Chemistry II: Introduction to Molecular Spectroscopy

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Module – 07
Lecture – 24
Introduction to Rotational Raman Spectra

Welcome back, to the lectures in Chemistry and the Introduction to Molecular Spectroscopy series that I been giving. So, in this lecture we will get to the practical aspects of the elementary aspects of Rotational Raman Spectra, and in the last 2 lectures. I talked about polarizability and the fact that it is a tenser, and it is connected to the, or it is measured. By which the induced dipole moment depends on the external electric field. So, now we will get to the actual spectroscopic details.

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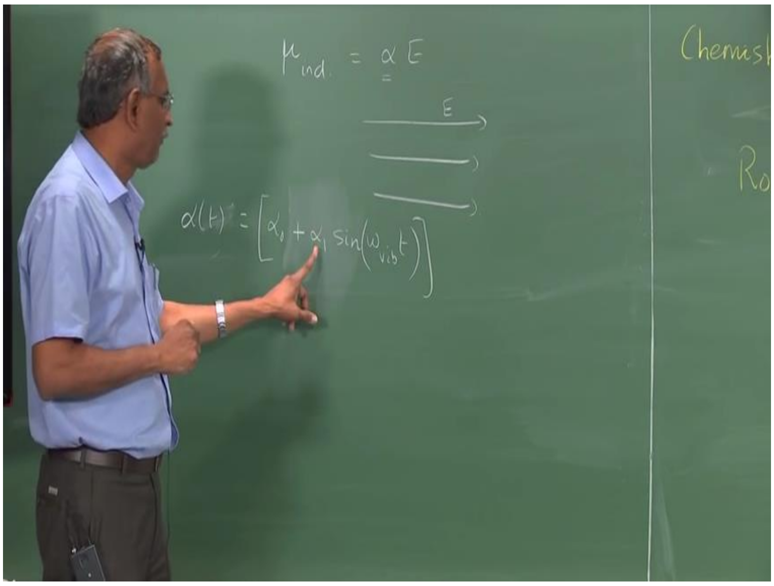

So, we will start from, the fact that mu induced is alpha times e. We will write it this way for the time being that is as a scalar and then we do the actual spectral intensity computation, we will use the factor alpha e is a tenser mu is proportional to alpha E. Now please, remember for a an external static electric field alpha is a constant, because the induced dipole moment depends on the electric field E, but alpha is not a static quantity. Because the molecule is not stationary the molecule is actually vibrating it is vibrating say with the frequency angular frequency omega. Let us call it as a vibration frequency. So, if the molecule is vibrating then alpha is actually also vibrating, is also changing in time by the simple relation alpha naught plus alpha 1 sin omega vibration times t. This is the polarizability as a function of time; this is due to the vibrations in the molecule.

In the case, of rotation of course, in a rigid rotation we do not worry about it we only worry about alpha 0. We do not need to know what alpha 1 is, but in general molecule undergoes both rotation vibration and. So, far we have been I mean our considerations have been simple enough to treat this has to different phenomena, 2 independent phenomena. So, if you do that then for the vibrational sake you will have both alpha naught and alpha 1 sin omega vibrational times t, but alpha naught will not be relevant for the vibrational spectroscopy for vibrational spectroscopy alpha one will be relevant, because that is a changing polarizability. Exactly, the same way the mu has to change during the vibration the nu induced also has to change during the vibration.

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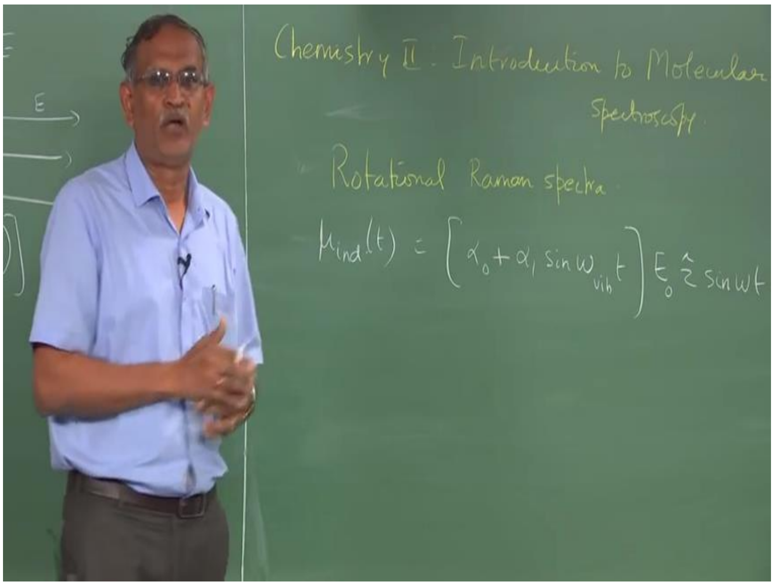

Therefore, the mu induced now will become as a function of molecular vibration it will become alpha naught plus alpha 1 sin omega vibration times t.

But, please remember in the case of the electromagnetic radiation, the electric field of the electromagnetic radiation is not a constant, is not a constant time. It is actually itself a sinusoidal function therefore, the electric field itself will be e naught in some direction say let us call it as a z direction if you wish. And it will be sin omega t. plus 5 if you want to put in as a phase factor, but we will consider very simple thing namely that the induced dipole moment changes during the vibration as a function of time due to two things. There are 2 oscillating components an oscillating component due to the vibration, and an oscillating component due to rotation. Now this is the physical picture now, what is the Raman Effect? We will start with this Raman Effect.

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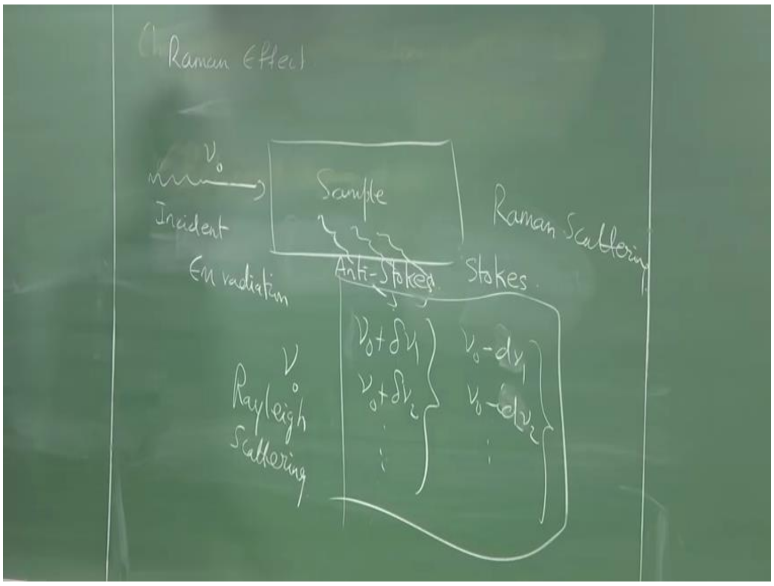

So, let us keep this in the background, when we need it we will come back to this. What is a Raman Effect?

Light of some frequency mu naught, radiates a sample. And this is some sample, the scattered light which comes out this a transparent sample therefore, what happens is a small portion of the light gets scattered bulk of the light is transparent and it goes straight through. And the very small portion of the light that is scattered seem to have not only the nu 0, which is the frequency of the incident light, incident electromagnetic radiation, but the scattered lights seems to have nu naught plus delta nu 1 nu naught plus delta nu 2.

That is all series of frequencies of radiation, which are emitted as well as nu naught minus delta nu 1 nu naught minus delta nu 2, I mean it is not the same delta some value now. So, if you want to write it as d nu 1, if you want to make it different it is d nu 2 so, on. So, that is also another group of frequencies, which are seen in the light that gets scattered, that is the scattered light has been modulated over the incident light frequencies, by these additional frequencies or this depleted frequencies. It is somewhat easy to understand this from the quantum mechanical stand point why light that falls on the system comes back with the a different frequency you have already seen that, because if you think about this as a photon and the photon frequency matches with some transition between rotational energy levels or transition between vibrational energy levels. It is possible that the photon gets absorbed and the scattered light may have some amount of energy reduced from it, to give radiation of this kind or an excited molecule which actually comes down to a lower energy level introduces an additional, a different photon with the frequency which is different from nu naught buy slightly more than that ok.

Now, there is also of course, nu naught a fairly large amount of light that is scattered does not have any intensity, does not have any change in the frequency. This nu naught to nu naught this is called Rayleigh scattering. These two together is called Raman scattering. This is the Raman scattering effect of course, the lines have very specific names light which has a frequency less than that of the incident frequency, this is this phenomenon of reduced frequency is called stokes phenomena or stokes radiation. And radiation which has a frequency, which is higher than the incident frequency due to the interaction of the radiation the sample whose energy levels are quantized and therefore, there is a lot of energy exchange in them leading to changes in the frequency this is called anti stokes phenomena. So, we will write that here anti stokes radiation. So, you get both you get the Rayleigh scattering you get stokes scattering, and you get the anti stoke scattering. Now, how do we understand this we understand this from the last line that we wrote before?

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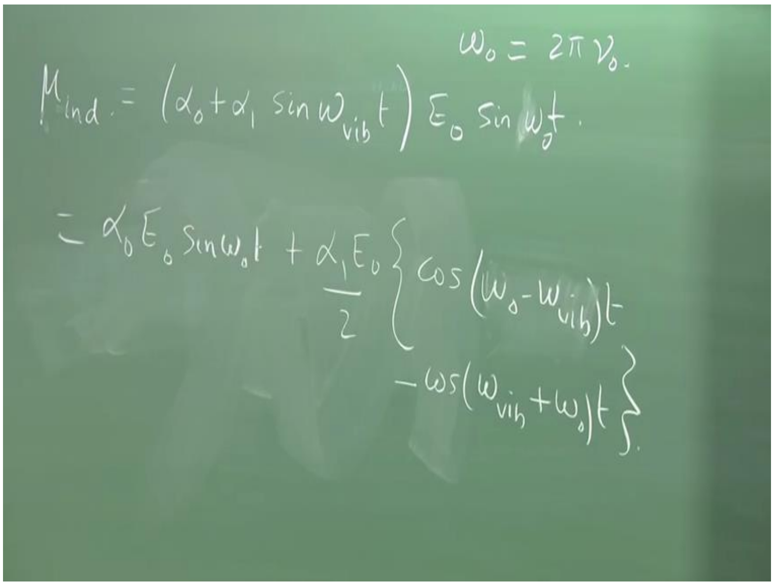

$$\omega_0 = 2\pi\nu_0.$$

$$\mu_{ind.} = (\alpha_0 + \alpha_1 \sin\omega_{vib} t)\, E_0 \sin\omega_0 t.$$

$$= \alpha_0 E_0 \sin\omega_0 t + \frac{\alpha_1 E_0}{2}\left\{\cos(\omega_0 - \omega_{vib})t - \cos(\omega_{vib} + \omega_0)t\right\}.$$

We introduced to the Raman effect, namely the induced dipole moment we wrote down is alpha naught plus alpha 1 sin omega vibrational t times e naught sin omega t. This is the radiation frequency this omega is what we call. Let us call this as omega naught, because we are using the symbol nu naught and the relation between omega naught and nu naught is, it is 2 pi nu naught this is angular frequency and this is the regular frequency in the form of hertz this is in terms of the angle ok.

Now, please remember sin a sin b is 1 half cos a minus b plus cos a plus b therefore, if you remember this relation. What you see here, from this one is alpha naught e naught sin omega naught t, that is the first term and then you have alpha 1 E naught by 2 times cos omega vibration minus omega naught t minus cos omega vibration plus omega naught t. Therefore, you see that the induced dipole moment now has components that correspond to dipole oscillating with the same frequency as the incident radiation. The dipole moment oscillating as the omega vibration minus omega naught meaning that omega naught is no longer omega naught, but it is changed by it is after all cosine. So, if you want to write this you can say omega naught minus omega vibration and this is also omega naught plus omega vibration therefore, the dipole moment thus has it is own oscillation and this results in the energy exchange and therefore, the radiation that comes out also has frequencies corresponding to the original the radiation of the original frequency nu naught and radiation with frequency differences corresponding to some vibrational motion internal vibration of the molecule internal vibrational motion of the molecule this is very elementary simplified picture to tell you why there is a modulation of the radiation that comes out see that frequencies are different and there can be many because we consider only one vibrational motion.

But molecules have more than 1 degree of freedom and also the molecules when they rotate the induced dipole moment undergoes rotation and the rotation induces it is own frequencies and rotation is connected to the alpha naught E naught because for a pure rigid rotor we do not have alpha 1 that is no vibration for the polarizability is the static polarizability, but the static polarizability is a second rank tensor it has x x component xy the yy component and zz component in the principle directions and therefore, there are three polarizability static polarizability components which are part of the induced dipole moment.

So, even if the molecule does not have a dipole moment the presence of the electromagnetic radiation induces a dipole moment, due to the fact that the molecule can actually polarize it itself to the positive part of the electric and the negative part of the electric field and continue to do that either through rotation or through vibration. So, since there is a an induced dipole moment even in the absence of vibration now there is a microwaves spectrum that one can see and that spectrum can be seen in the Raman lines in the next step.

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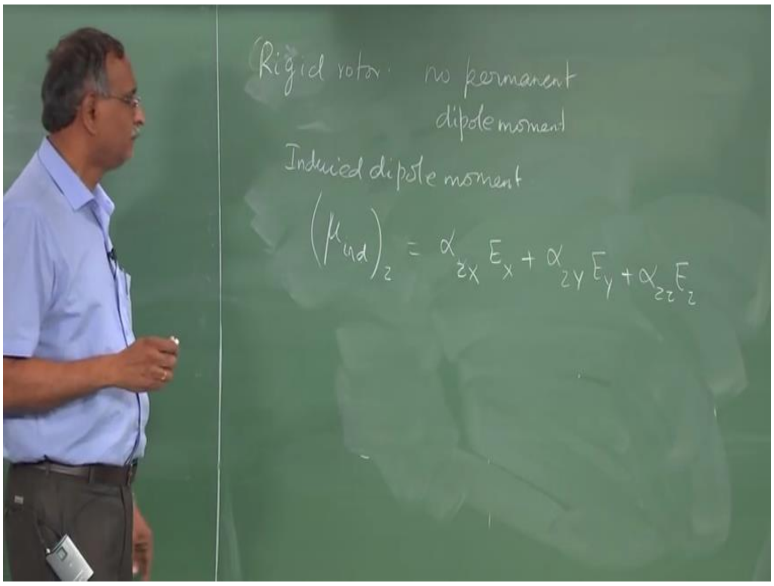

So, the rotational spectrum when the molecule does not have a permanent dipole moment it still has an induced dipole moment due to the electric field and the induced dipole moment also is proportional to the alpha. So, if you recall mu induced now, we will use the tonsorial form that we had used suppose we had mu induced in the z direction which is probably that direction of the symmetry axis of the molecule then, the mu induced is given by alpha zx ex plus alpha zy ey plus alpha zz ez.

Therefore, this is the one which causes the molecular rotational energies to be accessible by Raman spectroscopy because; now they have polarizability which is also rotating because of the molecule is rotating the polarizability tensor the quantity is also rotate the mu induced is directly given by 2 directions alpha zx or alpha zy or alpha zz barrier.

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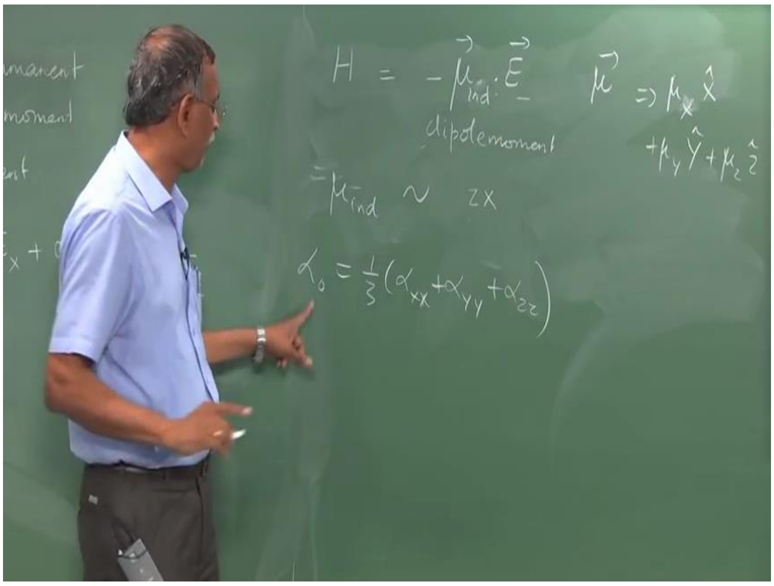

When we studied microwave spectroscopy the Hamiltonian that we were worried about had basically the interaction with the external electric field is mu dot E it is a scalar the mu is the dipole moment vector and e is the electromagnetic radiation and therefore, what you have is this mu is due to the mu induced and so, the Hamiltonian due to this mu induced is this and this Hamiltonian is responsible for that transition this is the one which leads to the transition between rotational levels.

So, this mu induced is now a function of 2 coordinates or 2 directions. So, it is like mu induced is like the molecular property of a coordinate z and a coordinate x earlier the mu in microwave spectroscopy was simply mu x of x plus mu y of y plus mu z of z and these were the dipole moment components in some chosen direction and xyz are the coordinate system that, we start with and therefore, these are the mu x mu y mu z are the components of the arbitrary dipole moment in the direction of the coordinate system here. The mu induced now depends on 2 coordinates.

Therefore, what this leads to is the selection rule of a delta j not plus or minus 1, but delta j 2 also there is a invariant component alpha 0 and alpha 0 is usually defined as one third of alpha xx plus alpha yy plus alpha zz and I told you that this quantity does not change between different coordinate systems. Therefore, this is called the scalar of the polarizability and this alpha naught which is a constant does not have any direction dependence everything has been summed here this constant therefore, also gives raise to what is called delta j is equal to 0 transition in microwave spectroscopy you do not have a delta j is equal to 0 because, there is no micro waves spectroscopy there delta j is plus minus 1 for a rigid molecule in the case of rotational Raman this the static polarizability, which does not have what is called scalar component; which does not have any direction leads to delta j is equal to 0 and the actual mu induced dipole which involves 2 directions leads to delta j is equal to plus minus 2.

Therefore, the selection rule for rotational Raman is 0 plus minus 2 and that is also for molecules which do not have a permanent dipole moment. Therefore, now you have a beautiful handle of being able to detect the microwave spectrum of hydrogen molecule the most elementary molecule that you have microwave spectra could not detect that Raman lines rotational Raman spectroscopy tells you how if the hydrogen the electrons between the 2 hydrogen atoms. If they are polarized due to the presence of the electromagnetic field then there is a polarizability that comes into the picture and this poilarizability has one scalar component and several Vectorial Tensorial components 2 in this case the stab parallel and perpendicular polarizability and this polarizability allows us to actually look at the rotational energy levels of hydrogen.

So, Raman spectroscopy is beautifully complimentary spectroscopies to study systems which are otherwise in accessible to the spectroscopic techniques. So, molecules which do not have permanent dipole moment are not seen in microwave all those molecules which have any measurable polarizability. I mean unless the bonds are extremely rigid and therefore, the polarizability is extremely small see if you are a very, very rigid they feel does not basically affect the electron density, but if the molecule is already undergoing some vibration and the you know 0 point vibration and the molecular bonds are slightly flexible then you the polarizability leads to an immediate measurement of the microwave spectrum of molecules. Now what is the microwave spectrum of molecule they have the following features.

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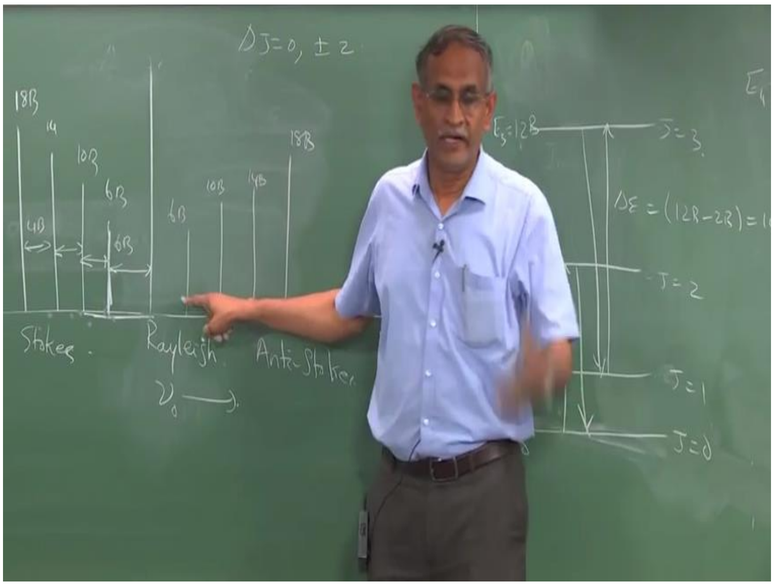

So, if the selection rules are delta j is equal to 0 plus minus 2 remember, we have what is called a nu naught this is the Rayleigh line the frequency that we have. So, that is the center frequency no modulation of the incident light that passes right through scattering equipment detects that right away. So, there is no change in that, now on either side we have delta j is equal to 0 or plus minus 2. So, which side is which let us write down the energy levels for a simple diatomic molecule?

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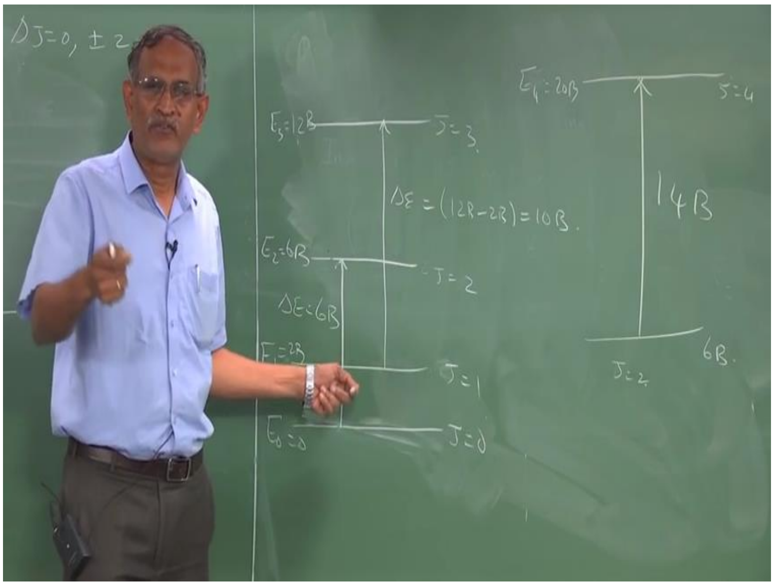

We have the energy levels e 0 which is 0 because j is 0 the next one e one is b j into j plus one it is 2 b j is equal to one it is 2 b therefore, the gap is 2 b, but then j is equal to 2 it is e 2 is 6 b same energy level spacing that we are familiar with micro wave. Now between 0 and 6 b you have a transition because delta j has to be 2 there is no transition between 0 and 1 there is no transition between 1 and 2 what about e j e 3 is equal to 12 b and this is j is equal to three there is a transition between 1 and 3 what is the difference between the 2 this is delta e is 12 b minus 2 b 12 b minus 2 b and that is 10 b; what is the lowest frequency that we would measure this delta e is the difference between 0 and 6 b therefore, this is 6 b ok.

What is the next one? Let us draw say j is equal to 2 here and that is a 6 b and the next let us draw j is equal to 4 j is equal to 4 4 is 4 into 5. So, it is 20 b the gap between j is equal to 2 and 4 is now; 14 b you calculate this you will see every difference that you can measure in Raman spectroscopy for rotational lines barring the first one which is 6 b will always be 4 b away from this 10 b 14 b 18 b 22 b and so on.

Therefore, what you will see n the rotational Raman line is on either side this is absorption of radiation therefore, what happens if this radiation is absorbed I mean supposing this is the frequency reduction n the scattered radiation then that is seen on this side of the frequency because; this is Rayleigh and this is the increasing direction on the frequency therefore, this is stokes side and this is the antistokes side therefore, the first line that you will see is 6 b the next line that you will see is 10 b from here 0 0 to no transition at this point j is 0 therefore, j is equal to 0 j is equal to 2 then, this is j is equal to 1 to 3 and then the next line is 14 b 18 b and so on. What about another side is exactly the same the other 1 is the emission of radiation because the transitions happens from higher energy state to lower energy state, but remember usually fewer molecules are there in the higher energy state and more molecules are there in the lower energy state.

Therefore, getting transitions down from very high energy state to very low energy because. So, few molecules are there the intensity of that such radiation that is the antistokes radiation usually weaker; than the intensity of the stokes radiation where nothing, but absorption is happening therefore, the radiation that comes out does not have those frequencies these are the nu naught minus 6 b nu naught minus 10 b nu naught minus fourteen b and. So, on therefore, I would say I would put something like 6 b eight b this is 6 b this is 10 b this is 14 b due to this process due to this process due to this process.

So, you see a very symmetric 18 b spectrum on either side of it for a rigid rotor the gap between the 0 and the first rotational line is 6 b and every other line is 4 b and what is b you know from microwave spectroscopy that for a rigid diatomic molecule that we are looking at the value of b is H by eight pi square ic.

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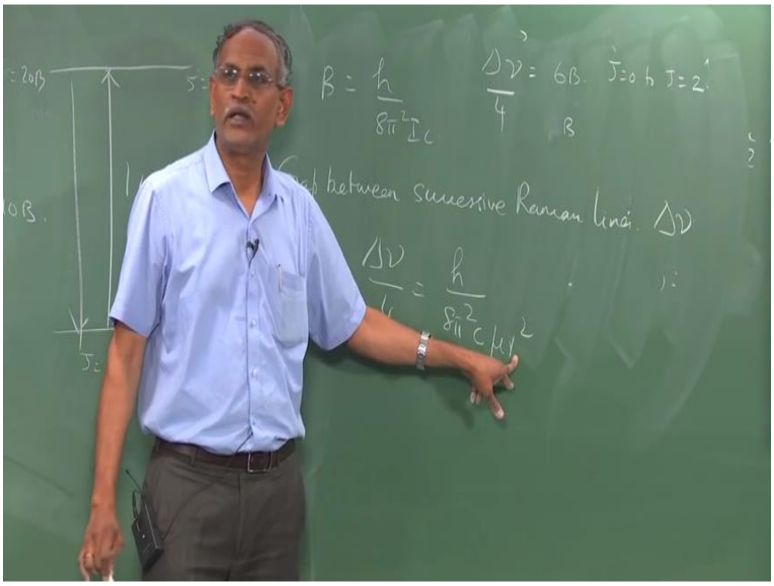

Therefore, if you have delta nu is equal to 6 b the first gap the first appearance of a rotational roman line hydrogen is a beautiful example and benzene; many other molecules all molecules which are homo nuclear no microwave spectrum every one shows off in the Raman in the gas phase and what you see is he first line 6 b is for j is equal to 0 to j is equal to 2 and the next line is every gap is 4 b. Therefore, delta nu by 4 is the gap between successive lines gap between successive Raman lines is 4 b and that delta nu and therefore, delta nu by 4 is h by 8 pi square c mu r square. You know the reduced mass therefore; you can calculate the bond length very, very accurately for the molecule.

If you can measure rotational roman lines this is as simple as what one can expect they were much more things in rotational Raman spectroscopy particularly; if the molecule is slightly non rigid then, there are centrifugal effects we never studied centrifugal effects in this course even in the pure microwave spectrum of molecules having permanent dipole moment. Therefore, I do not want to introduce that here, but remember this is the starting point of understanding the selection rules the selection rule being delta j is equal to plus minus to and the delta j is equal to 0 is right here no change.

So, what you see is that this is how to interpret elementary Raman spectra a looking at the spacing and then calculating the bond length or the vice-versa; if you know the bond length exactly where the Raman line will be and so on.

Now, in the next small bit I would talk about the vibrational Raman spectrum and then we will come to an end with respect to this particular course; on the molecular spectroscopy there will be one introductory lecture in another 3 or 4 days you will also see on electronic spectroscopy.

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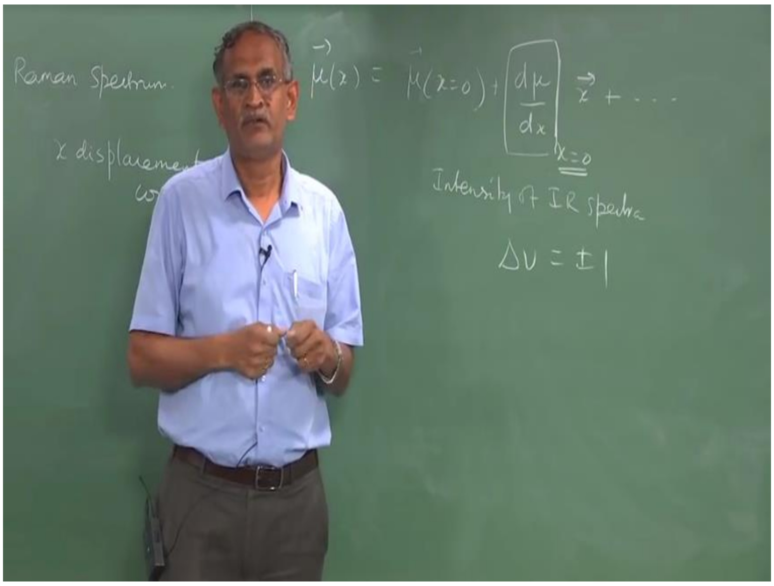

The last segment of this introductory lecture on Raman spectroscopy, we will look at vibrational Raman spectra also only for the very elementary case of a simple harmonic model or similar to that in the normal mode model for a poly atomic molecule. Now remember vibrational spectroscopy the intensity of the infrared transition is due to the rate of change of the dipole moment with respect to the displacement coordinate.

So, suppose x is the displacement coordinate and during that displacement the dipole moment changes it is the rate of change of the dipole moment with respect to displacement that is responsible and this is; how do we write that we will write in a formal way we will write mu at a position x is mu naught which is basically mu at x is equal to 0 no displacement. So, or at equilibrium displacement and then you have this is yeah plus d mu by dx evaluated at the displacement being 0 times x plus and so on.

It is this rate of change of dipole moment evaluated with respect to the equilibrium geometry that is responsible for the intensity of infrared spectra there are other terms like this rate of change that second degree then is a third degree and so on. That basically determines the extent to which the molecular motion is no longer harmonic, and it is highly non-linear and therefore, higher order terms come in, but if we restrict our self to this term this leads to the selection rule delta v is equal to plus minus 1.

This static dipole moment is irrelevant as far as the infrared spectrum intensities concerned because that is a fixed component there is no association with the position because it is a constant, but if the dipole moment keeps changing during the vibration you immediately see that that vibration mode is detected by the infrared spectrum that is this coordinate the rate of change the rate of change as well as this coordinate it is this which, is the molecular level operator I should say the position coordinate it is that.

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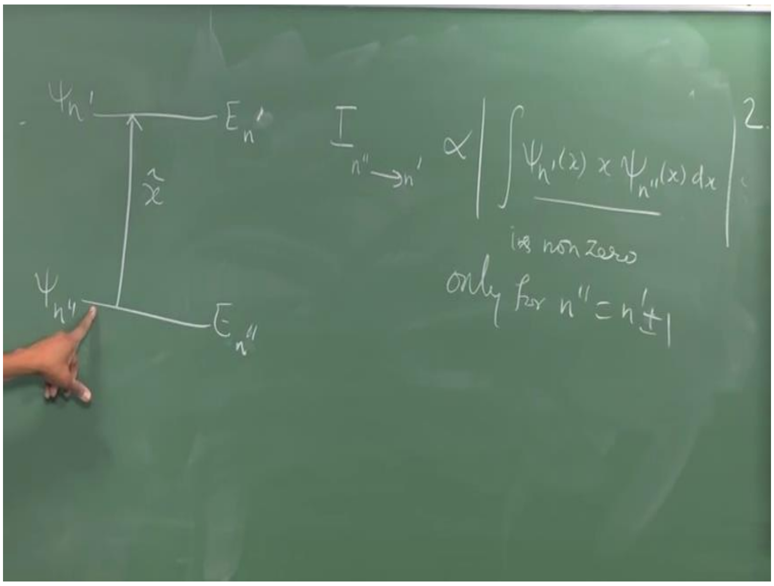

Which connects the vibrational Eigen function which contains one hermite polynomial to another vibrational Eigen function which contains another en prime en double prime and en prime. If these two have to be connected it is this, mu and technically it is the x operator which connects the psi n prime the psi n double prime to give you an intensity that of the transition between n double prime to n prime as being proportional to the absolute square of the integral psi n prime x x psi n double prime of x dx square.

Therefore you see that because it is linear it is x not x square not x to the one-half or anything else because; it is linear in the limit of what is call the harmonic approximation where the rate of change of dipole moment alone is sufficient for us to consider the motion that is because; the displacements are very small harmonic motion.

Therefore, the selection rules wholes because this integral is non zero only for n double prime is equal to n prime plus or minus 1. So, this is the essence of the vibrational intensity I might have talked about this in the lectures earlier if; I did not this is how we actually calculate the vibrational intensity the intensity is proportional to this square of what is call the matrix element between the state psi n double prime one of the energy states and it is next state psi n prime.

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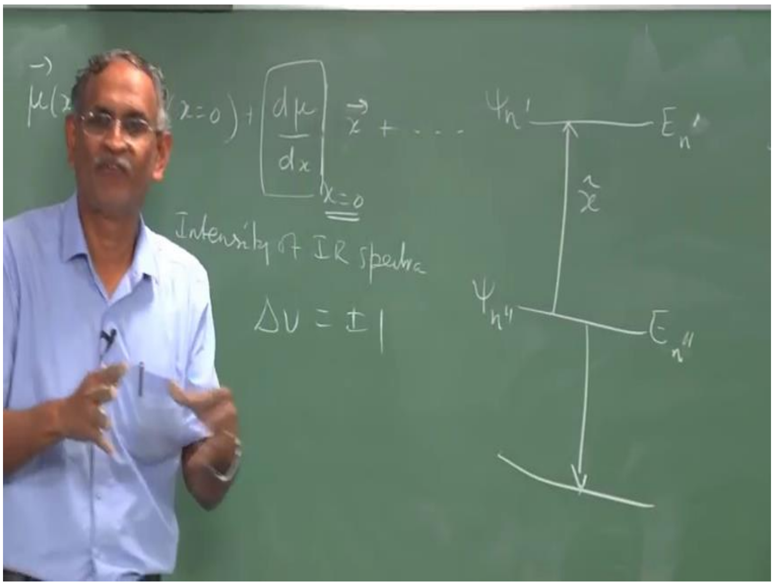

And therefore, this is also possible this is absorption this is emission therefore, delta v can be plus or minus 1 this picture does not change in the case of rotational in the case of vibrational Raman spectrum, why because of the following (Reference Time:35:00).

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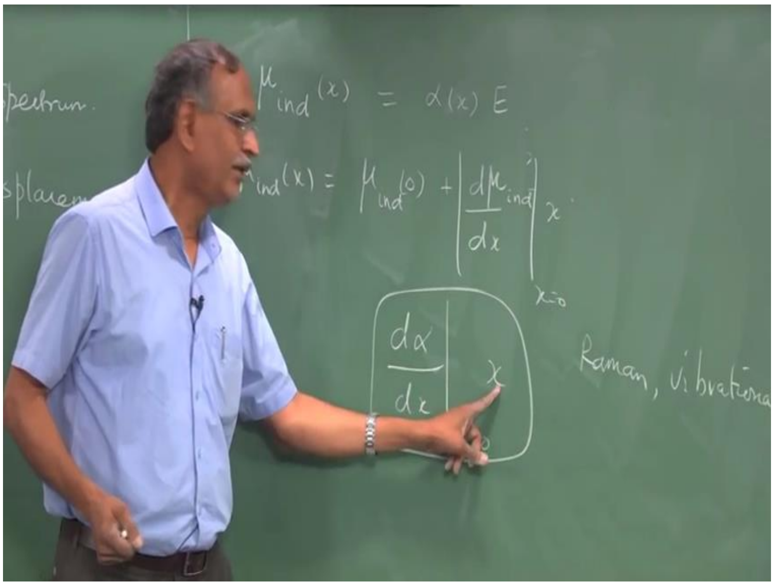

For vibrational Raman spectroscopy we are looking at mu induced. Now this mu induced is going to change also as a function of x please remember the polarizability is now absorbed in the mu induced x it itself and the mu induced x is going to involve alpha times r e and this is the alpha is the e. Hence that and so, what you have is d mu induced sorry let us write the other way around therefore, if we write mu induced x in terms of no there is when no (Reference Time:36:00) when there is no vibrational amplitude it will be mu induced 0 plus d mu by d x induced times x.

So, the molecular property that is responsible for vibrational motion is again this rate of change of the d mu index evaluated at x is equal to 0, which contains essentially the rate of change of alpha with respect to x. Because if, you substitute that you are going to get d alpha x x or whatever some quantity either the x quantity or the y quantity, but let us take the scalar quantity is d alpha by d x again, with respect to x is equal to 0 multiplied by the x, but please remember this d alpha by d (Reference Time:37:00) x is equal to 0 does not have anything to do with vibrational motion it is a static dipole the polarizability due to the external electric magnetic field.

Therefore, it is this component which is still responsible for Raman, but vibrational exactly the same way that the dipole movement must change during the vibration it is important that the polarizability changes during vibration and in that case this leads to the same matrix element type that, you have psi n prime of x x psi n double prime of x dx prime dx because; this evaluated with no displacement is actually independent of this x (Reference Time: 38:00), but it is needed without which you will not see this term at all if this is 0 this term will not be there.

Therefore, vibrational Raman spectroscopy requires essentially the polarizability to change during the vibration, but the matrix element that connects the vibrational states have made this elements are identical in terms of the Eigen functions of the vibrational state to the single coordinate x therefore, the selection role for vibrational Raman is also plus minus one no changes. But if you consider higher order terms and if you consider un harmonic terms and if you consider polarizabilies are very large if the molecule has a very large polarizability during due to the weakness of the forces between the different atoms.

So, that the (Reference Time:39:00) external electric field can actually pull these molecules apart from each other then it is possible that other terms the higher order of polarizability may get involved and so on. But the lowest level the vibration selection rule for Raman spectroscopy does not change by much. I mean does not change anything still delta v is equal to plus minus one, but there is a significant change in the rotational Raman spectroscopy where the selection rule is delta j is plus minus 2 and 0. So, these are usually a mentioned in any of the elementary text box, but I will leave this lecture with one last note.

I will make this as a statement and a very nice and simple explanation of this statement is of course, is already there in the one of the beautifully written elementary text box on molecular spectroscopy.

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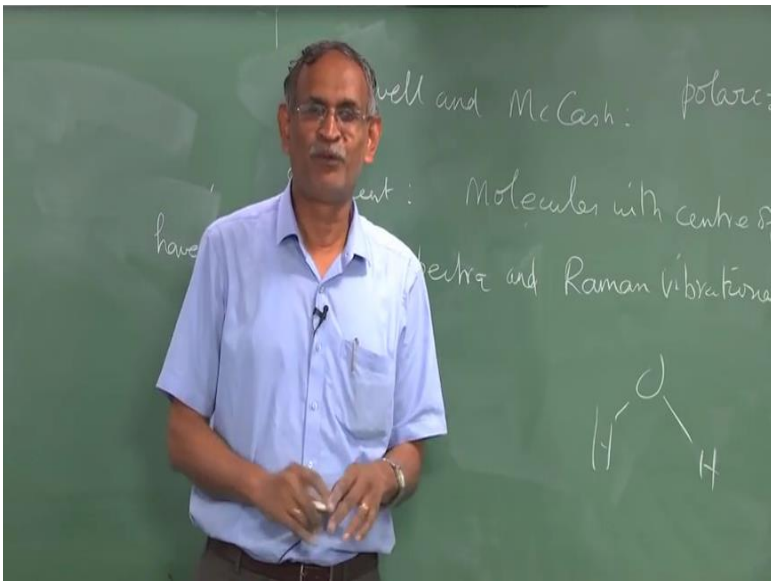

I have also referred to that book as a additional reference for you the book by Banwell (Reference Time:40:00) and mc cash Alian mc cash the statement that I would say make or the Raman spectroscopy is the following molecules, which have a center of symmetry with centre of symmetry those have ir spectra or Raman vibrational spectra, but not both meaning that, if there are many modes for example, carbon dioxide it itself elementary molecules even hydrogen for that matter hydrogen have a polarizability that changes during the vibration hydrogen (Reference Time:41:00). Vibration does not lead to any change in the permanent dipole movement which is always 0, but the induced dipole movement will be there for a molecule such as hydrogen therefore, hydrogen vibration motion cannot be seen by infrared spectrum, but there is a very nice and beautiful explanation in Bangwell and mc cash on how polazibality changes during the vibration from positive to 0 to negative.

Therefore, that leads to Raman vibration spectrum for that molecule this is the same thing with all molecules which have centre of symmetry such as carbon dioxide carbon dioxide has a centre of symmetry at carbon and it is symmetric stretch does not have any dipole movement change. But during the symmetric stretch the polarizability changes therefore, the symmetric stretch is not detectable by ir, but it can be seen in Raman spectroscopy (Reference Time:42:00) therefore, they are mutually exclusive molecules with centre of symmetry have mutually exclusive ir spectra and Raman spectra those vibrational degrees of freedom for which, the dipole movement change during the vibration they will be seen by the ir spectrum, but they will not be seen by Raman spectra Raman spectroscopy those degrees of freedom for which there is no dipole movement change; such as a symmetric stretch in carbon dioxide and many other symmetric stretches in every molecule which has a centre of symmetry, you will see them either some modes are ir detective and those modes which are ir detective, ir active some modes are ir active and those modes which are ir active or not Raman active and vice versa, but this is applicable only (Reference Time:43:00) in the case of molecules with centre of symmetry.

Water for example, has both rotational vibrational microwave and Raman rotational spectrum because it does not follow any of these things. I mean the dipole movement changes there is an induced dipole movement and therefore, there is a polarizability change in every one of these vibrations. Therefore, all three modes of water molecules are both Raman active and all three mode’s are also infrared active the molecule also has some microwave spectrum it has a rotational Raman spectrum.

So, many more things can be said and this is a great contribution by an Indian scientist in the early twenties and thirties to the evolving field of quantum mechanics and spectroscopy. Therefore, in later lectures we will study more of this ah in another course with some details. So, the actual calculations of some of these (Reference Time: 44:00) matrix elements and the polarizability matrix and so on. This sort of formally completes the lecture on infrared and microwave spectroscopy that I intended to give for this course I wish you all the best in the test and the tutorials as well as the examination and hope that you will come back to the next course that would be offered again in this area of sometime later by me.

Thank you.