Spectroscopic Techniques for Pharmaceutical
and
Biopharmaceutical Industries
by
Professor Shashank Deep
Department of Chemistry,
Indian Institute of Technology, Delhi
Lecture-10
Vibrational, Rotational-Vibrational, Raman Spectroscopy-II

Today, again I am going to discuss Vibrational Spectroscopy. So, in the last lecture we looked at how to calculate energy of vibrational levels and what are the selection rule.

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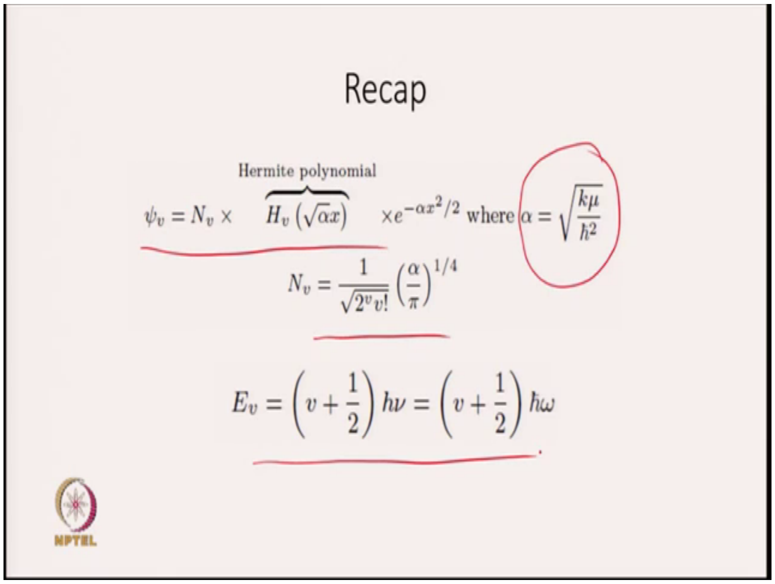

Recap

$$\psi_v = N_v \times \overbrace{H_v\left(\sqrt{\alpha}x\right)}^{\text{Hermite polynomial}} \times e^{-\alpha x^2/2} \text{ where } \alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

$$N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$E_v = \left(v+\frac{1}{2}\right)h\nu = \left(v+\frac{1}{2}\right)\hbar\omega$$

In this lecture, we will just first go through recap of the last lecture and then I will discuss Raman Vibrational Spectroscopy and application of IR spectroscopy for various purpose in various industry and in various applications. When we solved the Schrödinger equation for vibrational or harmonic oscillator, what we got is wave function, wave function is given by this formula where Nv is normalization factor and then you have Hermite Polynomial and multiplied by your exponential minus alpha X square by 2.

So, this is you are allowed wave function for vibrational level, Nv is given by this formula and then alpha is in terms of reduced mass and force constant. You can also calculate energy of various vibrational levels and that is given by your V plus half h nu or V plus half h bar omega. So, nu is your frequency and omega is angular frequency.

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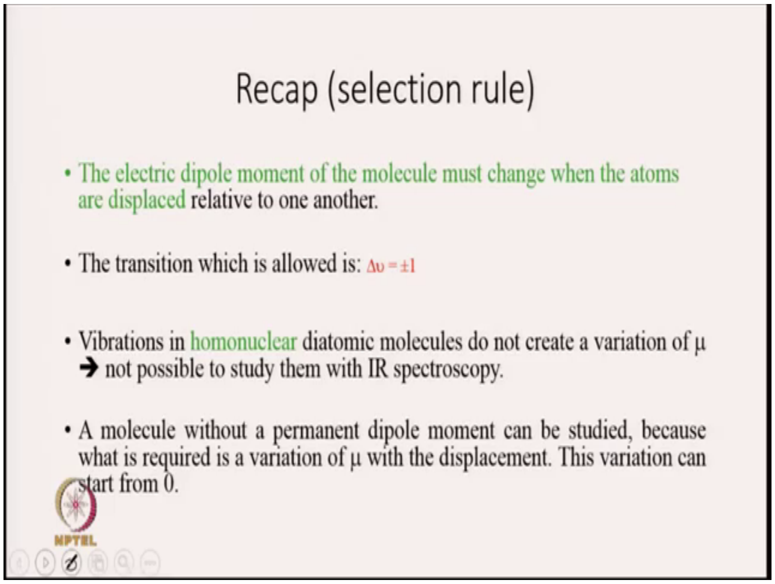

Recap (selection rule)

- The electric dipole moment of the molecule must change when the atoms are displaced relative to one another.
- The transition which is allowed is: $\Delta \upsilon = \pm 1$
- Vibrations in homonuclear diatomic molecules do not create a variation of μ → not possible to study them with IR spectroscopy.
- A molecule without a permanent dipole moment can be studied, because what is required is a variation of μ with the displacement. This variation can start from 0.

We also discussed in the last lecture about selection rule for vibrational spectroscopy. There are 2 selection rules, 1 which is known as Gross Selection Rule, which tells that, 'electric dipole movement of molecule must change when the atoms are displaced related to one another'.

So, during the vibration, electric dipole movement of molecule must change when only it can so, your Vibrational Spectroscopy. And the second is a Specific Selection Rule which tells you that 'transition is only allowed when delta V is equal to plus minus 1'. For homonuclear diatomic molecule, we discuss that vibration does not create change in your dipole movement, electrical dipole movement. So, homonuclear diatomic molecules cannot be studied through IR spectroscopy.

Molecule without a permanent dipole movement can be studied if there is a variation of dipole movement where the displacement and this (dis) variation can start from 0. For example, in CO2 molecule certain vibrational modes are IR active because your permanent dipole movement can change on the displacement. The application of your Vibrational Spectroscopy in the calculation of dissociation energy. So, we have already looked at what will be the energy of different vibrational levels when we consider your anharmonic oscillator.

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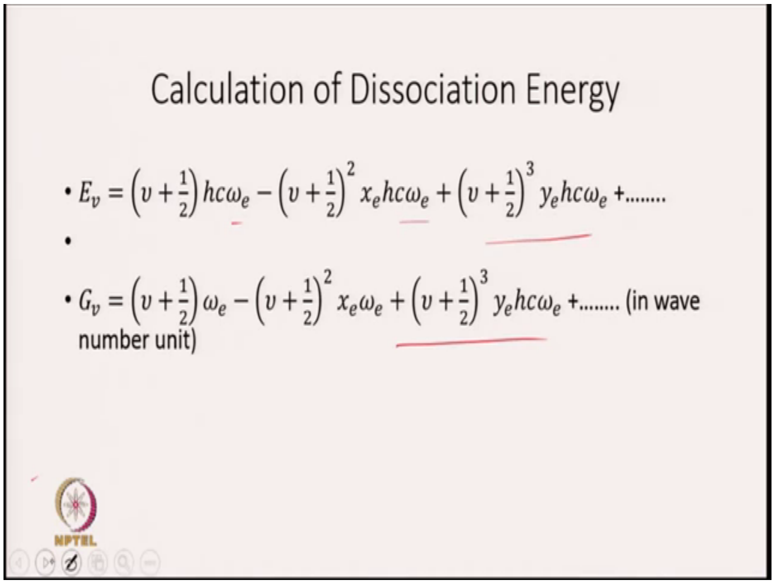

Calculation of Dissociation Energy

- $E_v = \left(v+\frac{1}{2}\right)hc\omega_e - \left(v+\frac{1}{2}\right)^2 x_e hc\omega_e + \left(v+\frac{1}{2}\right)^3 y_e hc\omega_e + \ldots\ldots$
-
- $G_v = \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e + \left(v+\frac{1}{2}\right)^3 y_e hc\omega_e + \ldots\ldots$ (in wave number unit)

So, for that your energy is given by V plus half hc omega e minus V plus half square Xe hc omega E plus higher energy terms, high energy terms. When we divide this energy term by hc, we will get energy of vibrational level in wave number unit, in wave number unit and that will be given by V plus half omega e minus V plus half square Xe omega E plus higher wave number term, higher wave number term.

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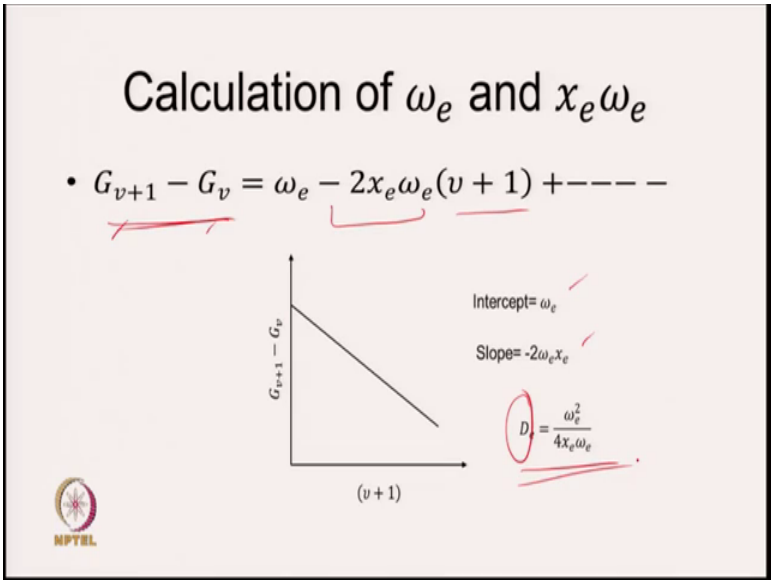

Calculation of ω_e and $x_e\omega_e$

- $G_{v+1} - G_v = \omega_e - 2x_e\omega_e(v+1) + \text{----} -$

Intercept= ω_e

Slope= $-2\omega_e x_e$

$D = \frac{\omega_e^2}{4x_e\omega_e}$

Now, one of the way to calculate We and Xe omega E is Gv plus 1 is energy of V plus 1 level in wave number unit minus Gv is energy of V level in wave number unit. When you subtract or when you take difference between these 2 values, these 2 terms what you will get is wave number of transition between level V to V plus 1, to V plus 1 and that can be obtained from Vibrational Spectroscopy experimental, experimentally you can obtain that and when you plot that verses V plus 1, what do we expect that it will give you a straight line with intercept omega e and slope minus 2 omega E Xe.

So, this is written here, now you see that if you plot this versus V plus 1, your intercept will be omega E and slope will be minus 2 Xe omega E. And that can be used to calculate your De, which is dissociation energy and the equation for this is given here. Now, we will discuss in the next slide, how we can obtain this relation.

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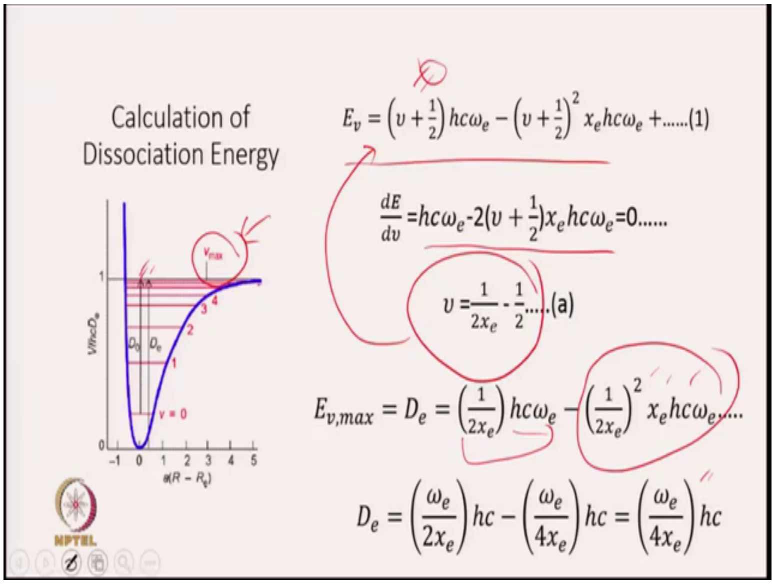

Calculation of Dissociation Energy

$$E_v = \left(v+\frac{1}{2}\right)hc\omega_e - \left(v+\frac{1}{2}\right)^2 x_e hc\omega_e + \ldots\ldots(1)$$

$$\frac{dE}{dv} = hc\omega_e - 2\left(v+\frac{1}{2}\right)x_e hc\omega_e = 0\ldots\ldots$$

$$v = \frac{1}{2x_e} - \frac{1}{2}\ldots\ldots(a)$$

$$E_{v,max} = D_e = \left(\frac{1}{2x_e}\right)hc\omega_e - \left(\frac{1}{2x_e}\right)^2 x_e hc\omega_e\ldots\ldots$$

$$D_e = \left(\frac{\omega_e}{2x_e}\right)hc - \left(\frac{\omega_e}{4x_e}\right)hc = \left(\frac{\omega_e}{4x_e}\right)hc$$

So, there are 2 different kind of dissociation energy, one is a difference of energy of vibrational level where the energy is maximum and your 0. Whereas, the second is your D 0, which is the energy difference between this and your V is equal to 0, energy corresponding to V is equal 0.

Now, to calculate V max and corresponding energy, what we will do is we will simply differentiate this energy term with respect to V, with respect to V. So, we expect that that will give you value of V max or value of V where energy is maximum value of V where energy is maximum. When you do that and you differentiate this equation 1 with V, what you are going to get is hc omega E minus 2 V plus half Xe hc omega E, higher terms are neglected and that should be equal to 0 if we want to know the V level where energy is maximum and when we do that, what we will get is V is equal to 1 by 2 Xe minus half, minus half and this is the V max.

Again V max is the vibrational level whose energy is maximum, whose energy is maximum, ok. So, EV max or which is basically known as De is basically obtain by putting this V value in Ev, in Ev, Now, you see that V plus half is equal to 1 by 2 Xe.

So, what you have to do is you just replace this V plus half by 1 by 2 Xe. When you do that what you will get is De or Ev max, energy of the maximum, energy of vibrational level where your energy is maximum is your 1 by 2 Xe or V plus half hc omega E minus 1 by 2 Xe square Xe hc omega E. So, this is basically omega E by 2 Xe hc minus if you simplify this what you are going to get is omega E by 4 Xe hc, 4 Xe hc which corresponds to omega E by 4 Xe into hc.

So, this is the way to calculate De and De is basically your maximum energy or energy of the vibrational level which corresponds to maximum energy, which corresponds to maximum energy.

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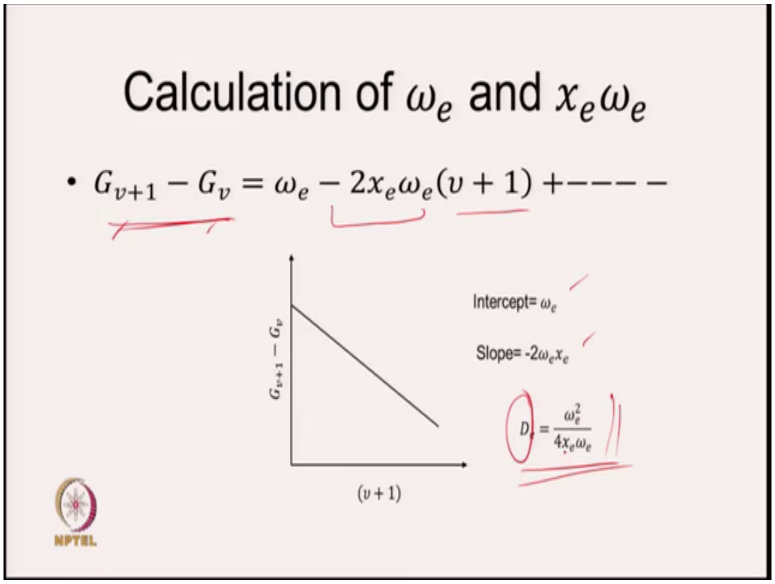

Calculation of ω_e and $x_e\omega_e$

- $G_{v+1} - G_v = \omega_e - 2x_e\omega_e(v+1) + - - - -$

Intercept= ω_e

Slope= $-2\omega_e x_e$

$D = \frac{\omega_e^2}{4x_e\omega_e}$

So, your De is, if you remember that De is equal to omega E square by 4 Xe omega E and here you can simply multiply their numerator by omega E and divide by omega E and it will be omega E square by 4 Xe omega E, 4 Xe omega E and that can be calculated by previously shown plot.

So, this is the way you can calculate De in wave number unit. So, this is De in your energy unit and if you divide by hc and you will get De in wave number unit.

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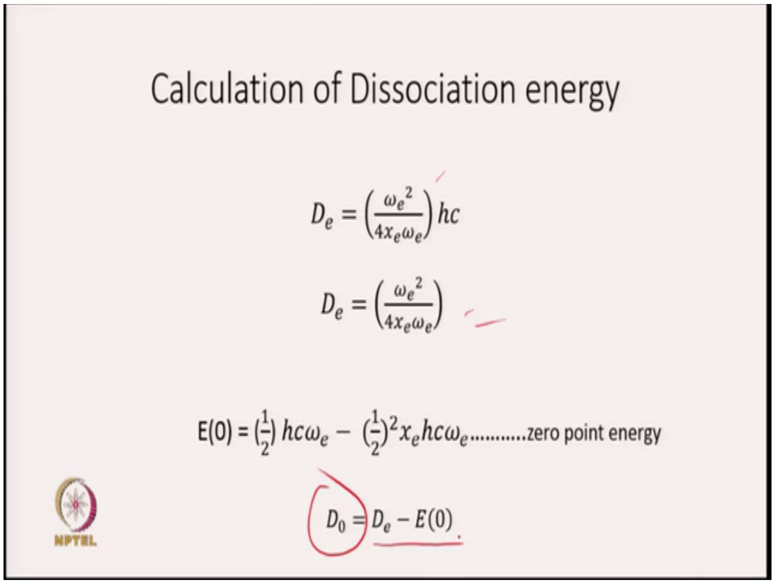

Calculation of Dissociation energy

$$D_e = \left(\frac{\omega_e{}^2}{4x_e\omega_e}\right)hc$$

$$D_e = \left(\frac{\omega_e{}^2}{4x_e\omega_e}\right)$$

$$E(0) = \left(\frac{1}{2}\right)hc\omega_e - \left(\frac{1}{2}\right)^2 x_e hc\omega_e \text{...........zero point energy}$$

$$D_0 = \underline{D_e - E(0)}$$

So, De is given by omega E square by 4 Xe omega E hc, this is in your energy unit whereas, if you divide by hc, you will get De in wave number unit and so, this is your De in wave number unit and if you subtract that by E naught, which is the energy of energy of V is equal to 0 or 0 point energy, then what you will get is or is known as your D0. So, D0 is equal to simply De minus E naught.

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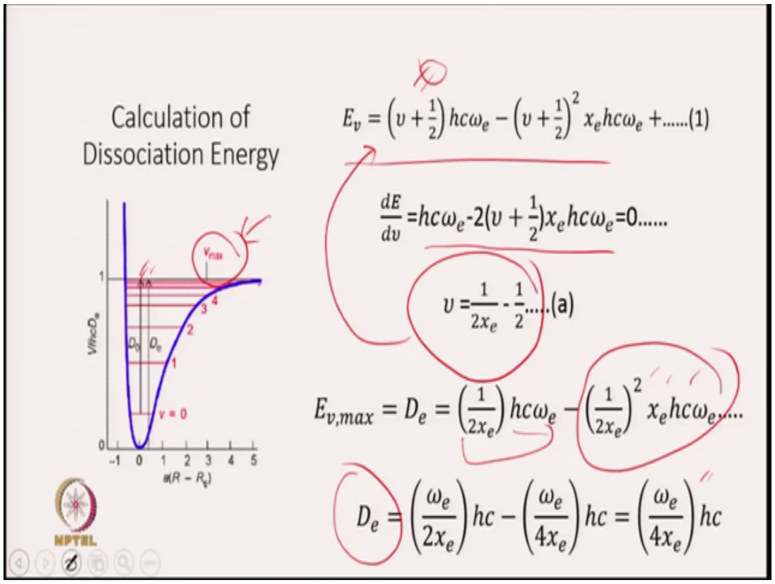

Calculation of Dissociation Energy

$$E_v = \left(v+\tfrac{1}{2}\right)hc\omega_e - \left(v+\tfrac{1}{2}\right)^2 x_e hc\omega_e + \ldots\ldots(1)$$

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$$D_e = \left(\frac{\omega_e}{2x_e}\right)hc - \left(\frac{\omega_e}{4x_e}\right)hc = \left(\frac{\omega_e}{4x_e}\right)hc$$

And if you see here, so, this is your energy of the vibrational level V, energy of vibrational level V where energy is maximum and this is your De whereas, De minus this 0 point energy, energy corresponding to V is equal 0 will give you D0 value.

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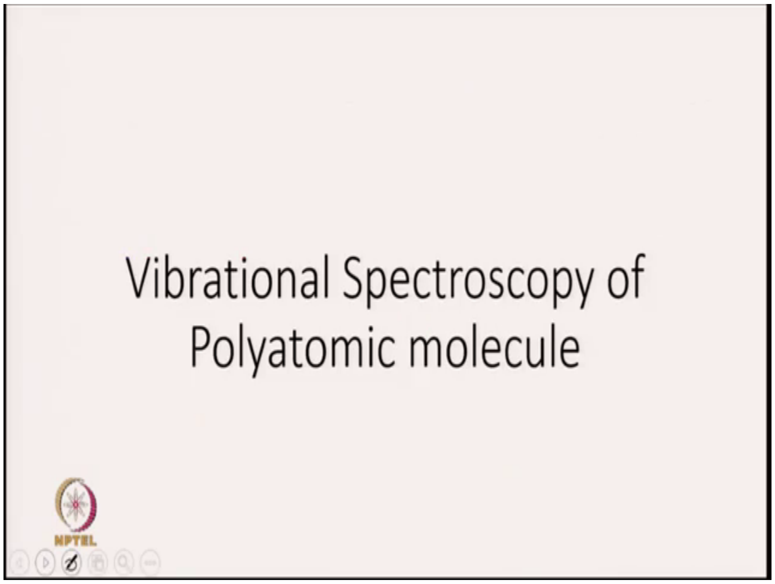
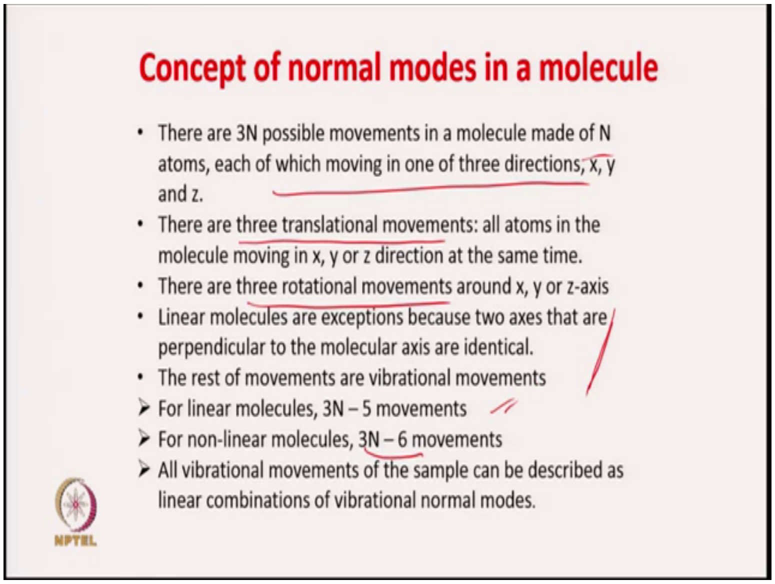


Vibrational Spectroscopy of Polyatomic molecule



Concept of normal modes in a molecule

- There are 3N possible movements in a molecule made of N atoms, each of which moving in one of three directions, x, y and z.
- There are three translational movements: all atoms in the molecule moving in x, y or z direction at the same time.
- There are three rotational movements around x, y or z-axis
- Linear molecules are exceptions because two axes that are perpendicular to the molecular axis are identical.
- The rest of movements are vibrational movements

➢ For linear molecules, 3N – 5 movements

➢ For non-linear molecules, 3N – 6 movements

➢ All vibrational movements of the sample can be described as linear combinations of vibrational normal modes.

So, till now we discussed Vibrational Spectroscopy of diatomic molecule. Now, we will discuss Vibrational Spectroscopy of polyatomic molecules. So, if you go for polyatomic molecule, first thing you need to understand is what in the normal modes. So, if there is N atoms in a molecule, there will be 3N possible movements and each, so, every atom moving in 1 of the 3 direction X, Y, Z. So, there is 3N possible movements out of that 3 are translational movements.

So, all atoms in the molecule moving X, Y, Z direction at the same time and so, you have a 3 translational movement. So, out of 3Nyou have a 3 translation movement and 3 rotational movement 3 rotational movements around X, Y or Z axis. So, out of 3N now, 3 is accounted for translational movement, 3 are accounted for rotational movement. So, left 1 is your 3N minus 6 movements and that is your normal modes of vibration in a molecule, in a polyatomic molecule.

For linear molecule, they are weight exceptions because two axes that perpendicular to molecular axis are identical and that is why they have only 2 rotational degree of 2 rotational movements. And so, total normal modes of vibration for linear molecule is 3N minus 5. All vibrational movements of the sample can be described as a linear combination of vibrational normal modes.

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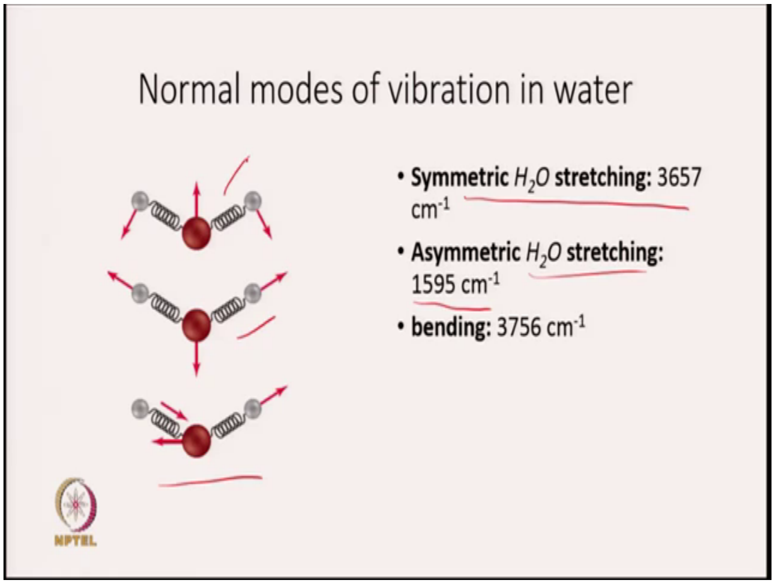

Normal modes of vibration in water

- **Symmetric H_2O stretching:** 3657 cm^{-1}
- **Asymmetric H_2O stretching:** 1595 cm^{-1}
- **bending:** 3756 cm^{-1}

Now, let us think about water. These are the 3 different normal modes of vibration, 1 is your symmetric is stretching. So, everything is going in 1 direction, the vibration of Symmetric H2O Stretching is around 3657 centimeter inverse. Then you have Asymmetric H2O Stretching hence 1 is going in this direction then other will the movement of other bond will not be symmetric, it will be just in opposite direction and so, you have Asymmetric H2O Stretching which have vibration around 1595 centimeter inverse and the last one is your the bending vibration and that happens around your 3756 centimeter inverse.

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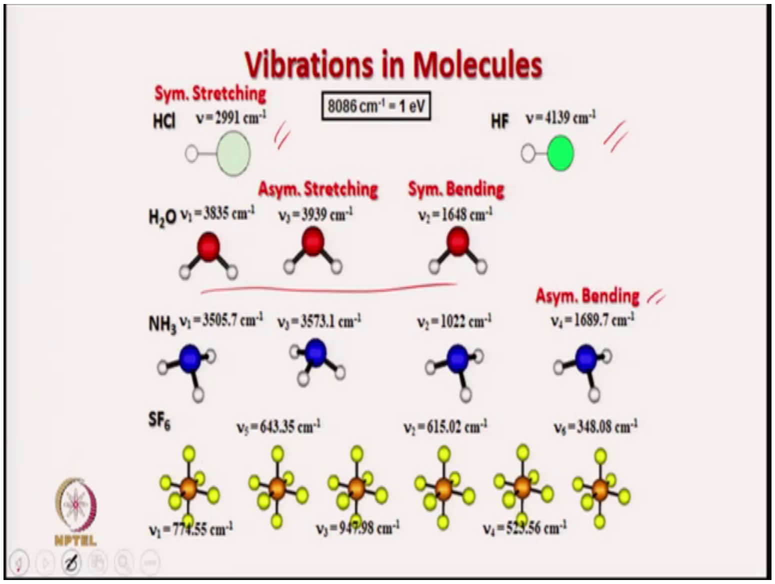

Vibrations in Molecules

8086 cm^{-1} = 1 eV

Sym. Stretching

HCl $\nu = 2991$ cm^{-1}

HF $\nu = 4139$ cm^{-1}

Asym. Stretching

Sym. Bending

H_2O $\nu_1 = 3835$ cm^{-1} $\nu_3 = 3939$ cm^{-1} $\nu_2 = 1648$ cm^{-1}

Asym. Bending

NH_3 $\nu_1 = 3505.7$ cm^{-1} $\nu_3 = 3573.1$ cm^{-1} $\nu_2 = 1022$ cm^{-1} $\nu_4 = 1689.7$ cm^{-1}

SF_6 $\nu_5 = 643.35$ cm^{-1} $\nu_2 = 615.02$ cm^{-1} $\nu_6 = 348.08$ cm^{-1}

$\nu_1 = 774.55$ cm^{-1} $\nu_3 = 947.98$ cm^{-1} $\nu_4 = 523.56$ cm^{-1}

Here, in this you can see there are several different molecule and their vibrational wave number is given for example HCl, symmetric stretching. So, it has only 1 kind of stretching. So, that is symmetrical stretching and your wave number is 2991 centimeter inverse. Similarly, HF molecule. So, for diatomic molecule, you only have 1 normal mode of vibration and for HF it is 4139 centimeter inverse.

For H2O you have a 3 different kind of vibration, we just discuss about that 1 is symmetric and other is asymmetric stretching and then your symmetric bending and this value we have already seen. For ammonia there can be 4 different kind of vibration, apart from symmetric stretching, asymmetric stretching, symmetrical bending, you have asymmetrical bending, which happens around 1689.7 centimeter inverse.

Similarly, you can go for go and calculate for other kind of molecules what will be the normal mode of vibration. The simple rule is for polyatomic molecule, which is not linear polyatomic molecule which is not linear, you have a nonlinear molecule.

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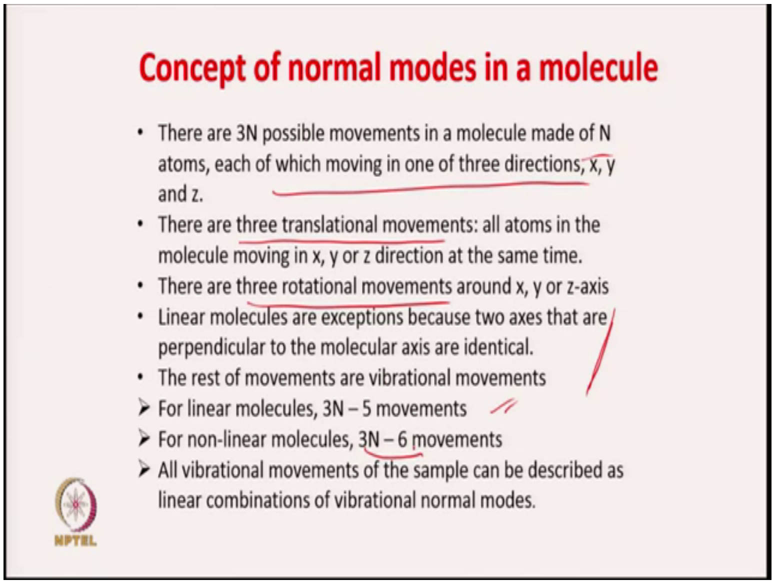

Concept of normal modes in a molecule

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- Linear molecules are exceptions because two axes that are perpendicular to the molecular axis are identical.
- The rest of movements are vibrational movements
- ➤ For linear molecules, 3N – 5 movements
- ➤ For non-linear molecules, 3N – 6 movements
- ➤ All vibrational movements of the sample can be described as linear combinations of vibrational normal modes.

Basically, you have 3N minus 6 movements or 3N minus 6 normal mode of vibration. For linear molecule, you have 3N minus 5 modes of vibration. So, for example, for HCl, you are going to have HCl as 2atoms. So, 3N minus 5 comes out to be 1 and that is what we saw in the case of HF and HCl. So, diatomic molecules are going to have only 1 normal mode of vibration. For H2O it is triatomic molecule and it is a nonlinear so 3N minus 6. So 3, normal mode of vibration, for ammonia, you have your 4 atoms, so, 3N minus 6, 4 into 3 minus 6. So, there are going to be 6 different kind of vibrations.

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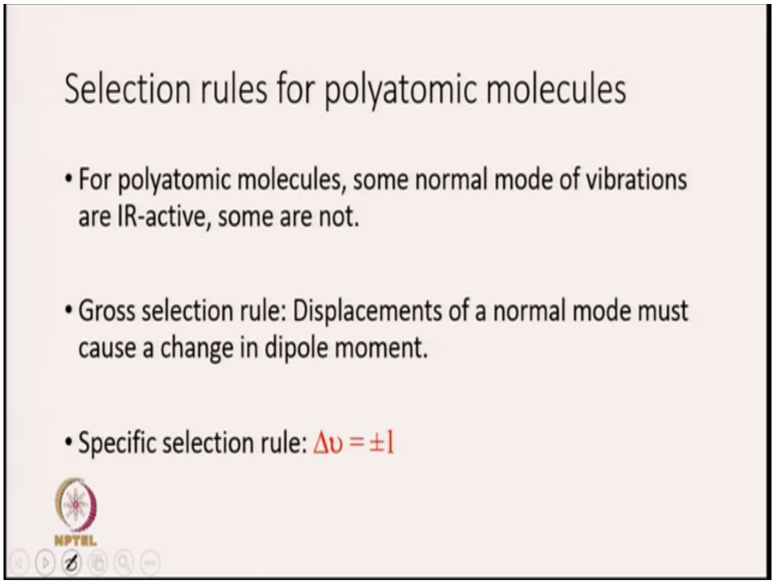

Selection rules for polyatomic molecules

- For polyatomic molecules, some normal mode of vibrations are IR-active, some are not.
- Gross selection rule: Displacements of a normal mode must cause a change in dipole moment.
- Specific selection rule: $\Delta \upsilon = \pm 1$

Selection rules for polyatomic molecules is similar to what we discussed for diatomic molecules, but for polyatomic molecules some normal mode of operation are IR active where, others are not. Gross Selection Rule is applicable here also. So, displacements of a normal mode must cause a change in the dipole movement only then you can see the IR spectra of that molecule. And then as specific selection rule is similar delta V is plus minus 1.

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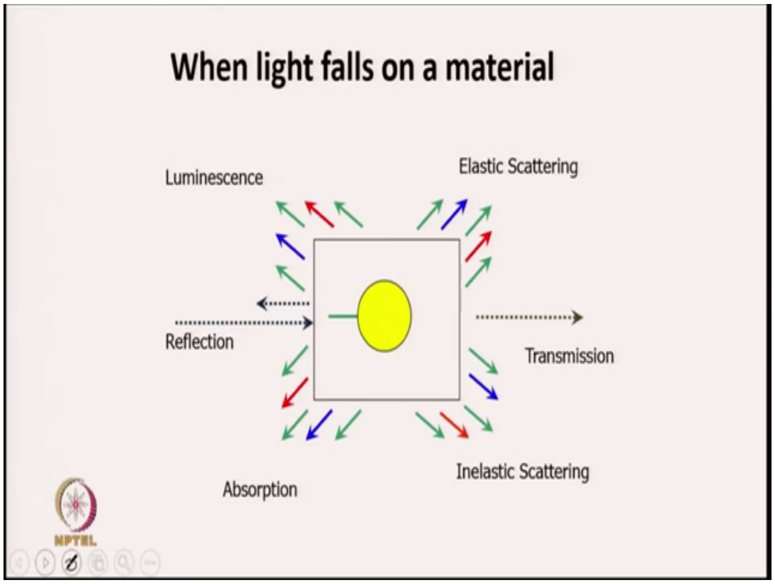

When light falls on a material

So, now, we will go to Raman Spectroscopy, so, Raman Vibrational and then we will discuss Raman Rotational Vibrational Spectroscopy. So, when light falls on a material we know that how EMR, electromagnetic radiation interacts with your sample, light can be transmitted, light can undergo your luminescence, light can get absorbed and scattering can happen, scattering is also of 2 types, elastic scattering and inelastic scattering.

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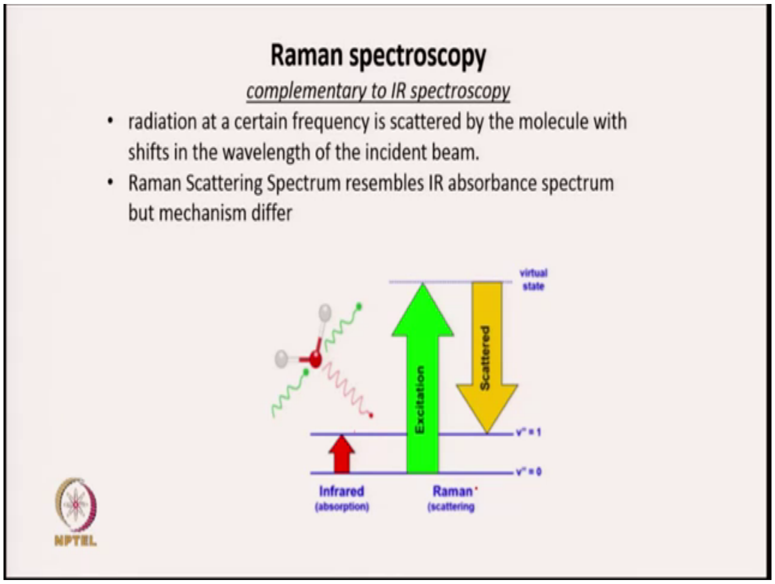

Raman spectroscopy

complementary to IR spectroscopy

- radiation at a certain frequency is scattered by the molecule with shifts in the wavelength of the incident beam.
- Raman Scattering Spectrum resembles IR absorbance spectrum but mechanism differ

So, Raman Spectroscopy is basically complimentary to IR Spectroscopy radiation at a certain frequency scattered by the molecule, the shift in wavelength of the incident beam, it resembles

IR absorption spectra, spectrum but mechanism differs. In IR Spectroscopy your particle is moving from one vibrational level to another vibrational level. In the Raman Spectroscopy when you excite the molecule, it goes to some virtual state and from the virtual state it comes back to one of the vibrational state. So, V double dash is equal to 1 by scattering. So, you can see gap is still remain same, gap is still remain same.

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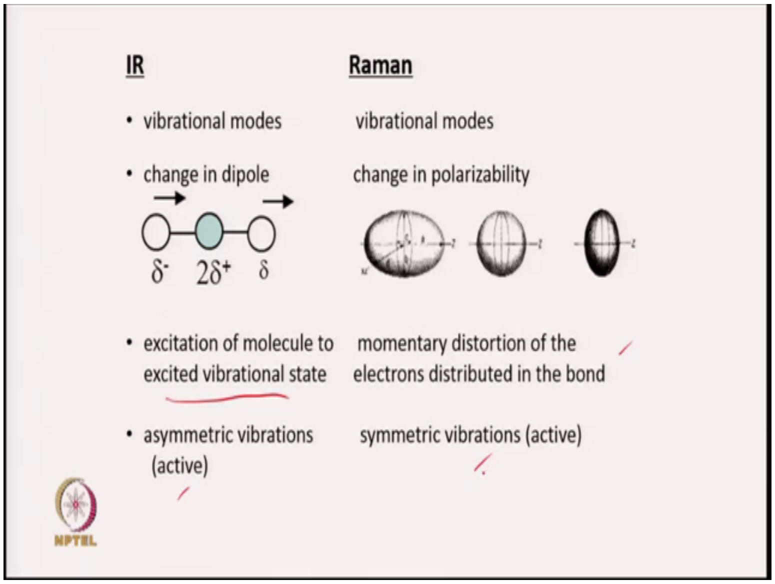

IR	**Raman**
• vibrational modes	vibrational modes
• change in dipole	change in polarizability
• excitation of molecule to excited vibrational state	momentary distortion of the electrons distributed in the bond
• asymmetric vibrations (active)	symmetric vibrations (active)

This is the difference between IR and Raman. We are looking at the vibrational modes only, but in IR change in dipole is important, whereas in Raman Spectroscopy, change in polarizability is important, we have already discussed Raman a bit in Rotational Raman Spectroscopy. So, I am not going to tell you in the detail, but we know that change in polarizability is important for Raman Spectroscopy.

Here, excitation of molecules happen to excited vibrational state, whereas in Raman Spectroscopy, momentary distortion of electron distributed in the bond and here is asymmetric vibrations are active, only asymmetric vibrations are active particularly for triatomic linear molecule. Here your symmetric vibrations are also active.

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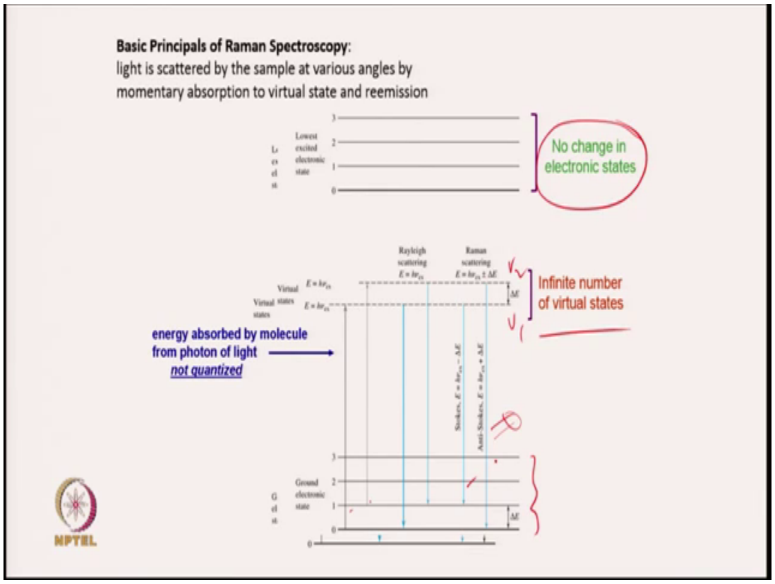

Basic Principals of Raman Spectroscopy:
light is scattered by the sample at various angles by
momentary absorption to virtual state and reemission

energy absorbed by molecule from photon of light → ***not quantized***

No change in electronic states

Infinite number of virtual states

So, Basic Principle of Raman Spectroscopy is light is scattered by the sample at various angle by momentary absorption to virtual state and then emission. So, absorption molecule does not go to a vibrational level, it goes to a virtual state and that is what it is seen here. So, no change in electronic history. So, first it must be kept in mind that in Raman Spectroscopy there is no change in electronic state. We are going from less ground state to a virtual state and there are infinite number of virtual state, it can go anywhere.

So, these are 2 virtual states you can see here, so first during excitation it goes to this, excitation can also take a molecule or a particle from a vibrational state 1 to this virtual state. And then So, this is your ground electronic state and there are this 4 vibrational state. So, from first vibrational state it can go to your some another virtual state and if suppose or absorption, it goes from 0 to this virtual state, it comes back to same ground state then you say that it is Rayleigh scattering.

Emission energy is equal to your h nu excitation. In this case in Raman Scattering, what happens that it does not come back to same vibrational level. It is now coming back, if you compare between this one and your this one, it is starts from excitation is from 0 vibrational state to this, suppose this is virtual V1 state, V1 and this is V2 state.

So, excitation is from 0 vibrational state to V1 virtual state. And if you see it is coming back from V1 virtual state to V is equal to 1 vibrational level not to V is equal to 0. So, E is going to be less and E is energy of emission is going to be h nu excitation minus delta E and delta is basically this difference, difference between V is equal to 0 vibrational level and V is equal to 1 vibrational level, V is equal to 1 vibrational level in Anti Stokes.

So, if you see here that there is excitation, the second excitation is from V is equal to 1 to virtual state V2, but when it is coming back, it is going from V2 to your V is equal to 0. So, here E is higher than h nu excitation and that is higher by delta E amount and this is called Anti Stokes Lines. So, you have 2 different kind of lines is Stoke Line and Anti Stokes Line.

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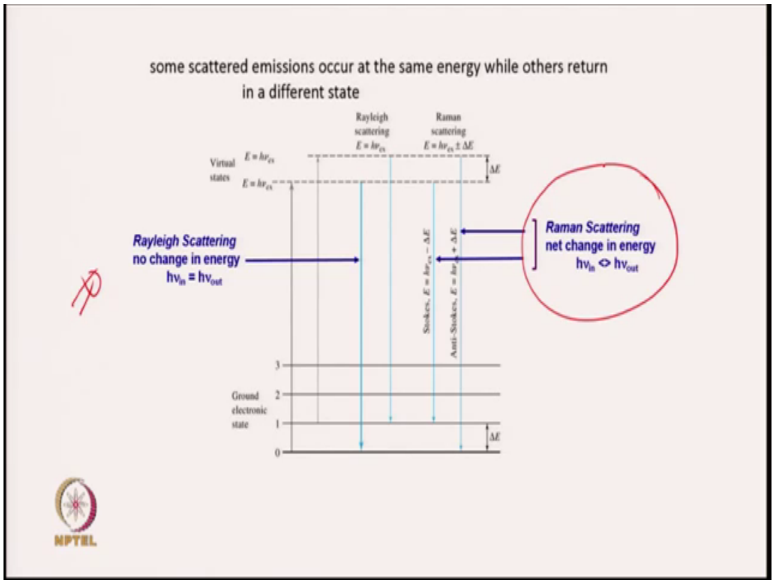

some scattered emissions occur at the same energy while others return in a different state

Some scattered emission occur at the same energy, while other returned to a different state. If it happens at the same energy, then you say that this is Rayleigh scattering, where h nu in is equal to h nu out. Whereas in Raman Spectroscopy, your there is a net change of energy and h nu in can be either less than h nu out or can be greater than h nu out. In one case you say that is a Stokes line and the in the second one you say that is Anti Stokes line.

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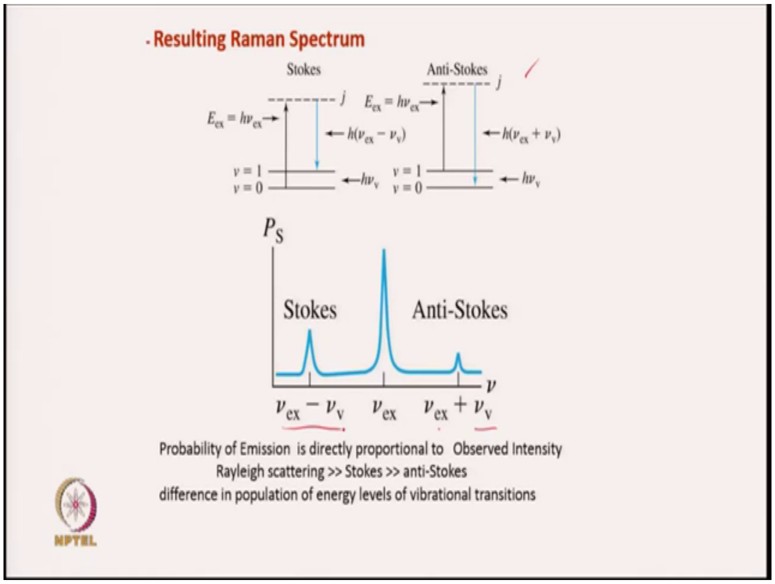

- Resulting Raman Spectrum

Probability of Emission is directly proportional to Observed Intensity

Rayleigh scattering >> Stokes >> anti-Stokes

difference in population of energy levels of vibrational transitions

So, resulting spectrum you can see Stokes line is this, where your E is less than E excitation, whereas in Anti Stokes line where E is greater than and your so, if you see frequency for Anti Stokes frequency is going to be higher and that is going to be nu excitation plus nu V. Whereas for a Stokes line you have smaller frequency which is nu excitation minus nu of vibrational V. Probability of emission is directly proportional to absorb intensity and Raleigh scattering is quite greater than Stokes and then less than Anti Stokes.

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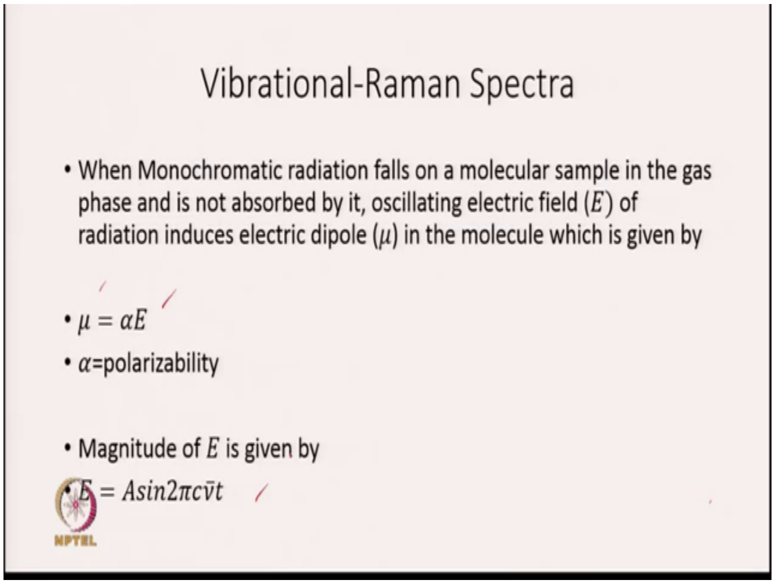

Vibrational-Raman Spectra

- 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
- $E = A\sin 2\pi c\bar{\nu}t$

So, let us discuss about Vibrational Raman Spectra. Theory is almost same as Rotational Raman Spectra. So, when monochromatic radiations falls on a molecular sample in gas phase and is not absorbed by it, oscillating electric field of radiation induces electric dipole in the molecule which is given by nu is equal to alpha into E, where alpha is your polarizability. Generally, the electric field, oscillating electric field is given by this equation is equal to A sin 2 pi C nu bar into T, where C is velocity of light and nu bar is the wave number (V) nu bar is the wave number.

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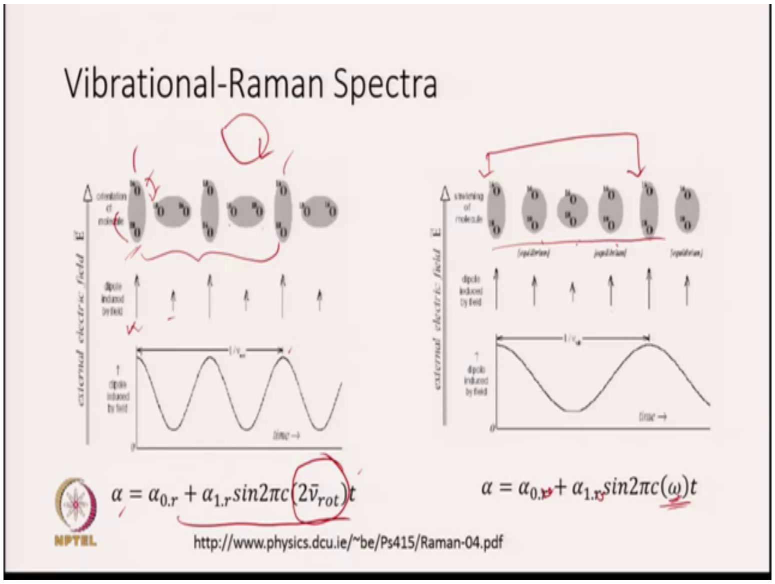

Vibrational-Raman Spectra

$$\alpha = \alpha_{0.r} + \alpha_{1.r} \sin 2\pi c \boxed{2\bar{\nu}_{rot}} t$$

$$\alpha = \alpha_{0.v} + \alpha_{1.v} \sin 2\pi c(\omega)t$$

http://www.physics.dcu.ie/~be/Ps415/Raman-04.pdf

So, now, let us think about how to express a polarizability. There is a difference between representation of polarizability in rotational spectrum in comparison to your vibrational spectrum. So, there is a difference between 2 different kind of motions. So, in the rotational spectrum, alpha is given by this equation where, alpha 0 R is polarizability when, at the equilibrium position, plus alpha 1 R multiplied by sin 2 pi C multiplied by 2 into nu bar rotation and then multiplied by t.

So this term is significant. If you go for vibration, you will get alpha is equal to, alpha 0 V you can say 0V, alpha 1V sin 2 pi C omega into T, where omega is again wave number, wave number where this is N number of vibration and this is the wave number of rotation. One thing you will notice that in this case it is multiplied by 2, whereas in this case it is multiplied by 1.

Now, question is why? So, let us think about a rotation of your O2 molecule and what we have done is, we have taken 16 O and this is 18 oxygen. So, this molecule when it is in this position, this is your the dipole movement and when it comes to horizontal position 18 O goes this side, so rotation is like this. So 18 O, 16 O then your dipole movement will decrease. Now, again rotate by 90degree. What you will get is 18 O up and 16 O down. So, again your dipole movement increases then on further rotation this 18 O will come here 16 O will come here.

So, you we are talking about this kind of rotation okay. So, 18 O will come here, 16 O will, 16 O will go here. In this condition also there is a decrease in induced dipole movement and then this is the position on further 90degree rotation what you will get is 16 O up and 18 O down and then you have higher dipole movement, higher dipole movement. So, now, you see that you started from this molecule and you are ending up with the same molecule and this requires 360degree rotation, 360degree rotation.

Now, let us look at how dipole movement is changing during this 360degree rotation at this position it is up then down and it is up here. So, what does that mean is during one 360degree rotation, it is going from first crest to third crest. So, first, second, third crest and what does that mean is, it is completing 2 cycles, it is completing 2 cycles. So, so during 360degree rotation, 2 cycles gets completed and that is why your wave number is written like 2 into nu bar rotation.

Whereas, during the vibration and now look at vibration what is happening 16 O, 18 O, so this is 1 complete vibration, this is your equilibrium position, this is your extension, equilibrium position, compression and then equilibrium position and then extension or stretching. So, you started with a stretching, you went to equilibrium position, you compressed it, you again went to the equilibrium position and finally, your molecule is this bond is stretched.

So, now you have gone from this position to this position. Now, you see if I plot this dipole induced by field during this 1 vibration, what I will get is here your dipole movement is higher, dipole movement is smaller, dipole movement is a smaller, dipole movement is higher and this is dipole movement is highest. So, you are saying that you started from 1 crest and you went to the another crest. So, from stretched mode to stretched mode, you are completing 1 cycle, only 1 cycle in contrast to the rotation, where 360degree rotation corresponds to 2 cycle. So, here you do not write 2 omega you write omega, where omega is wave number for, wave number for vibration.

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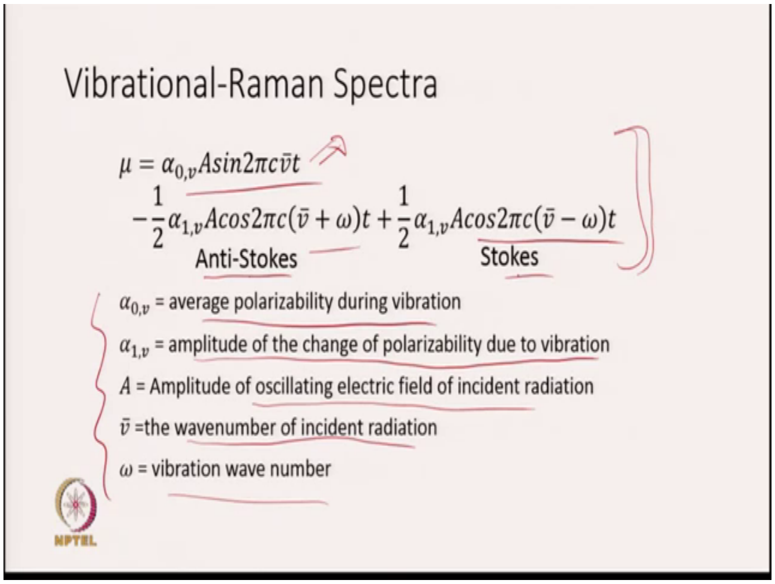

Vibrational-Raman Spectra

$$\mu = \alpha_{0,v} A sin 2\pi c\bar{\nu}t$$
$$-\underbrace{\frac{1}{2}\alpha_{1,v} A cos 2\pi c(\bar{\nu}+\omega)t}_{\text{Anti-Stokes}} + \underbrace{\frac{1}{2}\alpha_{1,v} A cos 2\pi c(\bar{\nu}-\omega)t}_{\text{Stokes}}$$

$\alpha_{0,v}$ = average polarizability during vibration

$\alpha_{1,v}$ = amplitude of the change of polarizability due to vibration

A = Amplitude of oscillating electric field of incident radiation

$\bar{\nu}$ =the wavenumber of incident radiation

ω = vibration wave number

So, if you multiply mu by E what you are going to get is 3 different terms and this I already explained you in Rotational Raman Spectroscopy, when wave number is your nu plus omega and you have Anti Stokes lines, when it is nu minus omega then you have Stokes lines. So, these are the different terms alpha 0 V.

I told you that corresponds to average polarizability during vibration, alpha 1 V is amplitude of change of polarizability due to vibration. A is amplitude of oscillating electric field of incident radiation, nu bar is wave number of incident radiation and omega is vibrational wave number. So, in the case of Vibrational Raman Spectrum, you again get 2 lines Anti Stokes, Stokes along with your Rayleigh line and the (frequency) wave number here corresponds to V plus omega and V minus omega, V minus omega.

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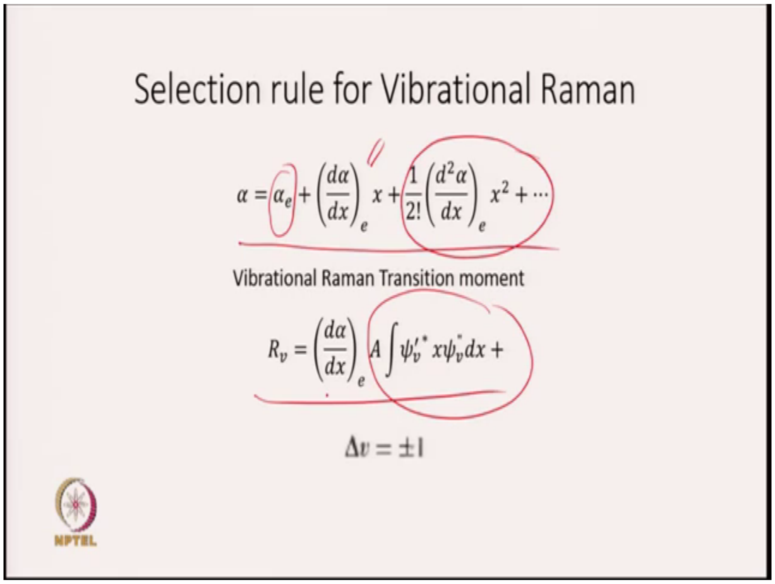

Selection rule for Vibrational Raman

$$\alpha = \alpha_e + \left(\frac{d\alpha}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2\alpha}{dx}\right)_e x^2 + \cdots$$

Vibrational Raman Transition moment

$$R_v = \left(\frac{d\alpha}{dx}\right)_e A \int \psi_v'^* x \psi_v'' dx +$$

$$\Delta v = \pm 1$$

Now, we can discuss about selection rule for Vibrational Spectroscopy. Alpha is the polarizability and alpha is also a function of X, alpha can be given as alpha E plus d alpha by dx E X plus 1 by 2 factorial d 2 alpha by dx at equilibrium into X square. So, this kind of calculation we have seen for Vibrational Spectroscopy. Same thing we are going to do it here. If we calculate vibrational Raman transition, the first terms when we put in this RV first term is going to be 0 because your 2 vibrational levels, V and V plus 1, wave function of 2 vibrational levels are orthogonal to each other.

So, first term well tends to 0, second term will remain whereas, third term we can neglect for a small displacement. So, vibrational Raman transition movement can be given by this equation RV is equal to your d alpha by d Xe and this integral multiplied by this integral. So, your polarizability alpha which polarizability must change with X if it is Raman active and so, this is one selection rule and the second one gives you delta V is equal to plus minus 1.

So, first term is not 0 when polarizability changes with your displacement, whereas second term will not be equal to 0 when delta V is equal to plus minus 1. So there are 2 selection rule, delta V plus minus 1 is called a ‘Specific Selection Rule’ whereas first one is known as ‘Gross Selection Rule’.

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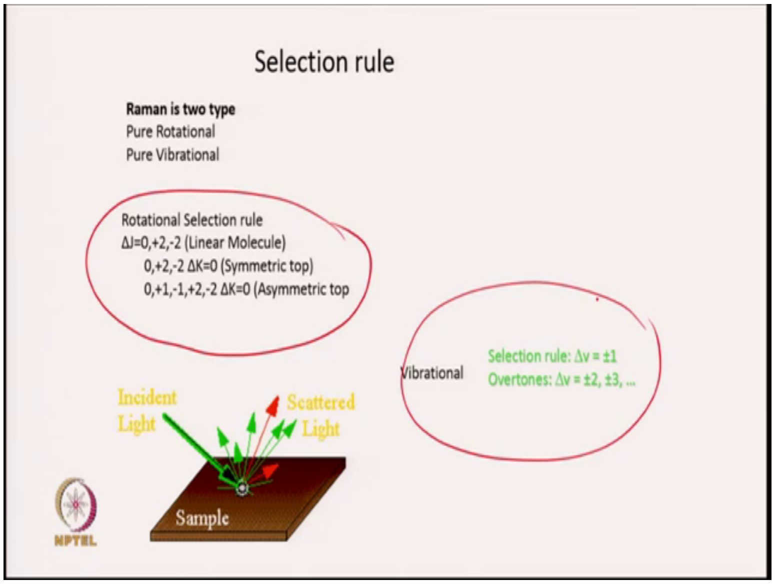

Selection rule

Raman is two type
Pure Rotational
Pure Vibrational

Rotational Selection rule
ΔJ=0,+2,-2 (Linear Molecule)
0,+2,-2 ΔK=0 (Symmetric top)
0,+1,-1,+2,-2 ΔK=0 (Asymmetric top

Vibrational
Selection rule: Δv = ±1
Overtones: Δv = ±2, ±3, ...

After this now, we know that Raman can be of 2 type pure Rotational Raman and pure Vibrational Raman. We have already discussed pure Rotational Raman and in this lecture, we discuss pure Vibrational Raman Spectroscopy. For vibrational, for rotational there are 3 different rules delta J is equal to 0 plus minus 2 for linear molecule, for symmetric top delta J is equal to 0 plus minus 2 and delta k is equal to 0 for asymmetric top, your delta J can be 0 plus minus 1 and plus minus 2 whereas delta k must be 0. So, this is the selection rule for rotational, for vibrational, then we have selection rule is delta V is equal to plus minus 1.

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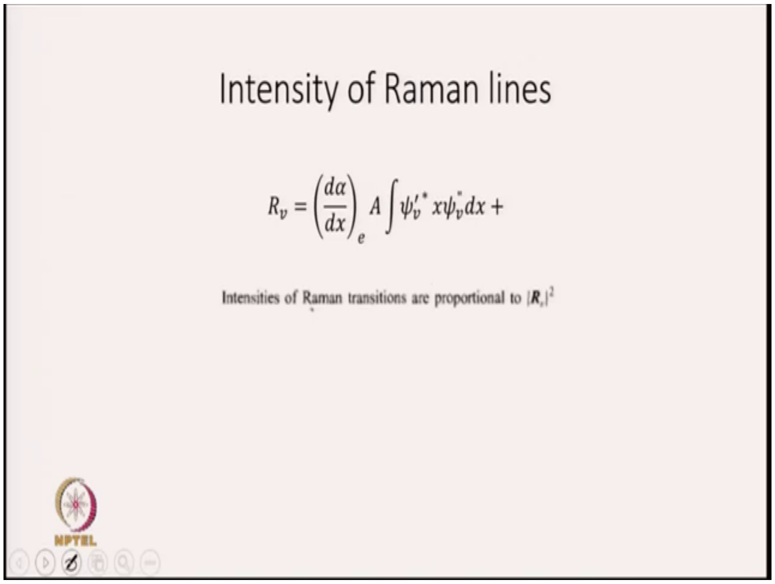

Intensity of Raman lines

$$R_v = \left(\frac{d\alpha}{dx}\right)_e A \int \psi_v'^{*} x \psi_v^{"} dx +$$

Intensities of Raman transitions are proportional to $|R_v|^2$

We can also know intensity of Raman line and we just calculated rotational Raman transition movement and that is given by this equation. Intensity is proportional to RV square and so, by looking at how RV changes, we can tell about intensity of Raman lines.

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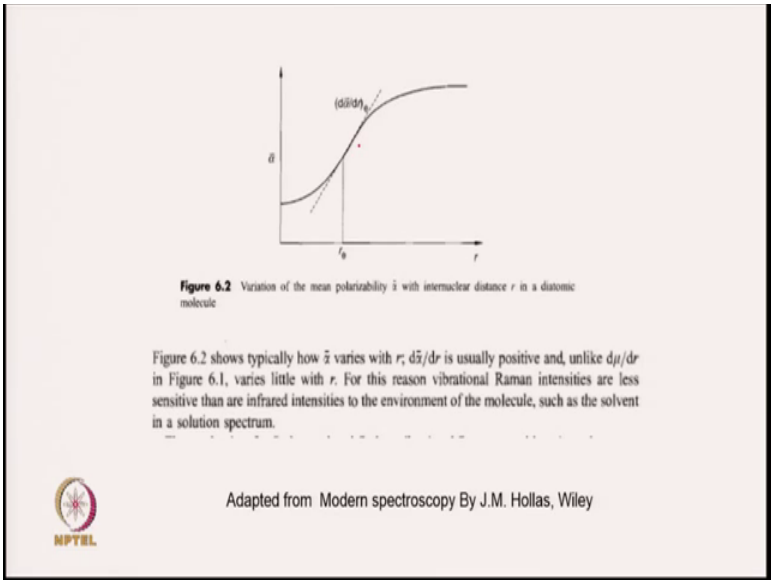

Figure 6.2 Variation of the mean polarizability $\bar{\alpha}$ with internuclear distance r in a diatomic molecule

Figure 6.2 shows typically how $\bar{\alpha}$ varies with r; $d\bar{\alpha}/dr$ is usually positive and, unlike $d\mu/dr$ in Figure 6.1, varies little with r. For this reason vibrational Raman intensities are less sensitive than are infrared intensities to the environment of the molecule, such as the solvent in a solution spectrum.

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

So, this is how alpha changes with X, alpha changes with X and so, depending on slope you can see position and the slope at that position you can calculate what will be the d alpha by dx square and that is basically proportional to your intensity. In contrast to Vibrational Spectroscopy, what we can see is that this d alpha by dR is mostly positive and it does not vary that much with R, it does not vary that much with R.

What does that mean is that Vibrational Raman Intensity are less sensitive than infrared intensities to the environment of the molecule such as solvent. So, please keep that thing in mind a peak is more intense based on the delta V is equal to plus minus 1 you also need to look at how polarizability changes with the distance and that also determines your intensity of the P.

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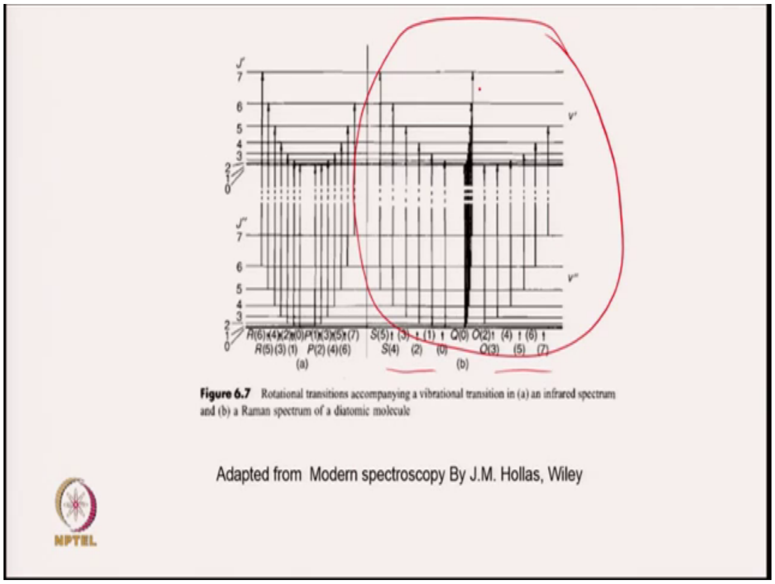

Figure 6.7 Rotational transitions accompanying a vibrational transition in (a) an infrared spectrum and (b) a Raman spectrum of a diatomic molecule

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

If you look at infrared Raman Spectroscopy for diatonic molecule, you will have your 3 different kind of transition. So, this is for diatonic. So, UCS is equal to your, here you are going from for example, take this case we are going from V double dash is equal to 5 to V double dash, V dash is equal to 7.

So, again Delta J is plus minus 2, we are going from your rotational level of 1 vibration to rotational level, to rotational level of another vibrational level, ok and so, this is Rotational, Vibrational Raman, Rotational Vibrational Raman and this can be of 3 types, what is known as SQ and so, this is your S type and this is Q and this is O which is here. In S you are going from 5 to 7, 5 to 7.

So, delta J plus 2, Delta J is plus 2. Here, you see, you are going from 7 to 5. So, this side you have delta J is minus 2 and in this case you are going from same place 7 to 7. So, delta J is 0. So, delta J is 0 corresponds to Q, peak whereas delta J is equal to plus 2 corresponds to S and delta J is equal to minus 2 corresponds to your O peak.

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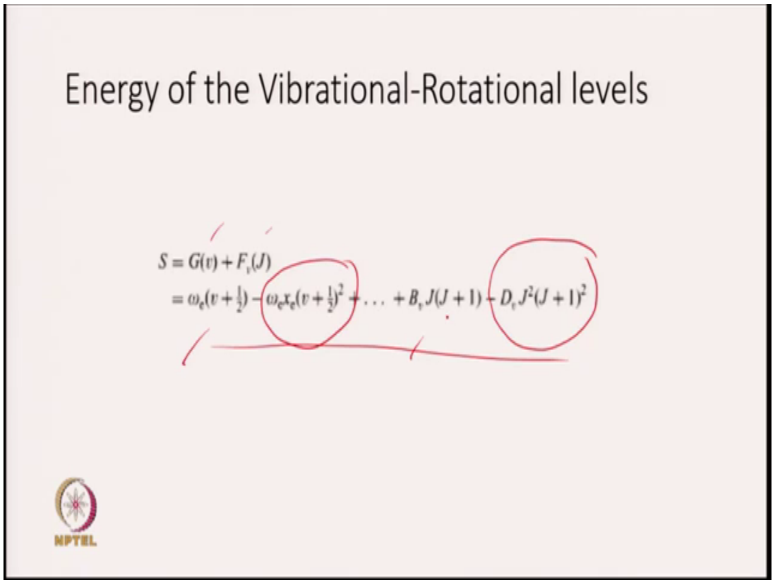

Energy of the Vibrational-Rotational levels

$$S = G(v) + F_v(J)$$
$$= \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \ldots + B_v J(J+1) - D_v J^2(J+1)^2$$

We know that energy of vibrational rotational levels, we have already discussed that and that is basically GV plus FvJ and that is given by this equation and now, we can apply delta J is equal to plus minus 2 to know what should be the wave number for your S transition, O transition and so, you see, this is if I neglect anharmonicity and if I neglect your centrifugal distortion, then we have 2 different part, 1 corresponding to vibrational and other corresponding to your rotational level.

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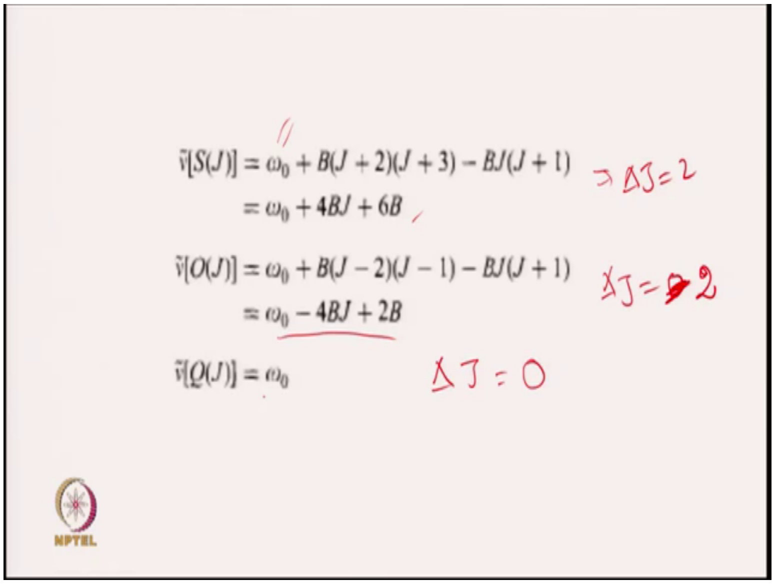

$$\tilde{\nu}[S(J)] = \omega_0 + B(J+2)(J+3) - BJ(J+1) \quad \Rightarrow \Delta J = 2$$
$$= \omega_0 + 4BJ + 6B$$

$$\tilde{\nu}[O(J)] = \omega_0 + B(J-2)(J-1) - BJ(J+1) \quad \Delta J = [illegible]\,2$$
$$= \underline{\omega_0 - 4BJ + 2B}$$

$$\tilde{\nu}[Q(J)] = \omega_0 \qquad \Delta J = 0$$

And then you can calculate nu bar or wave number for S, O, and Q transition, S, O and Q transition and here you can see that this is not going to change because your delta V is plus minus 1 and when Raman Rotational Vibrational Spectroscopy, but delta J is going to be your plus 2.

So, this is for delta J is equal to plus 2 and for that the wave number is given by omega naught plus 4BJ plus 6B, omega naught plus 4J plus 6B and then you can also calculate wave number for O transition is delta J is equal to minus 2, minus 2 and this is delta J is equal to 0, delta J is equal to 0. So, for O you will have this omega naught minus 4BJ plus 2B and for this you have omega naught.

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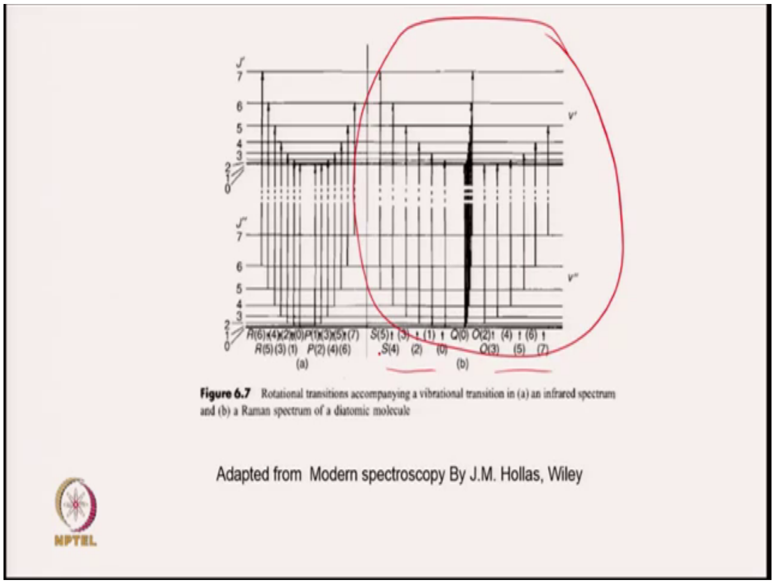

Figure 6.7 Rotational transitions accompanying a vibrational transition in (a) an infrared spectrum and (b) a Raman spectrum of a diatomic molecule

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

So, you can see that so, this is your Q and this is O and this is S. So, these are the 3 different kind of transition in Rotational Vibrational Raman Spectroscopy.

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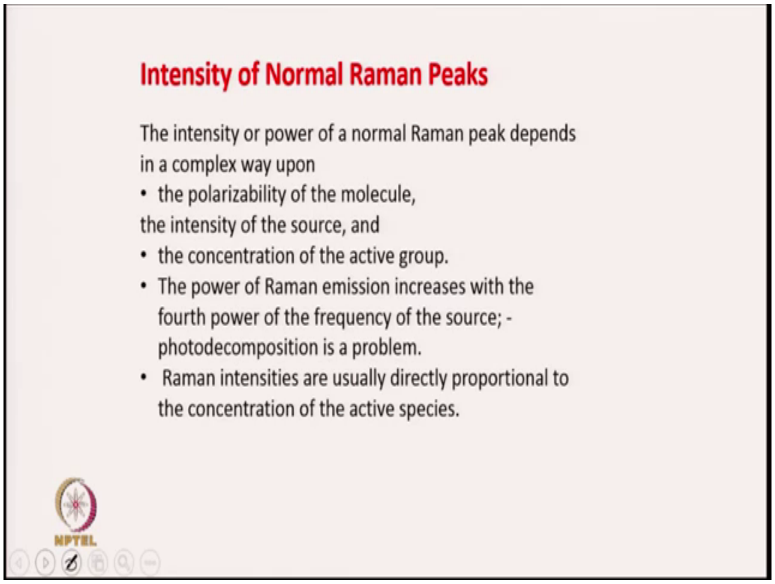

Intensity of Normal Raman Peaks

The intensity or power of a normal Raman peak depends in a complex way upon
- the polarizability of the molecule,

the intensity of the source, and
- the concentration of the active group.
- The power of Raman emission increases with the fourth power of the frequency of the source; - photodecomposition is a problem.
- Raman intensities are usually directly proportional to the concentration of the active species.

So, Intensity of Normal Raman Peak, just we discuss about intensity how we can calculate, we have to look at how polarizability changes with X that also tells you about intensity. Apart from that intensity of the source, the concentration of active group will increase your intensity of the peaks, the power of Raman emission increases with the fourth power of the frequency of the source and Raman intensity are usually directly proportional to the concentration of the active species. So, there are 2 other things which decides about intensity, one is power of the source and the second is concentration of active species.

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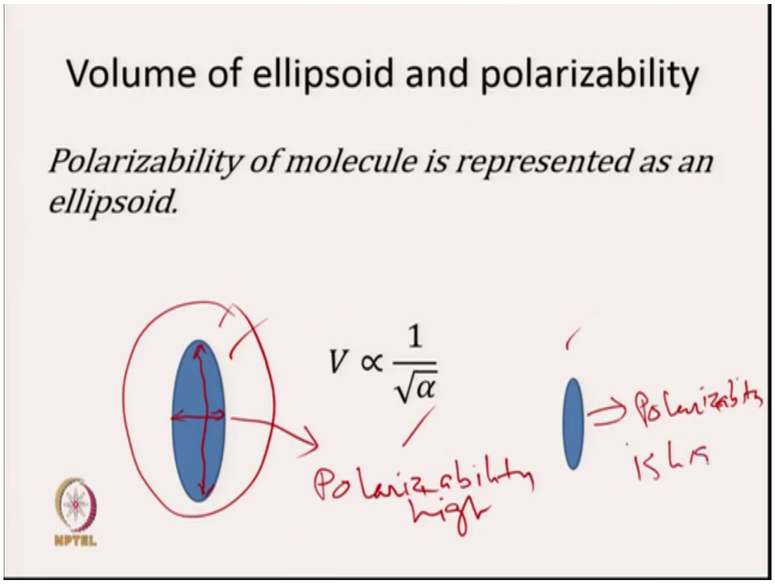

Volume of ellipsoid and polarizability

Polarizability of molecule is represented as an ellipsoid.

$$V \propto \frac{1}{\sqrt{\alpha}}$$

So, let us first understand what we mean by 'Volume of Ellipsoid and Polarizability'. It is important to understand polarizability, because then you can understand how a molecule is Raman active, Vibrational Raman active or not. Polarizability of molecule is generally represented at ellipsoid and volume of ellipsoid is inversely proportional to the square root of alpha where alpha is polarizability.

So, what does that mean is that if you look at this ellipsoid, so, in this direction your volume is less whereas, in this direction your volume is more. So, this is your minor axis and this is your major axis. So, what does that mean is in this direction, your polarizability is more, polarizability is more, your polarizability is high or more.

Whereas, in this direction, vertical direction your polarizability is less, since volume is proportional to 1 by root alpha, where alpha is polarizability. So, if volume is less it means polarizability is high. And now, you compare between these 2 volume of ellipsoid and you can tell that in this your polarizability is high, polarizability is high, lity is high, polarizability is high.

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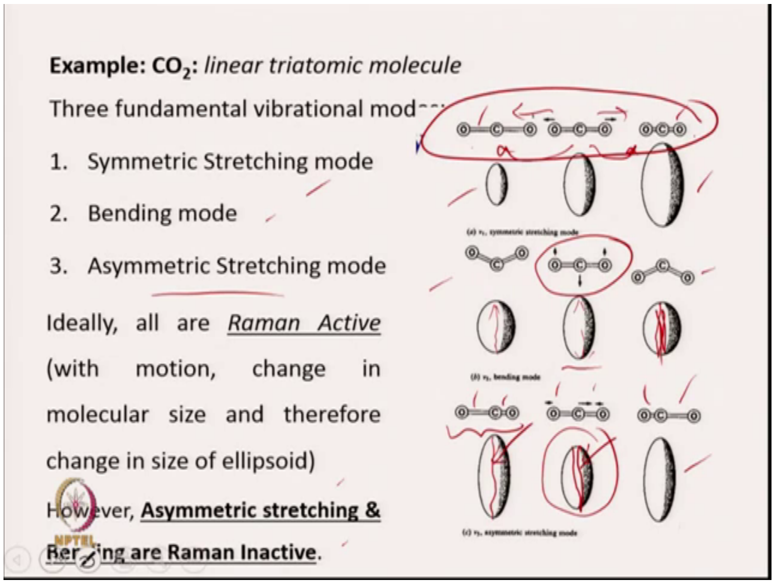

Example: CO$_2$: *linear triatomic molecule*

Three fundamental vibrational mod

1. Symmetric Stretching mode
2. Bending mode
3. Asymmetric Stretching mode

Ideally, all are *Raman Active* (with motion, change in molecular size and therefore change in size of ellipsoid)

However, **Asymmetric stretching & Bending are Raman Inactive.**

Now, let us think about if suppose I am looking at CO2 and I want to know whether different vibrational mode of CO2 is Raman active or not Raman active or not. CO2 has 3 fundamental vibrational mode. So, since CO2 (is) has 3 atoms, so, 3 and minus 6 is 3.

So, it has 3 fundamental vibrational mode. One is symmetric, symmetric stretching mode and that is shown here, shown here. So, this is a molecule and you are basically stretching this 2 bond, so extension this side this so stretching is happening. So, when stretching happens, you get this when contraction happens, you get this molecule.

So, both bonds are getting stressed, here both bonds are getting compressed. So, if that happens, you say that the molecule has symmetrical stretching mode, the second kind of mode is bending mode and here you can see that this is the normal molecule and if you take both up, then you will get this one, if you take both down then you will get this one.

So, this is your bending mode. And the third one is symmetric stretching mode. In that 1 bond is, 1 bond is getting stressed, while other bond is getting compressed. So in this case, this bond elongated, this bond get compressed, while in this case, this is compressed and this one is elongated.

So, you have 3 fundamental vibrational modes of CO2. Ideally, all are Raman active because you can see that there is a change in polarizability. But in reality, this asymmetric stretching and bending are Raman inactive. Now, let us first think about what is happening to polarizability. So, here you see you are stretching this bond, what does that mean is that the electron cloud is more polarizable, since, since there is a greater distance between nuclei and electron cloud.

So, you will see that volume of ellipsoid is, volume of polarizability ellipsoid is smaller, whereas in the contraction case polarizability is more, what does that mean volume of ellipsoid is going to be large, going to be large. Similar is the case with this bending mode in bending mode, you can see that here your cloud is elongated what does that mean is polarizability along the major axis is major axis is smaller, whereas in this case, polarizability along this direction is higher compared to this CO2.

Same thing here, polarizability along this axis is higher compare to your normal molecule or molecule in equilibrium position. Now, the third case asymmetric stretching mode. So, you can see here that, in this case, your polarizability is higher in the equilibrium, where in this one polarizability is going to be a smaller, so polarizability is polarizability is greater in the CO2 in equilibrium mode, polarizability is smaller along this axis along this axis, if you do asymmetric stretching and same case is here. So it looks like that polarizability is changing, but in reality, we will see that in the last 2 cases polarizability does not change.

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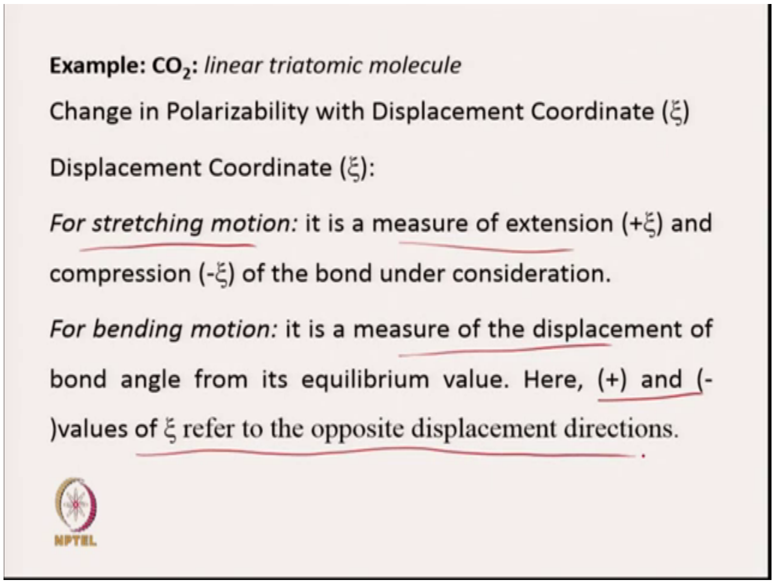

Example: CO_2: *linear triatomic molecule*

Change in Polarizability with Displacement Coordinate (ξ)

Displacement Coordinate (ξ):

For stretching motion: it is a measure of extension ($+\xi$) and compression ($-\xi$) of the bond under consideration.

For bending motion: it is a measure of the displacement of bond angle from its equilibrium value. Here, (+) and (-)values of ξ refer to the opposite displacement directions.

So, for that, what we need to do is we need to look at change in polarizability with displacement co-ordinates. So, to understand why the other 2 modes are Raman inactive, what we need to see is we need to look at change in polarizability with displacement coordinates. So, what I mean by displacement coordinates, that for stretching motion, it is a measure of extension and compression of the bond under consideration.

Whereas for bending motion, it is the measure of displacement of bond angle from its equilibrium value. So, what I mean is that plus and minus value of E refers to opposite displacement direction.

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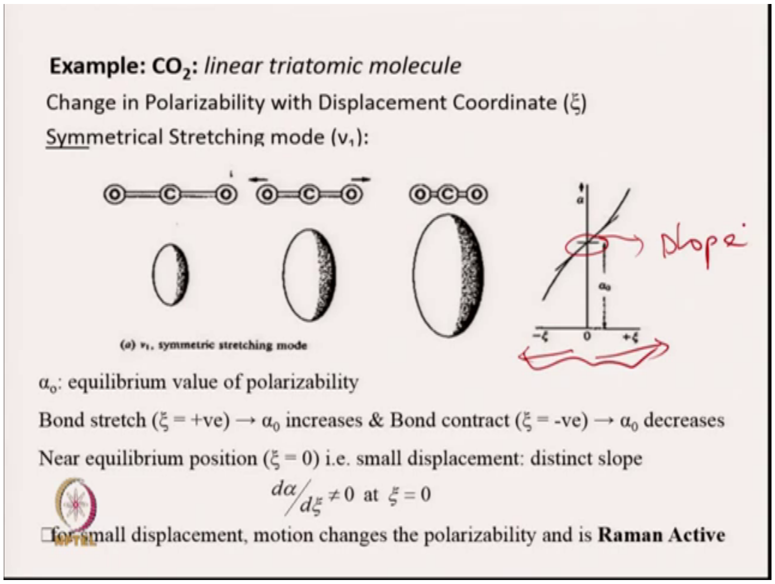

Example: CO_2: *linear triatomic molecule*

Change in Polarizability with Displacement Coordinate (ξ)

Symmetrical Stretching mode (v_1):

α_0: equilibrium value of polarizability

Bond stretch (ξ = +ve) → α_0 increases & Bond contract (ξ = -ve) → α_0 decreases

Near equilibrium position (ξ = 0) i.e. small displacement: distinct slope

$$d\alpha/d\xi \neq 0 \text{ at } \xi = 0$$

☐ for small displacement, motion changes the polarizability and is **Raman Active**

Once we know that, let us see the plot. So, this is plot for symmetrical stretching mode. And you can see that your epsilon is plotted against alpha. And now you see this is your equilibrium position. So, you are at this point.

And now what you are looking at what happens when you compress the bonds or stretch the bonds. So, this is your stretching and you can see that stretching, what happens, you are going towards plus E and plus E here your volume for ellipsoid is smaller and polarizability is higher. So you can see this polarizability is increasing. When you do compression, what you mean is you are looking at this side, negative side, negative side of extension and you can see that your volume of ellipsoid is larger, it means polarizability is smaller and so polarizability is dropping with the compression, with the compression.

So, if you look at this point, what we will see is near equilibrium position, if you look at a small displacement, it has a slope, so, you can see that there is a slope there is a slope. What does that mean is your for a small displacement, motion changes polarizability and thus, the symmetrical stretching mode is Raman active.

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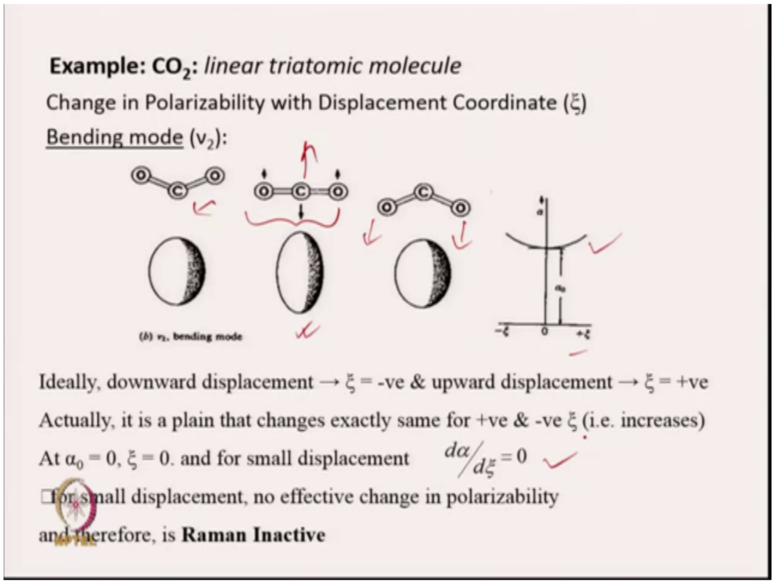

Example: CO_2: *linear triatomic molecule*

Change in Polarizability with Displacement Coordinate (ξ)

Bending mode (v_2):

Ideally, downward displacement → ξ = -ve & upward displacement → ξ = +ve

Actually, it is a plain that changes exactly same for +ve & -ve ξ (i.e. increases)

At $\alpha_0 = 0$, $\xi = 0$. and for small displacement $d\alpha / d\xi = 0$

☐ for small displacement, no effective change in polarizability and therefore, is **Raman Inactive**

Now, let us think about bending mode. So, I already discussed that, this is your equilibrium position, and your polarizability is going to be smaller and volume of ellipsoid is larger. So, now you are looking at plus E minus E. So, when you do suppose displacement in this direction, which is basically here, what you see is volume of ellipsoid decreasing, it means polarizability is increasing. So, polarizability is increasing.

Now, if you look at this case, where what we are doing is we are bending both CO towards downward and, and in that case, again, volume of ellipsoid is decreasing volume of ellipsoid decreasing and that means polarizability is increasing. So, you basically get this kind of curve, when you plot alpha versus E. Now, if you go at equilibrium position and try to draw a slope for a small displacement, what you will see that your slope is, slope is 0. What does that mean is d alpha by d E is equal to 0. So basically, for a small displacement, there is no effective change in polarizability and therefore, bending mode is Raman inactive. Bending mode is Raman inactive.

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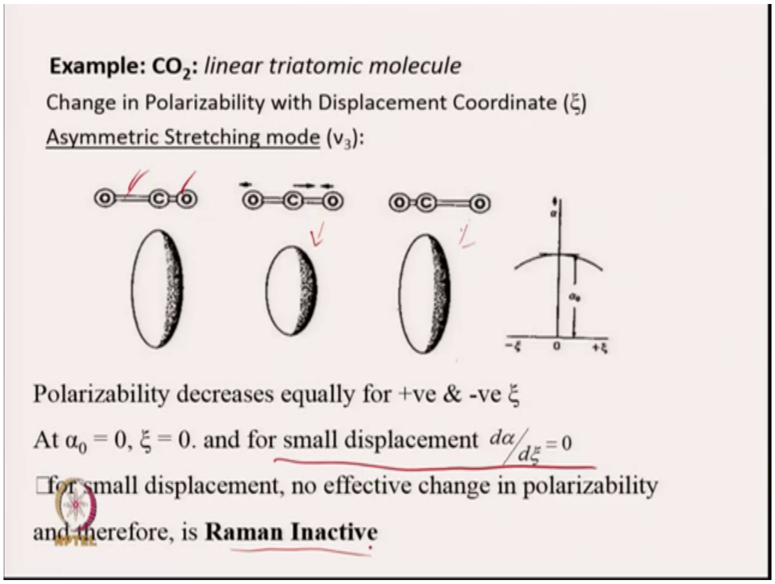

Example: CO_2: *linear triatomic molecule*

Change in Polarizability with Displacement Coordinate (ξ)

Asymmetric Stretching mode (v_3):

Polarizability decreases equally for +ve & -ve ξ

At $\alpha_0 = 0$, $\xi = 0$. and for small displacement $d\alpha/d\xi = 0$

☐for small displacement, no effective change in polarizability and therefore, is **Raman Inactive**

Now, let us think about the third case, asymmetric stretching mode. In this again, your equilibrium position, you have an equilibrium position, you have a smaller ellipsoid. What does that mean that alpha value is higher and if you do asymmetric stretching, what does that mean the extension of this bond and compression of this bond and we will get greater ellipsoid volume it means polarizability is decreasing. In this case also polarizability decreasing.

So, you get something like this curve when you plot alpha versus E. And now again, you can go at equilibrium position and look at the slope. Here, again slope is 0. What does that mean is for a small displacement, d alpha by dE is equal to 0. And what does that mean is for a small displacement, there is no effective change in polarizability. And what that means is that this mode is also Raman inactive.

So, basically, you have to look at the change in polarizability around equilibrium around equilibrium and you must have to think about a small displacement. And if slope is 0, it means that particular mode is not Raman active, if slope is positive or negative, it means polarizability is changing and when polarizability is changing hence it is Raman active.

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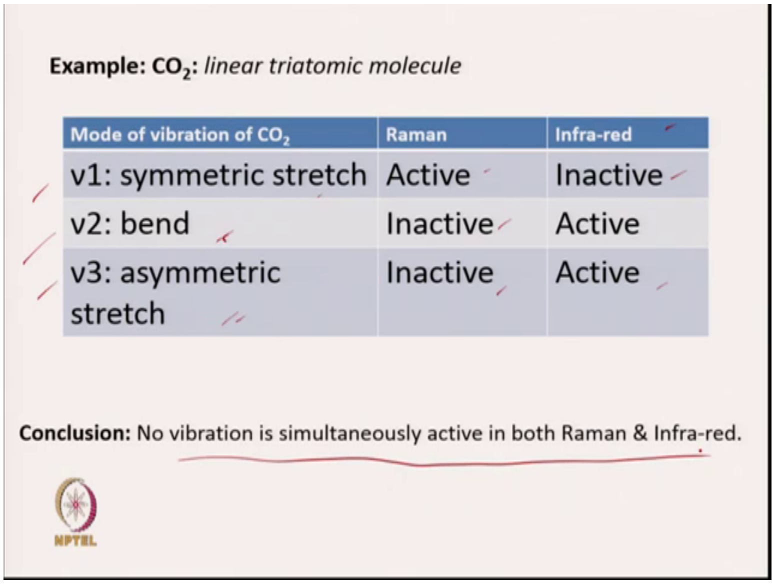

Example: CO_2: *linear triatomic molecule*

Mode of vibration of CO_2	Raman	Infra-red
v1: symmetric stretch	Active	Inactive
v2: bend	Inactive	Active
v3: asymmetric stretch	Inactive	Active

Conclusion: No vibration is simultaneously active in both Raman & Infra-red.

So, for CO2 molecule, we have looked at 3 different vibration mode, symmetrical stretching, bending and asymmetrical stretching. The first one is Raman active, but it is infrared inactive, whereas bending and asymmetric stretching are inactive, inactive modes in the Raman Spectroscopy, whereas they are infrared active.

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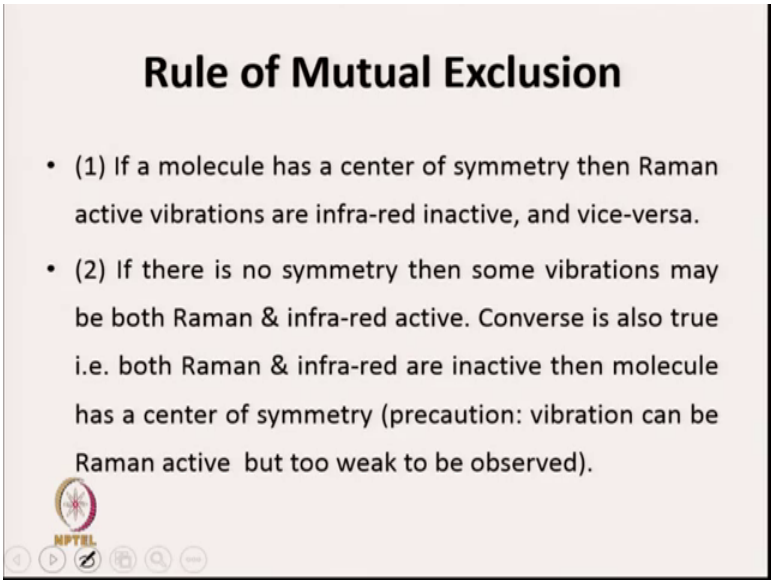

Rule of Mutual Exclusion

- (1) If a molecule has a center of symmetry then Raman active vibrations are infra-red inactive, and vice-versa.
- (2) If there is no symmetry then some vibrations may be both Raman & infra-red active. Converse is also true i.e. both Raman & infra-red are inactive then molecule has a center of symmetry (precaution: vibration can be Raman active but too weak to be observed).

So, conclusion is no vibration is simultaneously active in both Raman and infrared and that list to well known Rule of Mutual Exclusion, which says that 'if a molecule has a center of symmetry, then Raman active vibrations are infrared inactive and vice versa'. If there is no symmetry, then some vibration maybe both Raman and infrared active, converse is also true that is both Raman and infrared are inactive, then molecule has a center of symmetry.

So, this Rule of Mutual Exclusion is force molecule with a center of symmetry and when the molecule has center of symmetry, then either the mode is your infrared active or Raman active. It cannot be both Raman and infrared active molecule. So, this is all about theory part of IR spectroscopy.

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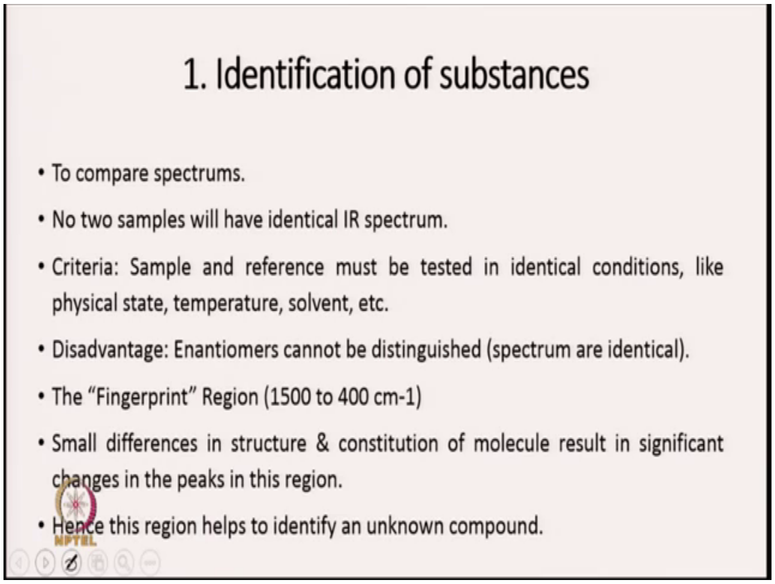

1. Identification of substances

- To compare spectrums.
- No two samples will have identical IR spectrum.
- Criteria: Sample and reference must be tested in identical conditions, like physical state, temperature, solvent, etc.
- Disadvantage: Enantiomers cannot be distinguished (spectrum are identical).
- The "Fingerprint" Region (1500 to 400 cm-1)
- Small differences in structure & constitution of molecule result in significant changes in the peaks in this region.
- Hence this region helps to identify an unknown compound.

Now, what we will do is we look at the application and IR spectroscopy has a wide range of application, most important one is your identification of substance. So, most of the organic molecule can be identified or particularly their functional group can be identified through IR spectroscopy, for that, you need to just compare a spectrum of your sample and reference sample. 2 identical, 2 samples are not going to have identical IR spectrum. So, you take 2 molecules and you try to see their IR spectrum that is not going to be same. You must certainly we are talking about when those 2 molecules are in identical conditions.

One disadvantage is that we cannot distinguish Enantiomer, Fingerprint region 1500 to 400 centimeter is very important, because when a small difference in a structure and constitution of molecule will show significant change in the peaks in the region, and so, it is very important to IR is a very important to to identify unknown compounds.

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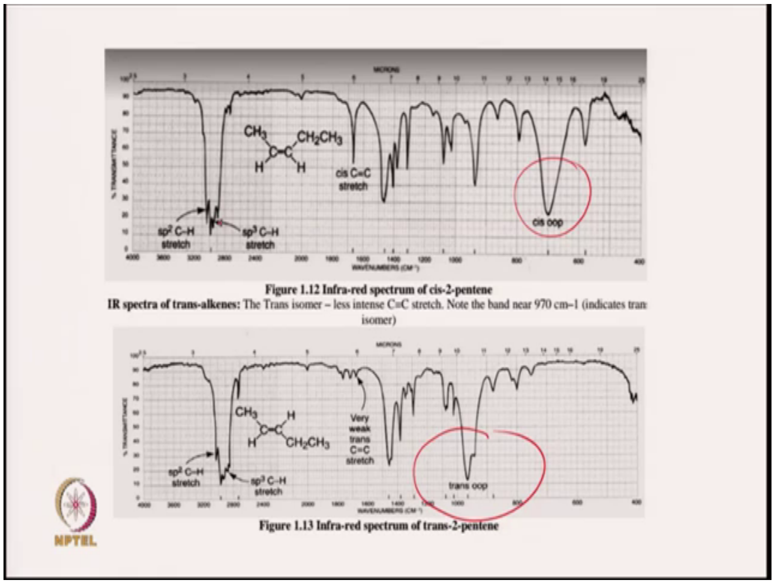

Figure 1.12 Infra-red spectrum of cis-2-pentene

IR spectra of trans-alkenes: The Trans isomer – less intense C=C stretch. Note the band near 970 cm–1 (indicates tran

isomer)

Figure 1.13 Infra-red spectrum of trans-2-pentene

I will give some examples to you. So, look at this molecule. So, here you have CH3 C double bond CH CH2 CH3 and this is at sis-trans, cis-2-pentene and your trans 2 pentene and you can see that there are a lot of differences in IR spectrum, particularly you see this cis you have here and 4 trans it is here. And similarly, you can look at the stretching SP 2 CH stretching, SP3 CH stretching. So, just by looking at you know, a spectrum of 2 pentene samples, you can tell that which 2 pentene has cis configuration and which one has trans configuration.

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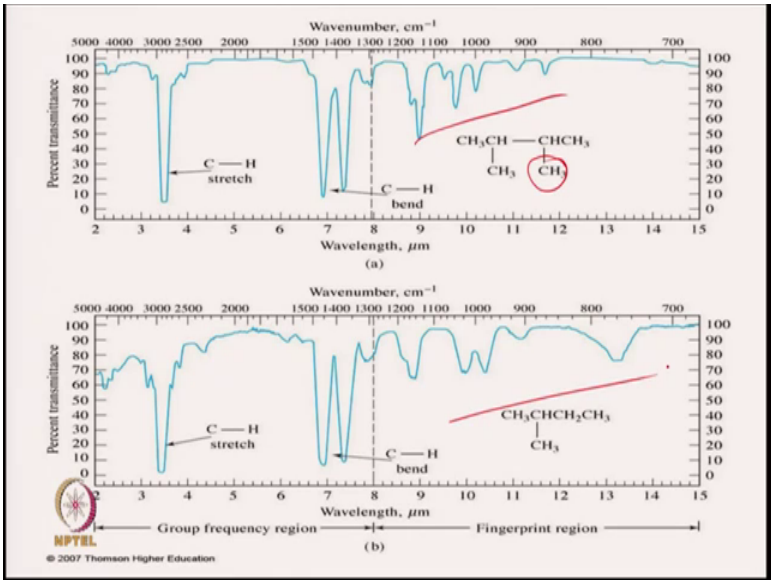

Now, look at this your 2, 3 hexane and this is your 2 pentane and 2, 3 hexane. Just a small change, one methyl group you have attached to this part and you see fingerprint region, it is a totally different, fingerprint region is totally different. And so, just by looking at fingerprint region, you can tell about which molecule is present in the sample, no 2 molecules has identical IR spectrum.

So, just by comparing with the already available data and the literature, you can know what molecule is there in the sample. This is simple method, IR is very simple method to distinguish between 2 polymers.

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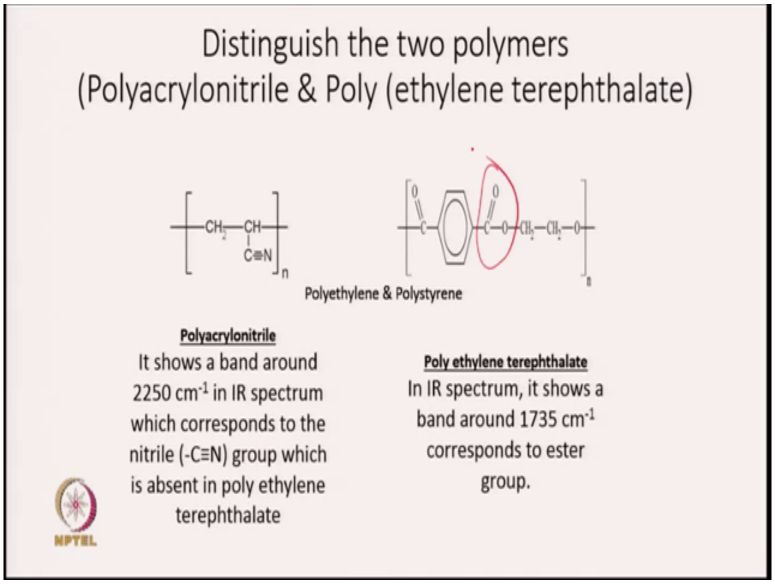

Distinguish the two polymers
(Polyacrylonitrile & Poly (ethylene terephthalate)

Polyethylene & Polystyrene

Polyacrylonitrile
It shows a band around 2250 cm^{-1} in IR spectrum which corresponds to the nitrile (-C≡N) group which is absent in poly ethylene terephthalate

Poly ethylene terephthalate
In IR spectrum, it shows a band around 1735 cm^{-1} corresponds to ester group.

For example, Polyacrylonitrile and polyethylene terephthalate. Just visually you cannot distinguish it, but just looking at IR you can distinguish between these 2 polymers, because this 2 polymers and different functional group. In first one you can see in polyacrylonitrile there is nitrile group and nitrile group, absorbs at 2250 centimeter inverse and get a band around 2250 centimeter inverse in IR spectrum if you have polyacrylonitrile sample. This polystyrene you have Ester group.

So, just by looking at frequency absorption of Ester group, which is around 1735 centimeter inverse, you can know that, whether you have polyethylene terephthalate or polyacrylonitrile. So, 2 polymers can be distinguished using IR spectroscopy, I will give a few more examples.

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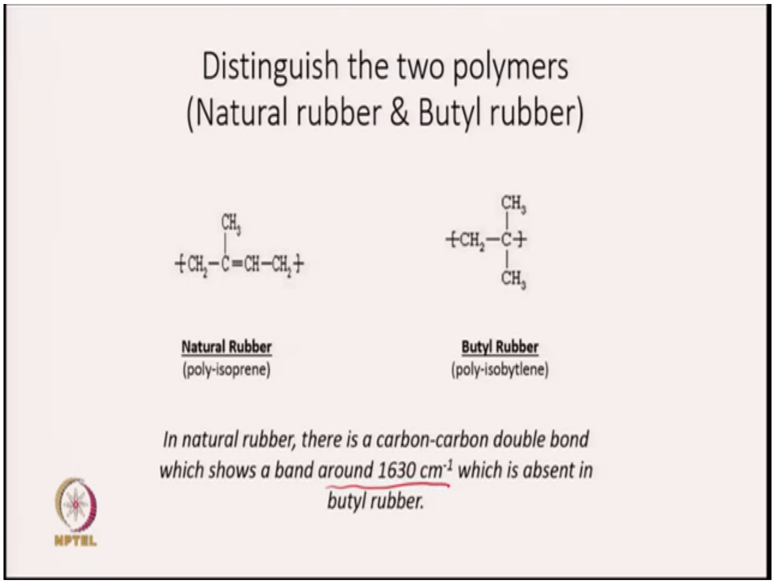

Distinguish the two polymers
(Natural rubber & Butyl rubber)

$$\left[CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right]$$

$$\left[CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\right]$$

Natural Rubber
(poly-isoprene)

Butyl Rubber
(poly-isobytlene)

In natural rubber, there is a carbon-carbon double bond which shows a band around 1630 cm^{-1} which is absent in butyl rubber.

For example, Natural rubber and Butyl rubber. We can differentiate between these 2 different kind of rubbers, because natural rubber is your polymer of isoprene, which has a double bond. Whereas, a butyl rubber is your polymer of isobutylene and you see here there is no double bond and your, in natural rubber you can see a band around 1630 centimeters inverse, which will not be present in butyl rubber.

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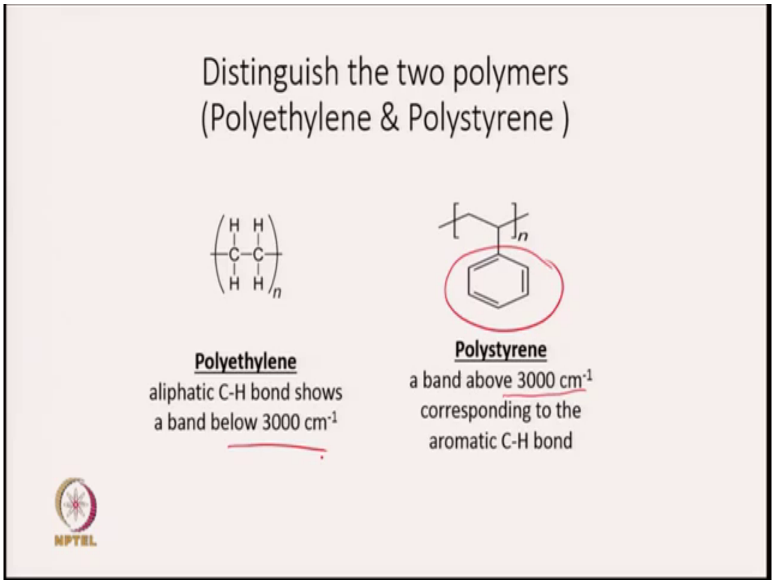

Distinguish the two polymers
(Polyethylene & Polystyrene)

Polyethylene
aliphatic C-H bond shows a band below 3000 cm^{-1}

Polystyrene
a band above 3000 cm^{-1} corresponding to the aromatic C-H bond

Similarly, we can distinguish between Polyethylene and Polystyrene as you can see that polyethylene is your polymer of ethylene molecule. Where is polystyrene polymer of styrene molecule and styrene has a aromatic benzene ring, aromatic benzene ring and for aromatic benzene ring CH comes above 3000 centimeter inverse, whereas, for aliphatic CH bond, your band comes below 3000 centimeter inverse. So, just by looking at simple IR spectrum of these 2 polymers, we can distinguish your 2 different, this 2 different polymers.

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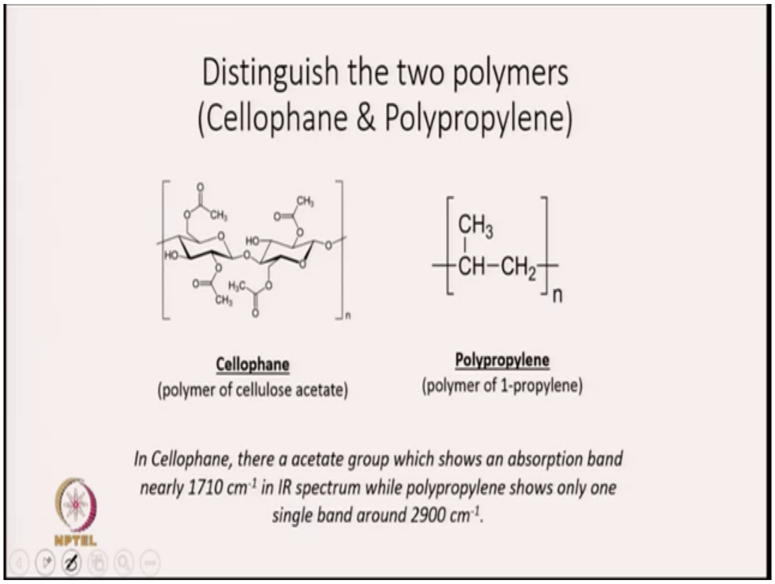

Distinguish the two polymers
(Cellophane & Polypropylene)

Cellophane
(polymer of cellulose acetate)

Polypropylene
(polymer of 1-propylene)

In Cellophane, there a acetate group which shows an absorption band nearly 1710 cm^{-1} in IR spectrum while polypropylene shows only one single band around 2900 cm^{-1}.

We can also distinguish between Cellophane and Polypropylene. Again Cellophane is a polymer of cellulose acetate, whereas, Polypropylene is polymer of 1 propylene, 1 propylene. So, now you can look at, in Cellophane, you have acetate group which shows an absorption band of around 1710 centimeter inverse. Whereas, for polyethylene this single band comes around 2900 centimeter inverse, just by looking at simple IR spectrum you can distinguish between these 2 polymers.

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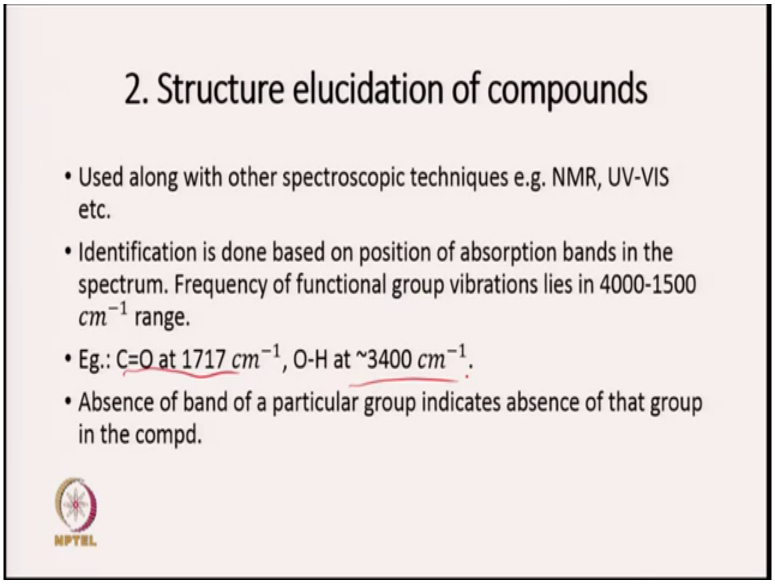

2. Structure elucidation of compounds

- Used along with other spectroscopic techniques e.g. NMR, UV-VIS etc.
- Identification is done based on position of absorption bands in the spectrum. Frequency of functional group vibrations lies in 4000-1500 cm^{-1} range.
- Eg.: C=O at 1717 cm^{-1}, O-H at ~3400 cm^{-1}.
- Absence of band of a particular group indicates absence of that group in the compd.

So, this is about finding out whether molecule or identify the molecule in the sample. The second thing is we can even get structure of the compound using IR and for that, we need to combine this with other spectroscopic technique like NMR, UV-visible. Particularly functional group can be very easily identified by use of IR spectroscopy.

For example, CO, Carbonyl band of absorbs around 1717, 1717 centimeter inverse, whereas you can find a bond around 3400 centimeter inverse if molecule has OH group. An absence of band of that particular group indicates absence of that functional group in the compound. So, for functional group prediction, IR is one of the most suitable and easiest method.

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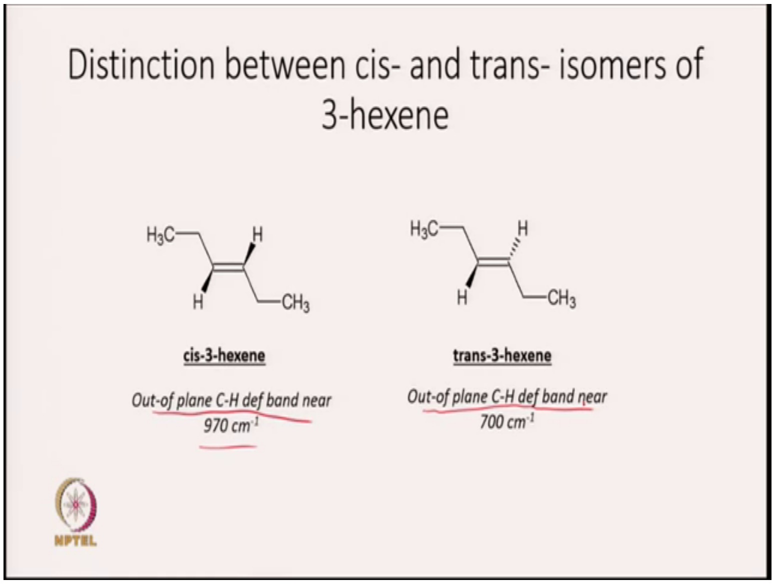

Distinction between cis- and trans- isomers of 3-hexene

cis-3-hexene

Out-of plane C-H def band near 970 cm^{-1}

trans-3-hexene

Out-of plane C-H def band near 700 cm^{-1}

One example I have already given that you know you can distinguish between 2 different isomers. Here again there is 1 case where you have since cis-trans isomer of 3 hexene and that can be distinguished by looking at the fingerprint region. In cis 3 hexene you will get out of plan CH deformation band near 970 centimeter inverse. Whereas, in trans 3 hexene in you will get CH deformation band near 700 centimeter inverse. So, cis and trans can be distinguished by use of IR spectroscopy.

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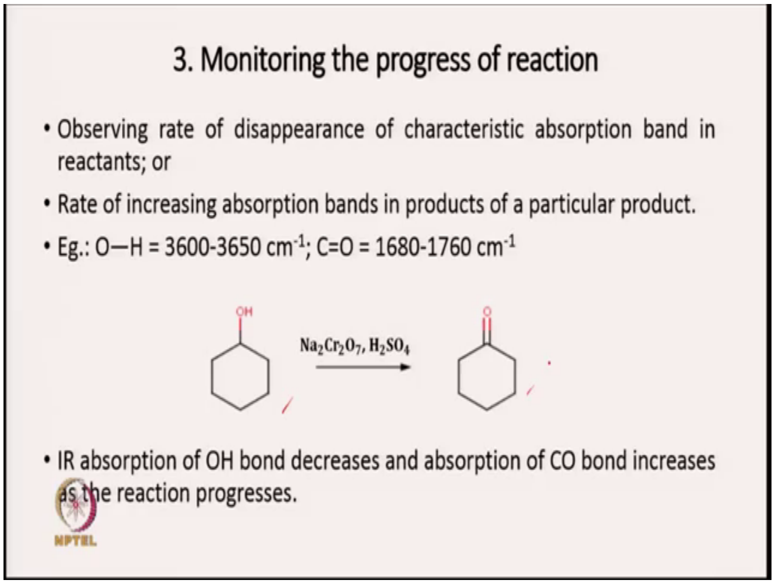

3. Monitoring the progress of reaction

- Observing rate of disappearance of characteristic absorption band in reactants; or
- Rate of increasing absorption bands in products of a particular product.
- Eg.: O—H = 3600-3650 cm^{-1}; C=O = 1680-1760 cm^{-1}

- IR absorption of OH bond decreases and absorption of CO bond increases as the reaction progresses.

The third application is Monitoring the Progress of Reaction, reaction progress can be simply monitored by using IR spectroscopy and it is quite simple, you can either look at disappearance of characteristic absorption band of reactants or you can look at increasing rate of increasing absorption band of a particular product. So, for example, if we are looking at this transformation, from alcohol to keto group, so, reactant has OH functional group.

So, you can look at rate of disappearance of alcohol and then you can study the kinetics. Whereas, you can also look at increase in absorption bond bond of CO to look at the monitoring of progress of reaction. So, suppose band around 3600 to 35 centimeter inverse disappears, then you know that your reaction is complete. Similarly, there is second example, where we can look at the progress of reaction.

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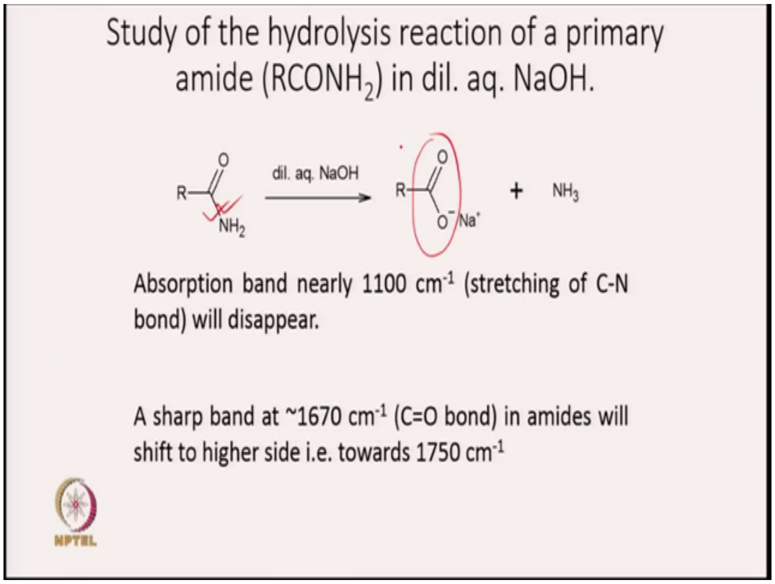

Study of the hydrolysis reaction of a primary amide ($RCONH_2$) in dil. aq. NaOH.

Absorption band nearly 1100 cm^{-1} (stretching of C-N bond) will disappear.

A sharp band at ~1670 cm^{-1} (C=O bond) in amides will shift to higher side i.e. towards 1750 cm^{-1}

So, this is simply hydrolysis in presence of aqueous NaOH. So, you can see that there is NH2 group and there is a CN bond. So, there is a CN bond. So, this CN bond absorbs around 1100 centimeter inverse and this is in the reactant and now, that is missing in your product, missing in your product. In product you have keto group converting to your the CO minus group.

So, what you will see with the progress of reaction that absorption band due to CN bond will disappear whereas your sharp band at 1670 centimeter inverse which is because of CO bond, CO bond in amide will shift to higher side because now you are going from CO bond in amide to CO bond in ester CO bond in ester and CO bond in ester basically absorbs at higher, higher wave numbers.

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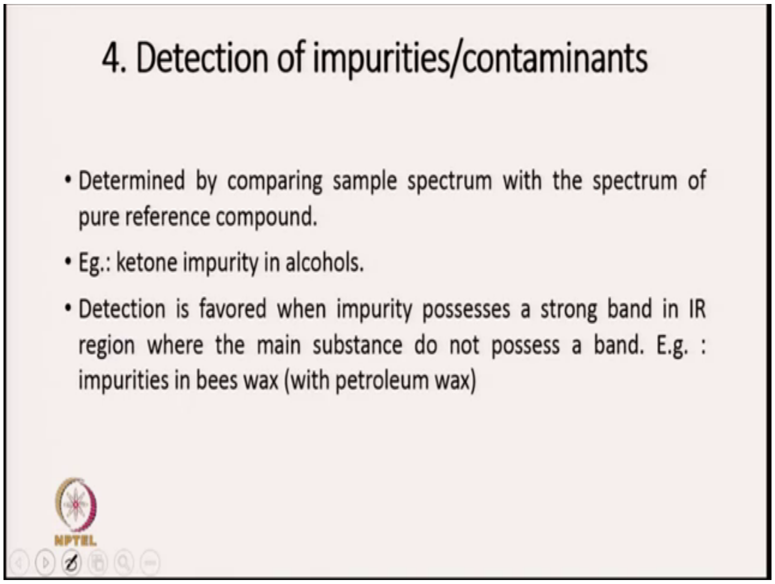

4. Detection of impurities/contaminants

- Determined by comparing sample spectrum with the spectrum of pure reference compound.
- Eg.: ketone impurity in alcohols.
- Detection is favored when impurity possesses a strong band in IR region where the main substance do not possess a band. E.g. : impurities in bees wax (with petroleum wax)

Apart from these 3 we can also detect the impurities contaminants and this is very important for particularly for quality of sample looking at quality of the sample. Generally, what we do is we compare sample spectrum with a spectrum of pure reference compound and by that we can know whether there is impurity or not. People try to look at ketone impurity in alcohol.

So, most of the alcohols has ketone impurity and just by looking at the absorption band of C double bond O, we can know whether that impurity exist or not and we can also do quantitative analysis. Generally, detection is favored when impurity possesses a strong band in IR region whereas, main substance do not possess band. Then only we can So, for example, when we are looking comparing between ketone and alcohol, ketone has a band due to CO, whereas alcohol has a brand due to OH which is absent in each other okay.

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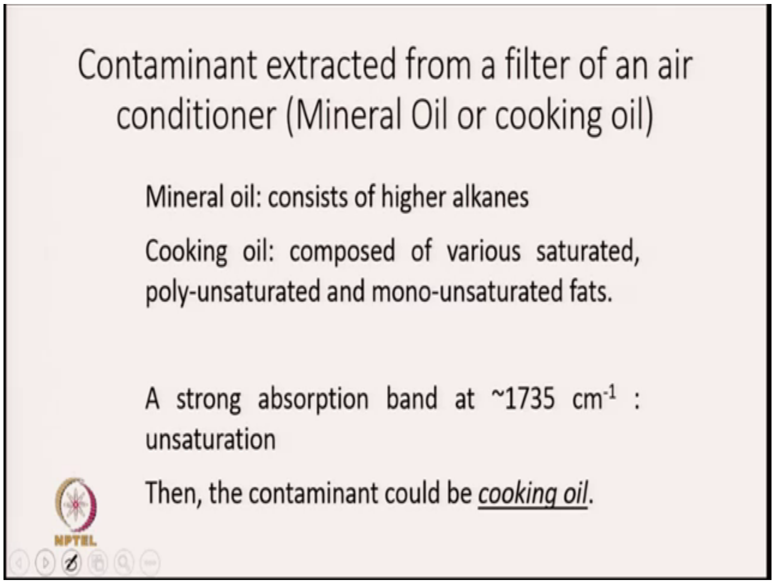

Contaminant extracted from a filter of an air conditioner (Mineral Oil or cooking oil)

Mineral oil: consists of higher alkanes

Cooking oil: composed of various saturated, poly-unsaturated and mono-unsaturated fats.

A strong absorption band at ~1735 cm^{-1} : unsaturation

Then, the contaminant could be ***cooking oil***.

So, there is 1 example where Contaminant extracted from a filter of air conditioner was looked at and it was tried to find out whether that contaminant is due to mineral oil are cooking oil. So, generally mineral oil consist of higher alkanes whereas, cooking oil has various saturated (un) unsaturated, polyunsaturated mono-unsaturated fats.

So, if you know this difference of a structure then you know that cooking oil must have your absorption band due to unsaturation and if your contaminant is from cooking oil, you will see a strong absorption band at 1735 centimeter inverse and that is because of unsaturation. Thus, contaminant, if we see that there is a band around 1735 centimeter inverse then contaminant must be contaminant could be cooking oil.

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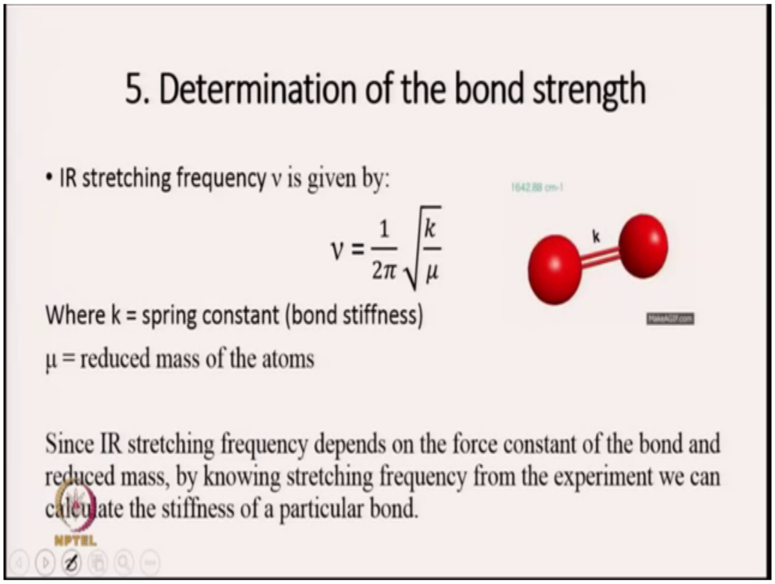

5. Determination of the bond strength

- IR stretching frequency ν is given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Where k = spring constant (bond stiffness)

μ = reduced mass of the atoms

Since IR stretching frequency depends on the force constant of the bond and reduced mass, by knowing stretching frequency from the experiment we can calculate the stiffness of a particular bond.

So, a next application of IR spectroscopy is Determination of the Bond Strength. So, IR stretching frequency, you know that it is given by 1 by 2 pi root k by mu. Where k is spring constant and mu is reduced mass of the atom. So, now again mu is related to R, your mu is related to R, whereas, K is related to bond strength.

So, just by looking at k, you can know that whether or by looking at k, you can determine the bond strength. So, if bond strength is high then k is going to be high. So, by knowing the stretching frequency from the experiment, we can calculate the stiffness of a particular band.

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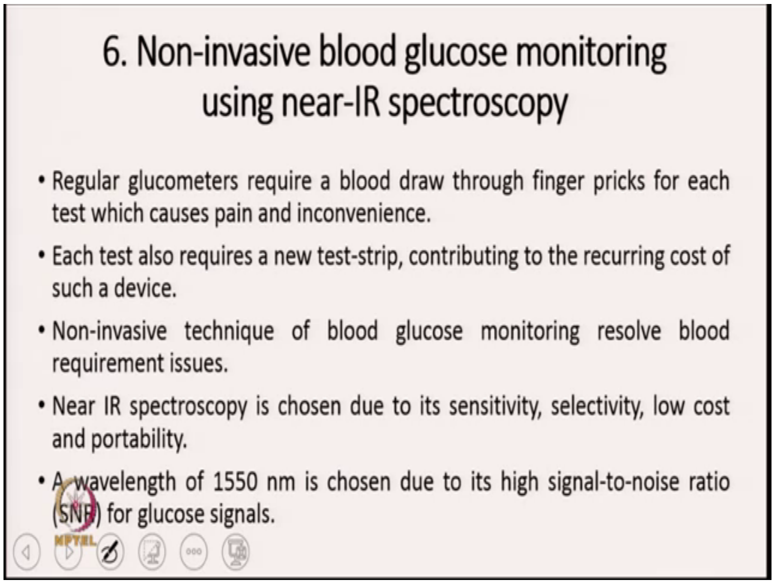

6. Non-invasive blood glucose monitoring using near-IR spectroscopy

- Regular glucometers require a blood draw through finger pricks for each test which causes pain and inconvenience.
- Each test also requires a new test-strip, contributing to the recurring cost of such a device.
- Non-invasive technique of blood glucose monitoring resolve blood requirement issues.
- Near IR spectroscopy is chosen due to its sensitivity, selectivity, low cost and portability.
- A wavelength of 1550 nm is chosen due to its high signal-to-noise ratio (SNR) for glucose signals.

There are other applications for example, if we are trying to look at blood glucose level and we generally know whenever we go to hospital, they take your blood and then look at your, then do some testing to know the blood glucose level, ok. So, for that you require a new test strip and that increases the cost of such a device.

This is a Non-invasive Technique and here your wavelength of 1550 nanometer is chosen due to high signal to noise ratio for glucose signal.

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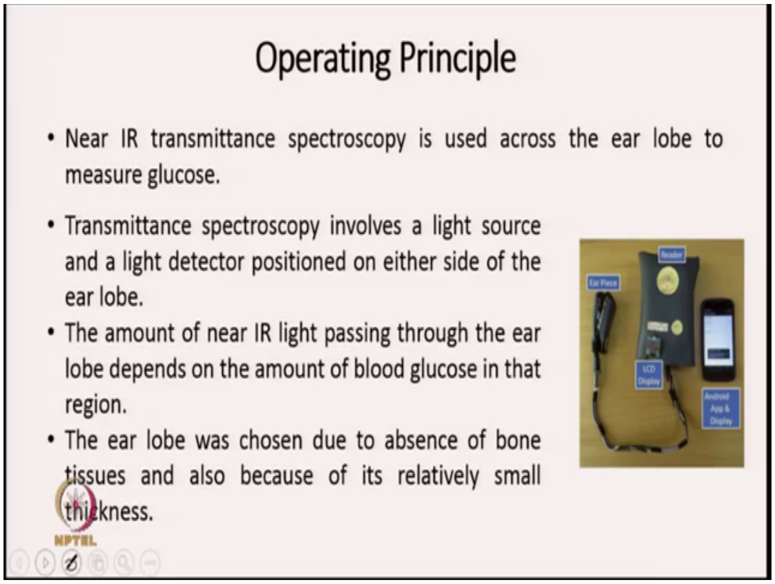

Operating Principle

- Near IR transmittance spectroscopy is used across the ear lobe to measure glucose.
- Transmittance spectroscopy involves a light source and a light detector positioned on either side of the ear lobe.
- The amount of near IR light passing through the ear lobe depends on the amount of blood glucose in that region.
- The ear lobe was chosen due to absence of bone tissues and also because of its relatively small thickness.

So, in this IR transmission your instrument is basically used across the ear lobe to measure glucose. So, you do not need a blood sample. And basically what is done is that a light source and a light detector is placed on either side of your lobe and then amount near IR light passing through the ear lobe depend on the amount of blood glucose in that region.

So, ear lobe was chosen due to absence of bone tissue and also because of its relatively small thickness. So, in this case, you can see that you know without taking the blood sample, we can know what is the glucose level in the blood. So, there are a lot of other applications of IR spectroscopy and in the next lecture will discuss some of them and but one thing is clear that you know for a chemical molecule IR spectroscopy, for analysis of chemical molecule IR spectroscopy is must and it is a your non-invasive technique.

And then, you know, it can (visily) very easily tell you about the functional group of the molecule. Thank you.