# Atomic and Molecular Physics
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## Lecture - 59
## Raman Spectroscopy (Contd.)

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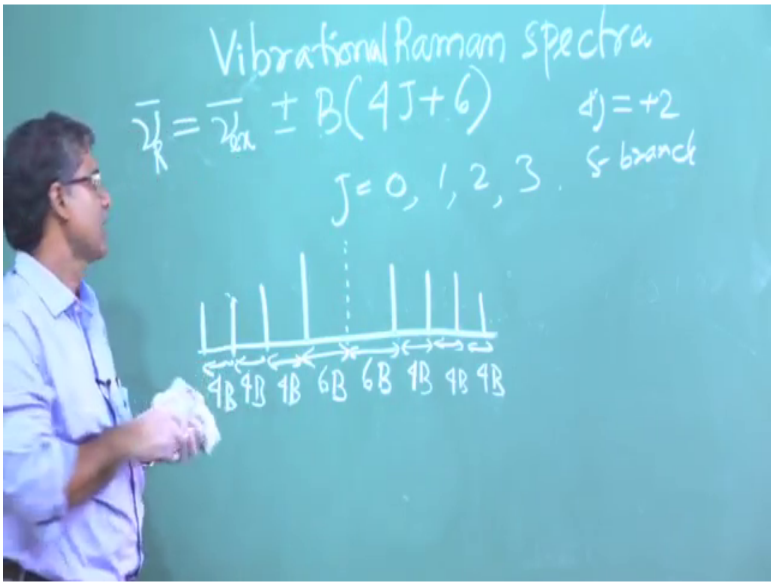

So, in last class, we discuss about the Rotational Raman Spectra. So, basically incident is called excited radiation ok. So, radiation excite the molecules ok. So, this if that is incident one; if I write this, excited radiation or excite radiation for exciting the molecules. So its wave number is nu ex bar ok.

So, then what we are getting? We are getting this plus minus that is the Raman Spectra Raman lines whatever we will get in spectrometer. So, if I write this R bar equal to this Raman lines ok. That will be this excited or plus minus this rotational part. So, that following the selection rule del j equal to plus 2 for S branch ok; for S branch; you will get you will get considering this one. So, I think I was getting B 4 J plus 6 ok. Now, J equal to 0 1 2 3 ok.

So, basically Raman spectra we will get that is J 0; when J equal to 0 ok. So, this part is 0. So, 6 B ok; so, nu 1; so, nu original from here for J equal to 0; I will get Stokes lines and Anti stokes lines for plus and minus for J equal to 0. So, one line I will get here and another line I will get here ok. When this separation is will be 6 B 6 B from 6 B ok. So, that will be the first Raman lines ok. So, that from these there shift this we tell general Raman shift the shift is 6 B ok.

So, for stokes line and anti stokes line it is from original. So, it is the higher and lower by 6 B first line. And then I will get second line; then I will get second line, third line etcetera intensity generally its decrease ok. And if you put J equal to 1; it is a 10 10 b. So, from here it is 10 B, right and this 6 B. So, this separation you will see this is a 4 B. So, and all other cases, if all other cases they are 4 B ok. In this case also, we will say plus would be that side this is a minus would 10 B 14 B this way. So, this is separation ok.

So, this is the things you will get. So, this is the rotational Raman spectra you will see this kind of spectra this for S branch. So, for other branch also one can one can see that, but intensity of these all lines will not be same.

So, just we measure this it is in terms of we plot basically Raman shift; what is from original? What is the shifting? What is the what is the shifting of this due to this rotation and other effects. So, in this case we are consider rotation. So, this first line from there; 6 B and this other one it is separation of 4 B. So, shifting will be 10 B 14 B 18 B etcetera ok.

So, basically that spectra in spectrometer we are measuring this shifting and if you may can measure the shifting then you will get the B value ah. And So, that is why it is an; this is what is the wave number of this, it is in the range of u v or visible range you know. So, that is why it is easy to handle and this spectrometer and one can easily get the information of B. And again I am telling this B from pure rotation you can you can get from microwave ok, and from here also one can get. So, here it is its more generally you know for any molecules one can get this information ok. Like oxygen, nitrogen molecules; that you cannot get from ultraviolet not ultraviolet that is the microwave spectroscopy ok.

So, anyway; so, already I have discussed about this. So, this is the rotational Raman spectra. One we will one has to just in this spectroscopy; measure this intensity at different wave length; measure this intensity at different wavelength or measure the wavelength basically that the spectrometer use this getting and then these different wavelengths are specially separated.

Now, from spectrometer itself one will where these lines are coming. So, this from detector one can identify at which angle it is coming. Now, from this angle to one can consider this calculate the wave number or wavelength or frequency, this getting that relation this sin theta equal to L lambda.

So, anyway; so, now, if I consider this Vibrational Raman Spectra Vibrational Raman Spectra; so, these are similar you know; Vibrational Raman Spectra these are similar. So, here this Raman spectra you will get this excited one and then this one will be modified this one will be modified ok.

So, in this case, what you have to see? So, that you have to you have to consider this for vibration this we know this nu bar; this vibration that was or or really this notation we have used E v that was ah. So, what was that? So, I think V plus half omega e bar ok. This is a equilibrium fundamental frequency. And then minus this anharmonicity constant and then V plus half square ok.

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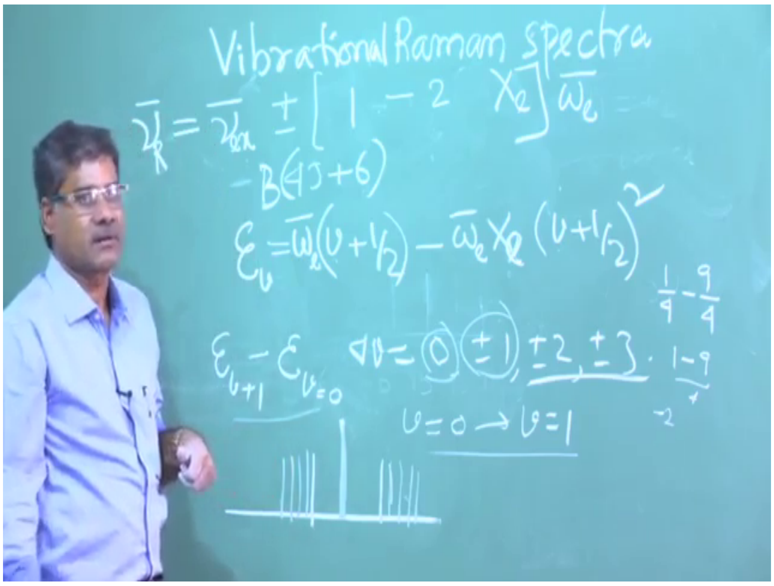

Now, in this case basically this del [vocalized-noise]; the selection rule one has to choose. So, the selection rule 0 plus minus 1 plus minus 2 plus minus 3 ok. So, in this case, vibration in vibrational case; so, this is the same selection rule as we have seen for earlier see it is not like rotational case. So, here this selection rule itself is valid; whatever we have seen for infrared spectroscopy for pure vibration, but it has non rigid of course, not non rigid this is the anharmonicity case that is why we have considered this one. For harmonic case, only it is not, this not the selection rule for harmonic unharmonic case, this is the selection rule ok. So, all transitions for the, but these as long as you will go the go towards the higher selection rule plus minus 2 plus minus three intensity will be very small and it will be difficult to detect.

So, that is why, when del nu equal to 0. So, it is will give basically you original lines ok. But mainly these del nu if we consider plus minus 1. So, just consider plus 1. So, nu equal to 0 plus minus 1 or plus 1. So, from nu equal to 0 state to nu equal to 1 state. So, if it goes from nu equal to 0 not nu V equal to 0 to V equal to 1 ok.

So, if you consider this transition or minus 1 will give this other way; so, from V equal to plus 1 to V equal to 0 or other equal to 1 to V equal to 2, V equal to 2 to V equal to 3. So, we remember. So, in this case, V equal to 0 to V equal to one. So, this called the fundamental lines ok, spectral lines and other is basically overtones; remember. And then hot band that we have discussed earlier. So, this for simplicity let us consider this is the fundamental one ok.

Now, due to this change if you just consider here, what we will get. So, this E v plus 1 minus E E v ok; in general, we have to consider this one and ah, but this also I would elaborate yes. So, V equal to 0, yes. So, this is in general. So, here you will have these all sorts of fundamental lines. Now, here if I if I consider V equal to 0. So, it will be E 0 and this will be E 1 ok.

So, that is the fundamental one and for other one one is so that will be overturns V equal to 1; then 1 to V equal to 2, V equal to 2 to V equal to 3. So, these are the overturns. So, if I just consider this fundamental one. So, here you put V equal to 0; V equal to 0, you put 0. So, it is a for here V equal to 0 and here whatever you will get and then you put V equal to 1 V equal to 1. So, here I will get V equal to obvious 3 by 2 minus V equal to 0; it is minus half. So, basically you will get you will get what you will get 3 by 2 minus half you will get 1. So, you will get basically omega e bar, right.

And other term it is a minus is there. So, it just it will be opposite. So, it is a half half square minus 1 means 1 means 1 means 3 by 2. So, 9 by this will be 0 means 1 by 4 minus 9 by I think 9 by 4. So, 1 minus 9 by 4; it will be 2 minus 2 ok.

So, I think another term this minus I think minus I think 2 2 omega e bar X e yeah that this kind of things you will get just one should do it. I think I have between correctly or so yes hopefully omega e 1 minus 2 X e 2 1 minus omega e 1 minus 2 X e yes. I have written correctly. So, omega e if you take omega e yeah outside, omega e outside so it is 1 omega e ok.

So, this now here the difference is. So, here what spectra we will get? So, this is the original one rely on; it is not Raman spectra original one E excited. Now, you will get fundamental lines plus of this omega e and minus of this. So, two lines you get this is a fundamental lines. This two you will get one stokes lines and another in naturally. So, these stoke lines and stoke this is modified with this by this ok. So, this is the. So, this shifting Raman shift it is coming because of the rotation ok.

Now, here this is a fundamental one I have considered and one can choose these other overtones and hot branch also, but their intensity generally less lower and you see this.

Now, what vibrational is there? If rotation generally most of the rotation also there. So, these this structure there is a fine structure of these vibrational Raman spectra. And this vibrational Raman spectrum; these fine structure is comes basically from the rotation. And then that how much it will; so, one has to did another term here one has to consider. So, this is the original say fundamental lines ok.

Now, these fundamental lines; now is for that for rotation one has to consider that one with here. So, that is the rotation part we have seen this is a 4 J plus 6 this B ok. So, now, these terms we will come will be will come there and modify this each line. So, this each line whatever earlier we have shown; this will be the original line coming from the vibration. Now, these lines will be modified it will show the each lines will be modified and it will show the fine structure of this of this lines and this is called basically the vibrational rotational Raman spectra; and or the fine structure of the vibrational rotational vibrational Raman spectra ok.

So, I think this is the things on yeah for this in Raman spectroscopy. So, whatever spectra we are seen that spectra Raman spectra and that is spectra is basically just it is a modulation of the incident radiation modulation of the incident radiation and that modulation is coming due to the vibration rotation of the molecules; we are quite familiar with the rotation and vibration of the molecules. And same things here we are considering, but only difference is that here these here initial radiation that we are choosing either in visible range or ultraviolet range and that it mean most of the cases ultraviolet range is considered.

And that is that that incident frequency of the radiation is just modulated with or modified with the information of the vibrational structure of the molecules, and rotational structure of the molecules, and that information we can get easily from the from the Raman spectrometer or analyzing the Raman spectra ok.

So, I think that is that is all about the Raman spectroscopy and that is this is the simplest version I discussed, but in this was purpose. So, this there are a lot of things people study using this Raman spectroscopy. And there are we just let me mention some other spectrometer with that with the very useful for studying the atomic spectra for studying the atoms and molecules ok.

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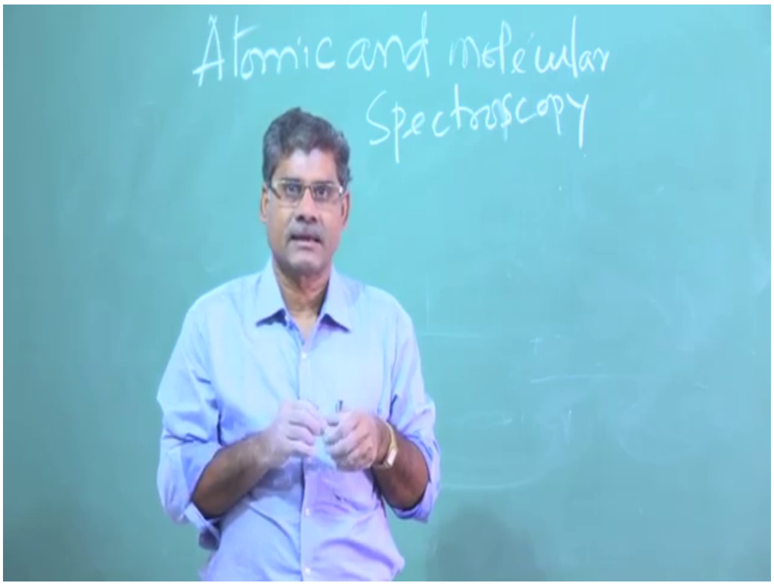

So, that is why it is; you tell Atomic and molecular Spectroscopy molecular Spectroscopy ok. So, whatever Raman spectroscopy I discussed that is the molecular spectroscopy. Another spectroscopy there are many spectroscopy known; already I mentioned micro spectroscopy, infrared spectroscopy, electronics spectroscopy, and then the special type Raman spectrum modular spectroscopy. I think XPS X-ray Photo Electron Spectroscopy ah. Then so, but there are many spectroscopy it is all are not for molecular. So, some are molecular for molecular some are atomic spectroscopy ok.

So, one more spectroscopy I think I will just discuss briefly and very interesting and it is it is also very popular. So, that is spin resonance Spin Resonance Spectroscopy, Spin Resonance Spectroscopy ok. So, that is that mostly it is not for molecular spectra for to study the molecules mainly it is used for studying the atomic to get the atomic information ok.

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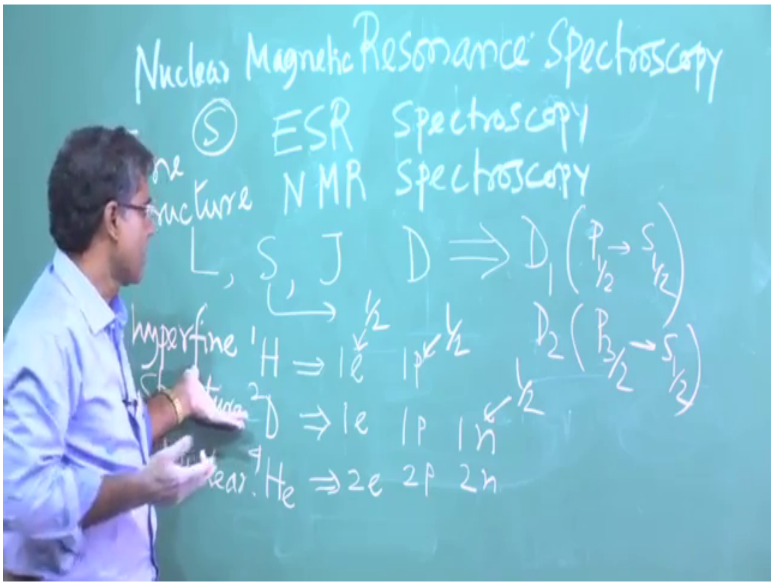

So, this is the as I told the Spin Resonance Spin Resonance Spectroscopy ok. So, spin resonance spectroscopy ok. So, this we are familiar with the spin of electron. So, if I put here electron, then it is Electron Spin Resonance Spectroscopy ESR is very famous spectroscopy and it is easy to use and very useful ok. So, then it is ESR Electron Spin Resonance Spectroscopy ESR Spectroscopy ok.

Another is if I replace this spin electron, if I put this Nuclear Spin Electron Spin and Nucleus Spin Nuclear Spin Resonance. So, it is called Nuclear Spin Resonance NSR it is really it is not Nuclear Magnetic Resonance people tell anyway this both are same both are same; so, Nuclear Magnetic Resonance Magnetic Resonance ok; so, this is called NMR N M R Spectroscopy.

So, it is called Nuclear Magnetic Resonance Spectroscopy ok, NMR Spectroscopy and another one Electron Spin Resonance Spectroscopy ESR. So, both are basically principle are similar ok. In one case, it is used the electron spin ok. Another case, it is used the nuclear spin ok. So, principle of the spectroscope is very simple just I will discuss this principle of this spectroscopy and yes.

So, we are quite familiar with the electron spin we have discussed a lot what we have we have seen that in atomic spectroscopy we have seen that this there are angular momentum; right L and then S spin and then total J right.

So, considering the spin of electrons we are able to explain the fine structure of the atomic spectra. So, now, spin is very important, spin is very important and considering the spin we are able to explain the fine structure the atomic fine structure. What is the atomic fine structure? You remember that say sodium D lines sodium D lines ok. So, these sodium D lines actually, it has two lines D 1 and D 2 D 1 and D 2 lines. And that we have seen D 1 and D 2 lines; it is transition between the this I think P half to S half and D 2 is P 3 by 2 2 S half ok. So, this is the. So, here J involve J means S involved ok. So that was we are able to explain the we are able to explain the fine structure of atomic spectra and that is because of the consideration of the electron spin. So, electron have spin half, right.

So, similarly; atom have electron and we have considered only electron ok. So, electron we have we have considered spin of the electron, but atom have the nucleus also; right, if we just consider the Hydrogen atom.

So, Hydrogen atom hydrogen atom it has we write one hydrogen atom means it has one electron and one proton right it has one electron and one proton and if I consider Deuteron isotope of this hydrogen. So, it is mass is 2. So, this basically one electron, one proton, and one neutron right Helium if I consider helium is 4; mass number is 4. So, it has basically two electron, two proton, and two neutron, right.

Now, as I told that we have we have considered the we have considered the spin of the electron in the atomic spectra without spin of electron whatever spectra we got, but that cannot explain this everything it cannot explain the fine structure of the spectra. So, now, that is why we considered the spin of the electron and it is there ok. Now, this we can explain the fine structure.

Now, additionally this after fine structure also it is seen this there are still splitting of these fine spectral lines and that is called the hyperfine structure. So, Fine Structure Fine

Structure Fine Structure that electron spin one has to consider; and to explain the hyperfine structure means still, it is not sufficient. So, this is called hyperfine structure hyperfine structure hyperfine structure. So, one has to consider the nuclear spin, one has to consider the nuclear spin ok. So, here one has to consider nuclear spin.

So, in nucleus protons and electron neutrons are there. So, spin electron it has spin half this photon also it has spin half neutron also this is spin half. So, to consider the hype hyperfine structure to describe the hyperfine structure; so, one has to consider the nuclear spin of proton spin of neutron ok. So, that means, in the system atomic system we have spin electron spin as well as nuclear spin means protons and neutron spin and these they interact with each other there is a interaction among them ok. So, this interaction we have to consider and we have to get the resultant total spin, total angular momentum spin angular momentum of the of the system ok.

So, then only we have one can explain this hyper hyperfine structure of that. So, this is basically hyperfine structure that is because of the nuclear spin which interact with the electron spin and so that I will discuss in next class. So, here let me stop.

Thank you.