Chemistry II: Introduction to Molecular Spectroscopy

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Lecture - 27
Review of Elementary Vibrational Spectroscopy

Welcome back to the lectures we move on to the last section of this namely the review of elementary vibrational spectroscopy carried out over several lecture modules in this course.

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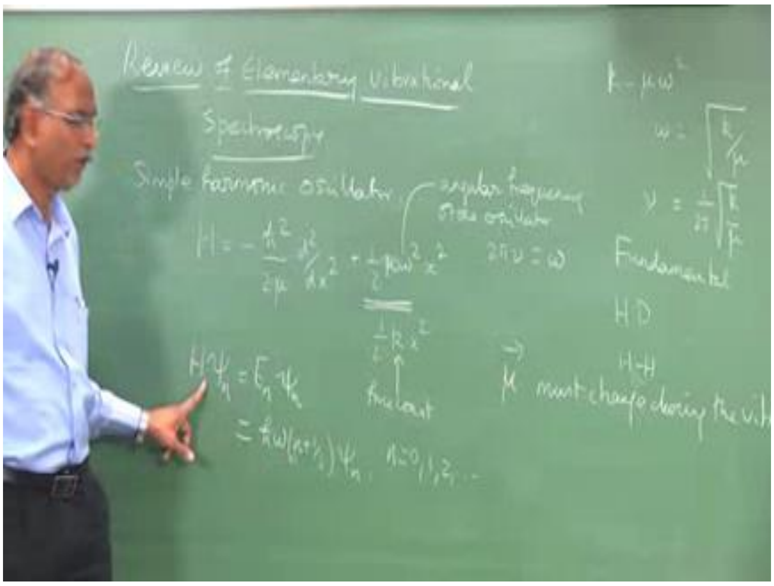

The important starting point for us was the simple harmonic oscillator model. And I recall that I had a fairly elaborate session on the quantum mechanics of the harmonic oscillator model, I gave you the energy level expressions as well as the wave functions for the harmonic oscillator. Now recall the harmonic oscillator Hamiltonian is the kinetic energy 2 mu d square by dx square and this being p square operator by 2 mu plus half m omega square x square and this is nothing, but half k x square, where k is the force constant, and omega is the I am using mu. So, let us use mu here and omega is the angular frequency of the harmonic oscillator of the oscillator therefore, and it is given by 2 pi mu that is equal to omega he relation between k and angular frequency obvious from here.

Namely k is equal to mu omega square therefore, omega is k by mu and the frequency nu is 1 by that is a square root here 1 by 2 pi square root of k by mu.

So, given the harmonic oscillator frequency from the experiment and knowing what the molecule is therefore, calculate we are able to calculate the mu it is possible for us to calculate the force constant. Such exercises were given to you for different molecules simple diatomic molecules, they gave you the, what is call the fundamental frequency this is call the fundamental harmonic oscillator frequency. And the fundamental frequency is related to the force constant that it is this proportional to the square root of the force constant, it is proportional to the inverse of the reduced mass therefore, if we have molecules such as HD and H 2 and we know that the force constant between the two hydrogens and the hydrogen and deuterium are approximately the same, then the reduced mass for this two species are different produced masses are different and therefore, the harmonic oscillator frequencies will also be different.

In fact, nu of isotope 1 divided by nu of isotope 2 is in very straight forward to show that it is a reduced mass of the isotope 2 divided by the reduced mass of isotope 1. Such exercises were also given to you to give an idea that how by a very simple mass shift, it is possible for the harmonic oscillator to have the slightly different frequency and that is particularly important for isotopic species where the chemical nature the force constant which determines the chemical association between the two atoms does not change by much therefore, keeping the force constant it is possible for us to calculate the shift in the harmonic oscillator frequencies and vice-versa I think such calculations were given.

Now, the one important difference for harmonic oscillator from the microwave spectroscopy in terms of the absorption of radiation infrared radiation in this case is the fact that the dipole movement mu must change during the vibration.

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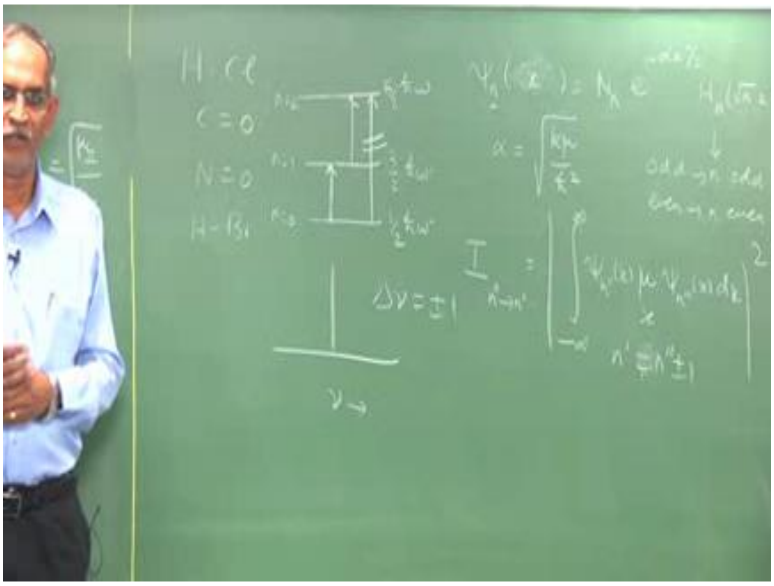

Therefore, molecules which have permanent dipole movements such as HCL CO then NO H Br I mean all those molecules? During vibration they already have a non 0 dipole movement and during vibration the dipole movements also change, it is the change in dipole movement during vibration which leads to vibrational energy absorption and the vibrational states are all given by the expression as the eigenvalue for this Hamiltonian H psi n is equal to En psi n and En is h bar omega n plus half psi n. This omega is the same as the angular frequency therefore, you see that the harmonic oscillator has introduced a new quantum number n whose values starts from 0 1 2 etcetera.

And even when n is 0 the harmonic oscillator still has what is call the 0 point energy namely half h bar omega and that is important that is a quantum mechanical outcome the application of quantum mechanics leads to this kind of prediction that there is a 0 point energy for the molecule even at 0 Kelvin. T he harmonic oscillator energy levels are all equidistant because the lowest energy level when n equal to 0 is half h bar omega n equal to 1 is 3 half h bar omega and n equal to 2 is 5 half h bar omega and so on.

Therefore, n the harmonic oscillator approximation there is no vibrational spectrum for diatomic molecules there is a single line because the transitions between n and n plus 1 are the only allowed positions leading to one line in the frequency this to this or this to this or this to that and so on. The transition between vibrational levels which differ by more than one is not possible within the harmonic oscillator frame work and one has to introduce what is known as the molecular anharmonicity the vibrational motion is no longer harmonic, that is the vibrational motion is no longer half k x square, but there will be other terms like x cube and x to the power four and other types of terms and these basically distort the vibrational motion from harmonic motion to un harmonic motion. We looked at the vibrational wave functions also we wrote them as psi n a constant root alpha x as a normalization constant which depends on the quantum number n and exponential minus alpha x square by 2 and the hermite polynomial with the argument root alpha x where alpha is square root of k mu by h bar square.

So, k and mu are the parameters of the harmonic oscillator therefore, alpha is determined by the nature of the oscillator this is the planks constant and it is the same alpha that goes here and alpha has the dimensions of one by length square x is the displacement from equilibrium therefore, this is length square alpha has one by L square has a dimension. So, root alpha x is dimensionless and this hermite polynomials where given to you as odd and even depending on whether n is odd or n is even. This formulas are given to you in the lecture notes and therefore, you might look at the wave functions because the transition movement I between transition n and n prime, the initial state lets write it as n double prime to the n prime is given by the absolute square of the transition movement integral namely psi n prime of x let us see psi n prime of x here psi n prime of x mu psi n double prime of x dx between minus infinity to plus infinity d absolute square.

And mu being proportional as a displacement the rate of change of mu has to change during the vibration and that extent is given by the displacement itself, the displacement connects a wave function n prime and n double prime to give you non 0 values for this integral only if n prime is equal to n double prime plus or minus 1, for all the other values the dipole movement does not lead to connecting a y wave function n to a wave function n double prime which is far away it is required the gap that is required to be just one. Because of the fact that the dipole movement that we have is proportional to the displacement and this is within the harmonic model therefore, the selection rule for harmonic oscillator is delta v is equal to plus or minus 1 this is not to be forgotten.

So, this is the harmonic model that we have and then there was the slight improvement from the harmonic model by considering anharmonicity in the form of a Morse oscillator.

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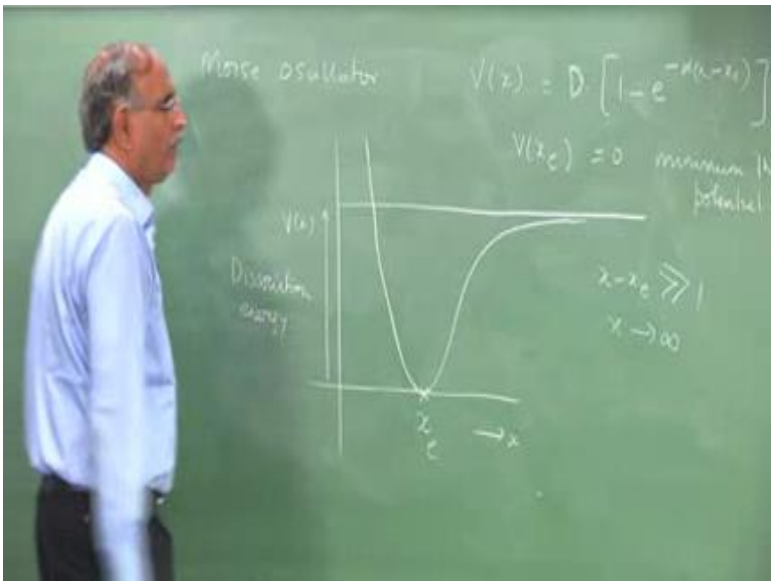

For the Morse oscillator we wrote down, the Morse potential proposed by Philip Morse first, namely the displacement the potential has the function of the displacement is a constant times his functional form 1 minus e to the minus alpha x whole square I would write this as x minus x e whole square, where V at to the equilibrium distance xe is 0. You can see that right away when x is equal to xe this term is the exponent is 0 therefore, the exponential of 0 is 1, 1 minus 1 0 therefore, the vf so, this is called the minimum in the potential.

The Morse oscillator model allows us to consider molecular dissociation as a result of vibration, because if you plot the Morse oscillator potential as a function of the potential energy as a function of the displacement coordinate this is xe and this is x you would see that the potential is minimum and then it raises until it reaches a (Refer Time: 12:13) and also it raises to a very steep value for x less than xe, because when x is less than xe this is negative and there is no minus sign therefore, the exponential alpha becomes positive keeps increasing as this becomes more negative therefore, you see that as x becomes more and more I mean less and less than the equilibrium distance when the atoms compressed together very closely. You see that the potential raises very steeply that is given and you can also see the value of d as nothing but, when x minus xe is very, very large or x goes to infinity, ideally as a mathematical formula when x goes to infinity this whole exponential goes to 0 therefore, what you have is 1 whole square and so, you have d and d is essentially the asymptotic value and this d with respect to this value is called the dissociation energy. Because at that extension of x the molecule the atoms do not come back therefore, they permanently separated from each other and this is called the dissociation energy.

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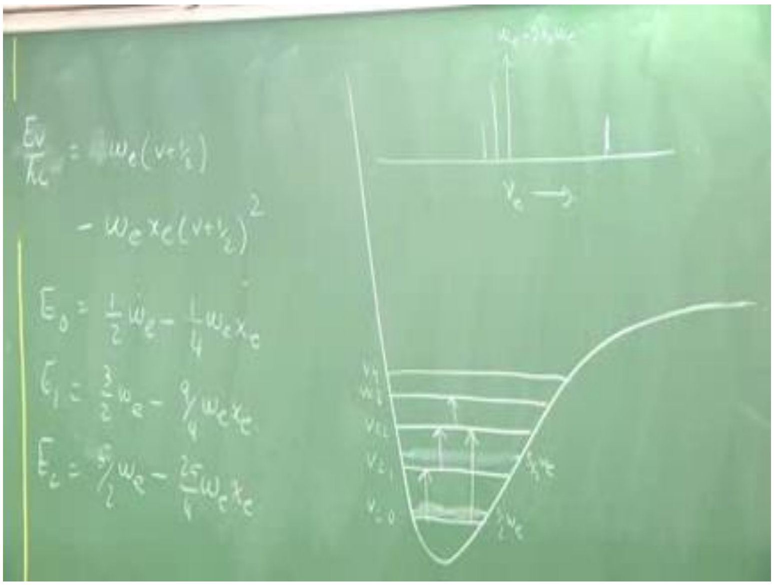

The Morse oscillator also led to a very unique form of the energy expressions, you might recall the energy level associated with the Morse oscillator were given by h bar omega e times v plus half minus let be, I think I used only EV by HC to keep in mind that this is only a frequency factor the centimeter inverse or a wave number and then we have minus omega exe v plus half square. I think this is the expression I probably use in the lecture notes and you can see that the vibrational quantum number v is 0 1 2 etcetera.

Immediately what you see is that E naught is no longer half omega e, but it is half omega e minus 1 by 4 omega e, x e because of this term and E 1 is 3 halves omega e minus 9 by

4 omega e XE because this is 3 by 2 whole square. And likewise if I write e 2 it is 5 by 2 omega e minus 25 by 4 omega e x e. The picture that the Morse oscillator immediately gives raise to from this kind of energy level expressions is the following, you by remember that he energy levels become closure to each other.

So, if I have to plot the lowest energy as the half omega e minus 1 by 4 omega e x e the next energy level is not omega e, but there is also the difference between the 2 which is 2, 9 by 4 minus 1 by 4 is 8 by 4 there is a minus 2 omega e x e. So, ideally if you have to write this as half omega e this as 3 by 2 omega e is no longer that this is slightly lower than that half omega e by this factor 1 by 4 and this is even lower. Therefore, you see that the Morse oscillator energy levels close in. The next energy level, if you look at e 2 is closer to e 1 then e 1 is closer to e naught and like wise you can see that. So, this is v equal to 0 v equal to 1 v equal to 2 3 and 4. So, what it means is that the gap between successive energy levels is no longer the same between any given pair.

So, you can see that this is not equal to that Morse oscillator also allows in principally jump from 0 to 2 and therefore, what you see in vibrational spectra is that a center line corresponding to this which is of a very large intensity, and then smaller lines which correspond to a slightly lower intensity, and every weak line which is approximately at the twice. So, if you write this as the new VE. So, this is the first line corresponding to the difference between e naught and e 1 which is omega e minus 2 x e omega e. And therefore, if we note two of these differences we have two unknowns mainly omega e and XE. So, the differences we can calculate these unknowns therefore, we can attain the anharmonicity parameter for the Morse oscillator using the Morse model, and the nice thing about the Morse model is that, the molecule for very large values in principle can be associate.

The harmonic model does not allow that please remember the harmonic model is essentially that, no matter how far away the atom is how high in the potential energy is the atom will always come back to its equilibrium and move around the equilibrium this thus the prediction of the harmonic model, which does not work in reality of course, and therefore, what you see as the Morse model as a very nice way of accommodating the actual molecular behavior. There are other models there are other anharmonic models due to cubic and harmonicities quartic anharmonicities etcetera and we will not in this particular course worry about those things and I did not even introduce them. Those are important when you want to study the high resolution infrared spectroscopy of gas waves molecules of very highly resolved spectra then you need to worry about all those terms therefore, this is a precursor to understanding some of those things later.

Now, we will just very quickly move on to the polyatomic vibrational motion and review what we have done, but before we do that again please remember that for vibrational spectroscopy of the harmonic oscillator level the selection role is delta d is equal to plus minus 1 and it requires the dipole movement you change during the vibration for the more oscillator, there is no dipole movement selection rule all energy levels can be connected by the dipole movement operator, but the intensities of vibrational levels decreases very sharply, as you go from v is equal to 0 to v is equal to 1 to v is equal to 2 and so on therefore, the lines becomes less intense as you go further away, but there are lines unlike that of a harmonic oscillator.

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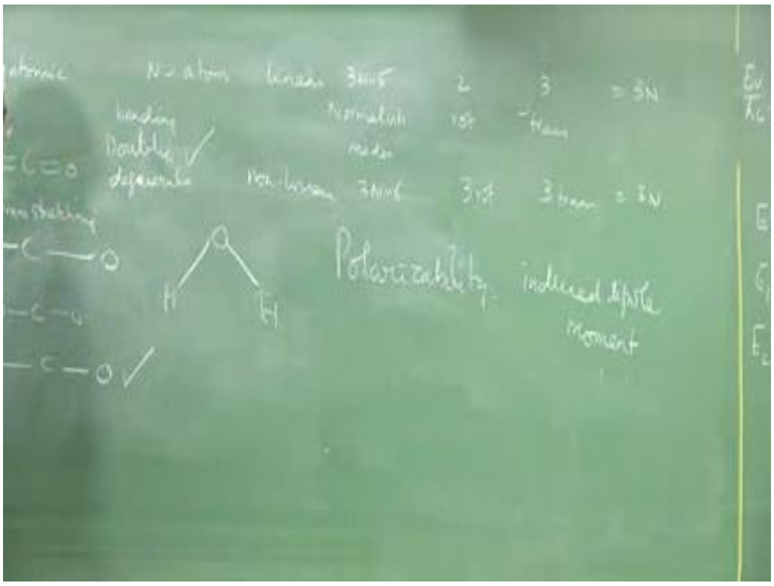

Now, if you look at the poly atomic molecular systems for vibrational degrees of freedom. I told you immediately that and N atom molecule linear there are 3 n minus 5 normal vibrational modes and you recall for linear molecule there are 2 rotational modes and there are 3 translational modes leading to a total of 3 n for non-linear molecules. There are 3 n minus 6 normalized normal vibrational modes 3 rotational degrees of freedom and 3 translational degrees of freedom giving the estimate total of 3 n degrees of freedom. And we were only looking at harmonic oscillator model for all the 3 n minus 4 or 3 n minus 4 6 degrees of freedom and the harmonic oscillator model is; obviously, called the normal mode model in this particular case.

And the if I recall I gave you a large number of animations and the simple example of a carbon dioxide, or ozone or water. These examples are given for specific reasons namely, in the case of ozone all the three atoms which are vibrating about their equilibrium positions of the same mass therefore, the vibrational displacements of each one of the atom about its equilibrium is the same as the other in the case of water molecule these are lighter atoms and this is oxygen is heavier atom.

Therefore, the vibrational amplitudes of the lighter atoms are slightly more in the vibrational period, that of the heavier atom is much less and in the case of a linear molecule you realize that there are one there is one additional vibrational degree of freedom and that led to what is called the double degenerate bending mode. For all linear molecules one bending mode is o c o bending in this plane and the other bending mode is the carbon going behind the board and the oxygen coming in front that is also a bending mode and both of them have the same energy and the bending mode frequencies are lower than the stretching mode frequencies.

The stretching mode for carbon dioxide where two of them is symmetric stretching and this is called the symmetric stretching. Then there is this unsymmetric stretching or asymmetric stretching in which one of the bonds is lengthened and the other is shorten this was very special as well as the bending mode, because both of these induce a dipole movement in the molecule during the vibration therefore, the dipole movement changes from 0 to here 0 here to a finite value and then goes back to 0 as the molecule completes one vibrational motion. This change in the dipole movement means that this degree of freedom and the bending degree of freedom or both infrared active, the symmetric switching move for carbon dioxide does not involve any change in the dipole movement from its original value of 0, because carbon is in the middle of both these oxygens thus center of mass charge center as well as the mass center therefore, there is no dipole movement. So, when the molecule undergo symmetric stretch both the oxygens go away from the carbon and the same extend and then come back to the a equilibrium position on the same time therefore, for symmetric stretch does not involve any change in dipole movement it is not high or active.

And this is true for a large number of linear molecules and molecules which have no dipole movements, such as tetrahedral molecules c h 4 or the planar triangular I mean with an atom in the middle of triangle center b h 3 kind of molecule. Those are molecules which do not have any dipole movement for certain type of vibrational motions, but the fact that there are dipole movements introduced during other is symmetric stretches means that those modes or infrared detectable, and we see down in the introduction spectroscopy quite a number of such examples were given to you, and with this I think we sort of came to an end in telling you that vibrational spectroscopy are the level of which we are we have introduced to a sufficient to understand most importantly the relation between the force constants the reduced mass and the vibrational frequencies.

The last lecture involved roman spectroscopy which was slightly different from all the other things are been did roman spectroscopy is the spectroscopy due to scattering of light not due to absorption of light. So, when light falls on a sample which is something likes this and if you measure the light that is scattered in a perpendicular direction, the light that is scattered has frequencies which are modulated which are changed from the original frequency of the light that excited irradiated the sample.

And these changes are on either side of the frequency they can be a radiation with an increased frequency than the original one and those are called the anti stoke lines, and the radiation which has a frequency which is lower than the frequency of the original one which is called the stokes radiation. And the radiation of exactly the same frequency as the incident radiation was called Rayleigh frequency. And roman spectroscopy introduce the concept of polarizability, as and the induced dipole movement as the reason for the observation of roman spectrum.

The induced dipole movement is proportional to the externally applied field or the electromagnetic field that falls on the radiation that falls on the substance and therefore, this is directly proportional to the magnitude and the proportionality constant polarizability was introduced to you as a tenser of rank two of course, we did not make use of that property in the lecture, the brief lecture that we had we use the scalar property and for roman spectroscopy to be observed it is important that molecules have one polarizability for microwave region for rotational lines of roman spectrum to be observed static polarizability is required.

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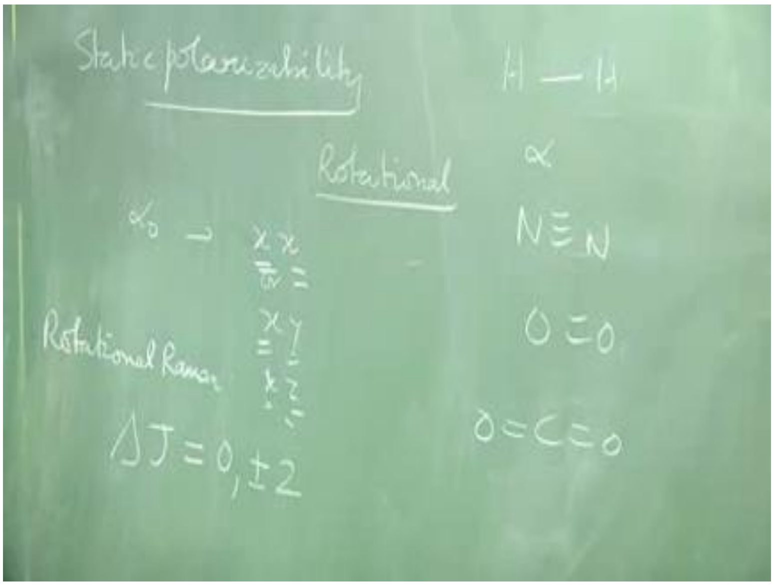

Therefore, when hydrogen for example, undergoes rotation in the presence of an electro external electric field the stretching the separation of the hydrogen atom leads to what is called the polarization of the two hydrogen atom about the electric field. It introduces an alpha this alpha is static and this static polarizability is responsible for the rotational roman lines. Therefore, the presence of non 0 alpha means that even homo nuclear diatomic molecules N triple bond N oxygen all homo nuclear diatomic molecules and even molecules, which do not otherwise have a dipole movement and cannot be detected using microwave spectroscopy can be actually detected using roman spectroscopy and the relation then the reason for that is the presence of polarizability, that is the extend that the molecule can be polarized in the presence of the external field.

I also reminded you that the polarizability leads to a selection rule being a second rank tenser even the static polarizability is like XX or XY or XZ two quantities two directional displacement and therefore, the selection rule for roman spectroscopy is either 0 or plus minus 2 or micro wave rotational roman lines. In the case of microwave spectroscopy we were only looking at the dipole movement of the molecule, here the induced dipole movement being proportional to the polarizability, it is the polarizability which is responsible for the rotational lines and that being a second rank tenser leads to a selection rule of plus minus 2 and therefore, rotational roman lines are always seen between J and

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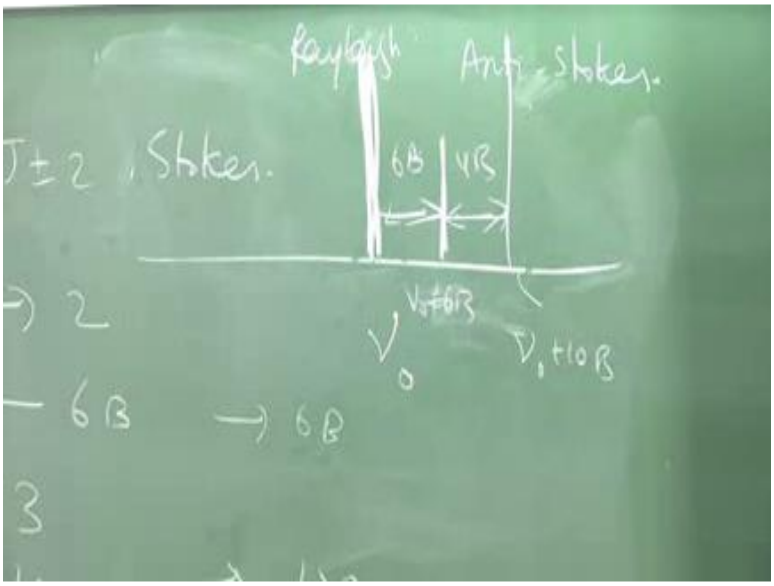

J plus or minus 2, if you start from 0 the first line is 2 and you remember this is energy is 0 this is 6 b and therefore, the first line has an energy of radiation. The radiation that is seen in the roman spectrum has the characteristic frequency of 6 b. The next one if you look at, say 1 to 3 this is 2 B and 3 is of course, 12 B the difference between the 2 ways and B then you have 2 to 4 which is this is J these are all J and 2 to 4 is 6 B to 20 B and therefore, you have the next line 14 B.

Therefore, you see successive roman lines come from the 6 B they are of by 4 B to the next line 10 B and from 10 B the next line is at 14 B therefore, the roman spectrum if you look at it the Rayleigh line which does not have any frequency shift new 0, is now shifted by the anti stocks lines namely, new naught plus 6 B as the first gap and then it is new naught plus 4 B. This is 10 B this is new naught plus 6 B and this is new naught plus 10 B and the gap between the 2 is 4 Bb this is 6 B. And the same thing happens in the anti stokes region, when this is sorry this is the anti stoke region same thing happens in stokes region when essentially the energy is absorbed by the molecules, then that frequency is missing in the radiation and you can see that happens here, when energy is dumped by the molecules in to the radiation from coming down in the energy that increases the radiation frequency on the side.

So, this is stokes and this is anti stokes, this is Rayleigh line. Most important thing for roman spectroscopy for us to remember was the fact that the polarizability is important and in the case of rotational roman lines, the static polarizability results in this kind of selection rule. For vibrational spectroscopy it is again the change in the induced dipole movement and correspondingly it is the change in polarizability, from the static polarizability during the vibration that was required and therefore, that need not change the selection rule for infrared roman active lines. Roman active vibrational modes the selection rules or the same as the infrared active selection rules namely, delta b is equal to plus minus 1 therefore, vibrationally the only difference between the roman spectroscopic lines and that of the infrared lines is that, molecules which have a center of symmetry seem to choose mutually exclusive spectroscopies either this or that.

So, molecules which have a center of symmetry have vibrational modes which are either roman active or infrared active, but not both, but molecules which do not have a center of symmetry and which do have a permanent dipole movement or both roman active and also IR active. Thus for example, for water molecules we have roman lines as well as infrared lines for carbon dioxide we do not have the roman line for the symmetric stretch and the infrared line is for the anti symmetric or the asymmetric stretch and the bending mode. So, these are some of the elementary properties that come from the polarizability. The nature of polarizability and its change with respect to the vibrational mode from that happens in a molecule. So, with all of these elementary ideas now been told to you and hoping that you have followed some of these lectures. I wish you all the best and I hope that you will continue this study of spectroscopy in a more profitable way in the future in to other areas as well as in to more advanced areas I wish you all the best.

Thank You.