysis of biological sample. In biological samples, more than 50 percent water is present, which is your weak Raman scatterer and usually do not interfere with the Raman measurement, which is not the case in the IR kind of measurement.

They can be used to distinguish between cancerous tissue from normal tissue and people have used is to differentiate malignant tumors from normal breast tissues and it has also been used to look at neoplastic changes in a mouse model.

So, in this lecture, we are able to see the some the Theory of Rotational Spectroscopy and Rotational Raman Spectroscopy and also we have looked at the application of these spectroscopy in both chemical analysis and biological analysis. So, in the next class we will discuss the Infrared Spectroscopy. Thank you.