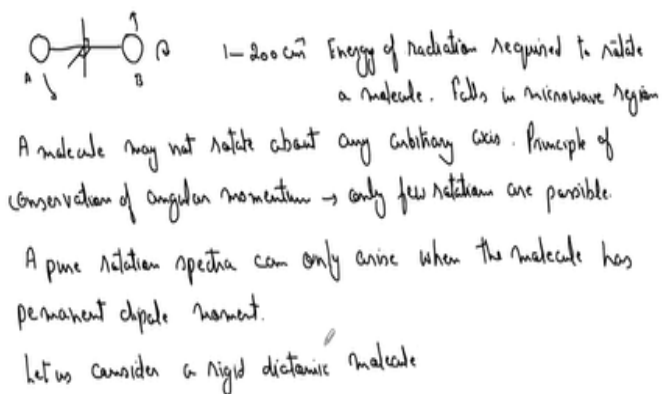**Symmetry and Group Theory**
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Lecture -58
Introduction to Spectroscopy Part- II

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Now, you can also think of, in typical cases, you do not find atoms tied to a rigid body, but two atoms tied with a bond. So, now these two can describe a rotation. For example, if I am displacing this body, let us say atom A and atom B this side. This gets displayed like this and then you have a rotation motion like this, else it can also do a rotation like this. But that rotation does not bring a change in the orientation of the molecule, it will it does not look like specially in case of quantum objects, it does not look like as if anything is happening to the molecule.

Another is, like, so basically axis which is perpendicular to the bond axis, this axis and this axis both are perpendicular to these bond axes. So, the rotations can happen only about these two axes not about the internuclear axis that rotation is not counted. So, energy required to create this kind of rotations are very very small. And typically, are in the range of 1-200 centimeter inverse, energy of radiation required to rotate.

And now these energy falls in microwave region of the electromagnetic spectrum. So, hence, this is called as rotational or microwave spectroscopy. So, also, we should also note down here that the molecule, but will not go into those details, but just for completeness I am mentioning, a molecule may not rotate about any arbitrary axis. There is a law called principle of conservation of angular momentum, which dictates only few rotations are possible.

So, this is not in the scope of this course, so you will find this discussion in a spectroscopy course or you can actually go and study any spectroscopic textbook you will find details of this. But for completeness I am just mentioning it here, only few rotations are possible. So, we should also mention that a pure rotation spectrum can only arise when the molecule has permanent dipole moment.
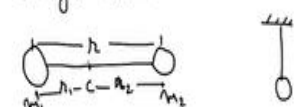
So, why dipole moment is required we will see that. So, dipole moment, basically what you are doing is you are trying to interact let the electromagnetic radiation interact with the rotating molecule. Now, there should be some sort of interaction which should happen. Now that interaction comes because of the dipole moment we will see how? So, let us consider a rigid diatomic molecule. See this has nothing to do with group theory I am just giving you a basic spectroscopy introduction because you have not gone through spectroscopy course.

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So, this is nothing to do with group theory. So, this is true for any general spectroscopy. So, let us consider a rigid diatomic molecule with masses m1 and m2. So, rigid means that the bond length is not going to change so, it is like a rod. There is no vibration, which we are considering here, rigid means no vibrations. And the length of this is r which is from the center of the two atoms.

So, this, length is r and let us say that the center of mass is C. Then you can call it as r 1 and r 2, distance from center of mass to the center of atom. So, just like a rigid atom which is tied to by a thread like a simple pendulum, which is tied by a thread to a rigid body support. So, now this atom is actually moving about this rigid support. So, here the atoms are moving about the center of the mass.

So, the motion is about the center of the mass. So, that is why we have considered somewhere in the middle, we do not know where it could be. It will depend on the individual atom if it is a homonuclear it will be in the center if it is heteronuclear it will be depending on the overall mass distribution. Now independent rotation of this molecule can change the orientation.

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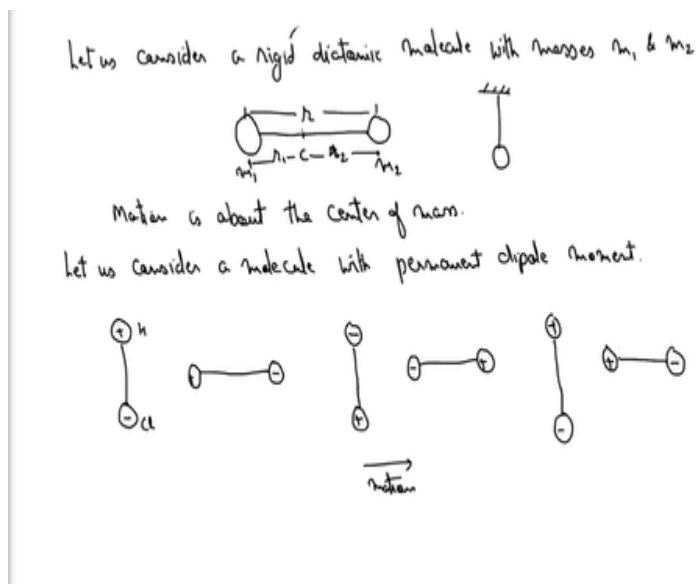
So, let us consider a molecule with permanent dipole moment, we should all be aware of we have already discussed the application of group theory in dipole moment. So, dipole moment is separation of permanent unbalance of charge in the molecule or separation of charges. So, if it is

HCl molecule, so you have a positive charge let us say proton and negative charge let us say chloride.

Now, if the molecule changes its orientation by undergoing rotation. So, let us say you come to this position that is plus and minus. And then you go opposite, you go minus plus and then you go opposite before minus plus. And again, you go opposite minus plus and again you go, so it is a periodic motion, periodic motion plus minus like this.

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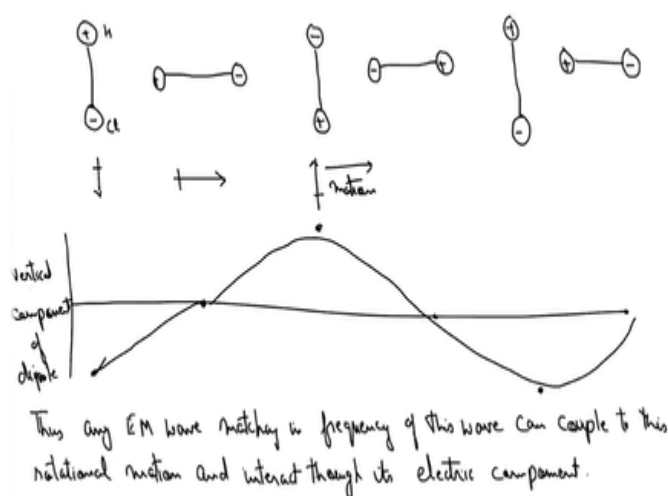
Now if you try to see, if you try to draw the direction of the dipole or the vertical component of the dipole, you get something like a wave. So, if I am trying to draw the vertical component of the dipole, you will get something like this. So, it will be negative here zero here let us say because the vertical component is zero vertical component is downwards something like this. Here it is like this so vertical component is zero.
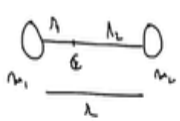
Vertical component is now upside, so you will get something like this, zero again, negative and zero again. And now if you try to match these points, you will end up getting a sine wave. So, what you have drawn here is vertical component of dipole. So, basically it tries to create some sort of a fluctuating electric field around it by doing this rotation. Now if you provide electromagnetic radiation, which is having same energy.

So, the two waves if they are having same energy they will tend to interact and, in that sense, that once this light is interacting it will cause a change in the rotational frequency or rotation of this molecule. So, thus any EM wave matching in frequency of this wave can couple to this rotation or rotational motion and interact through its electric component.

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Homo nuclear molecules → No dipole moment → No rotational spectrum

Use of rotational spectroscopy to determine bond length.

Center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2$$

The moment of inertia is defined by, a quantity that determines the torque needed for a desired angular acceleration.

$$I = m_1 r_1^2 + m_2 r_2^2$$

So, once you interact, there will be a change in rotational energy levels and if there is a change in rotational energy level populations, then you will see that there will be a rotational spectrum. So, if you see homo nuclear molecules, no dipole moment for example, H2 gas. There is no dipole moment and no rotational spectrum. So, a spectrum can come only if there is a permanent dipole moment that we have already seen.

So, now let us try to work out a formula where we can use rotational spectroscopy to determine the bond length of the molecule. So, use of rotational spectroscopy to determine bond length. So, we have defined center of mass, so, there was a center of mass somewhere in the middle I said let us call this a center of mass you have r 1 and r 2, m 1, m 2 and this whole distance is r. So, all the distances are from center of the atom.

Now center of mass how do you define where is the center of mass? Center of mass is defined by equating the moments on both segments of the molecular axis. What do I mean? So, I mean that we can say m1 r1 is equal to m2 r2. So, mass into the corresponding distance from center of

mass should be equal to mass into r2. So, if the two masses are equal r 1 will be equal to r 2 and hence it will come in the center.

If the two masses are not equal, it will be proportional to the masses. Also let us also see what is the moment of inertia like in here? So, the moment of inertia is defined by so, what is moment of inertia? It is a quantity that determines the torque needed for a desired angular acceleration. So, moment of inertia, let me write down it is a quantity that determines the torque needed for a desired angular acceleration.

Also, it is an additive property that means if there are multiple atoms in the molecule. So, moment of inertia about the center of mass will all be additive. So, that will give you the total moment of inertia of the molecule. So, what do I mean? So, it means m1 r1 square, so this is it is also called as second moment of mass first moment of mass (wrongly said as force, it is simply moment of mass) which is m1 r1 equal to m2 r2. The second moment of mass is moment of inertia, which is m1 r1 square plus m2 r2 square.

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So, as I said this is additive property and moment of inertia is calculated about the center of mass and it is calculated for all the atoms present in the molecule. So, here we are talking about a diatomic molecule. So, both the atoms will contribute to moment of inertia. Now we also know

m1 r1 equal to m2 r2, so I can always write it like this m2, r2, r1 + m 2 r 2 square, I am trying to decrease the number of variables here. So, I have substituted m 1 r 1 equal to m 2 r 2 here.

Since m 1 r 1 is equal to m 2 r 2 alright, sorry I can also do the same thing here m 1 r 1 r 2. So, now if I take r 1 r 2 outside, I will get m 1 + m 2 over here. Also, I can say m 2 r 2 = m 2 r - r 1. So, now I can substitute r 2, so let us see so, I can say in this equation m 1 plus m 2 into r 1 can be written as m 2 into r. So, then I can also say r 1 is equal to m 2 r divided by, so this is a basic algebra nothing fancy about it, so you are just playing around with two equations here, m 1 plus m 2. And similarly, r 2 can be written as m 2 r m 1 + m 2.

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So, now what do we have here? So, we will get now expression of I, can be now written as m 1 m 2 r square. So, I am trying to eliminate r 1 and r 2 here, so that we can get to the expression of bond length, so r upon m 1 + m 2, substituting these two into the top one r 1 and r 2 if I substitute you will get this. Now this can be written as mu r square, now what is mu here? Where mu is equal to m 1 m 2 divided by m 1 + m 2 or we can say 1 by mu is equal to 1 by m 1 + 1 by m 2 and it is also called as reduced mass.

So, I is equal to mu, basically now it looks like as if you have reduced the diatomic molecule into a mono atomic molecule tied to origin or rigid body without any mass. So, all the masses now concentrated into one body and the distances from origin. So, something similar to simple

pendulum case now. So, then we can say that the rotation of rotation of diatomic molecule is equivalent to rotation of a mass mu at a distance r from the origin C.

So, now there is no center of mass the whole thing is now concentrated about the single atom, so, we are reduced the problem to one way.

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The quantized rotational energy levels for this diatomic molecule is given

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{where } J \text{ is the total angular momentum quantum no.}$$

$$\Delta E = E_{J+1} - E_J = \frac{h^2}{8\pi^2 I}\left[(J+1)(J+2) - J(J+1)\right] = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

$$\bar{\nu} = \frac{h}{8\pi^2 I_c} 2(J+1) = B2(J+1)$$

$$\text{where } B \in \frac{h}{8\pi^2 I_c}$$

So, now again I am going to use the result of Schrodinger equation directly. I am not going to go into details of how do you get that. So, the quantized rotational energy levels for this diatomic molecule, the maths can be little boring but the end result is very fantastic. So, just bear with me a little more, is given by E J where J is the rotational level and E is the corresponding energy of the level is equal to h square upon 8 pi square I and J J + 1;

Where J is the total angular momentum quantum number. So, again, I am not going to go into those details. Now that transition between the two J levels is given by delta E, the energy difference between this is given by and the selection rules actually tell that the transition can only happen between two consecutive J levels. That is E J + 1, so you can only talk about these energy levels.

When you talk about E J + 1 to E J or E J + 2 to E J + 1 and so on so forth. So, for general case let us look at E J + 1 - E J which will be equal to, if you do this calculation, so you will have h

square upon 8 pi square I J + 1, J + 2. So, now I have instead of J I have written J + 1, so this becomes J + 1 this becomes J + 2 - J J + 1. And this can also be written as h nu or h c by lambda, which is the wavelength of the light which we are using, the microwave here.

It can also be called as h c nu bar. So, now we have this expression for delta E, so nu bar if we want to just talk about nu bar, so h c will come down, so you will have h upon 8 pi square I c and in the brackets here you have 2 J + 1. If you solve this you will get 2 J + 1, hc will come down, so you will get nu bar is equal to this. Now you can also write this as B times 2 J + 1 where B is equal to h upon 8 pi square Ic.

So, if you see that all of these are constants here. So, if you determine B you can determine I if you determine I you can determine r, which is the bond length. So, let us see how from spectroscopy you can determine the value of B for any given molecule.

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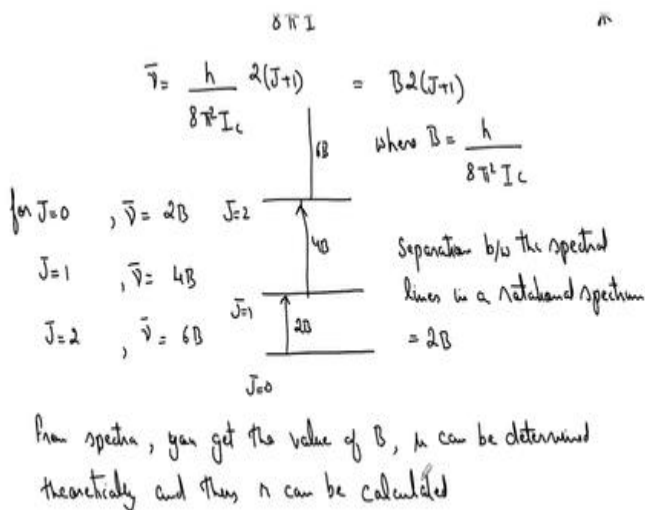
Not for any given molecule for molecules which will show a rotational spectrum. So, now for J = 0, the nu bar can be calculated as 2B J = 1 nu bar = 4B, J = 2, nu bar = 6B and so on. So, that means if you look at the transitions J = 0, J = 1, J = 2. So, this spectral line would come at 2 B nu bar number, nu bar is in centimeter inverse. So, this will come at 2 B difference so this can be obtained from like you can put in the value of J = 0 and then you will know this is 2 B.

Similarly, you will get 4B here and if you keep on going, we will get 6B and so on. So, separation between spectral lines in our rotational spectrum is equal to 2B. So, that means you can determine once you record a spectrum you will notice that the spectrum, the difference between the spectral lines will be equal to 2B, of course, we are talking about only pure rotational spectrum.

So, once you see that this difference is 2B, you can determine the value of B, once you have determined the value of B you can determine the value of I, the reduced mass can be determined by theoretical values. Because you know the mass of the atoms and hence the bond length can be determined just by looking at the rotational spectrum, so we can say from spectra you get the value of B, mu can be determined theoretically and thus r can be calculated.

So, this ends today's discussion of rotational spectroscopy. Next class, we will take up similar introduction of very brief introduction, this is no way a comprehensive introduction because this is not a spectroscopy course. So, we will give a brief introduction of vibrational and Raman spectroscopy. And then we will move to the application of group theory to spectroscopy, that is all for today. Thank you.