Fundamentals of Spectroscopy

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Lecture-13
Rotational spectroscopy: Diatomic Rigid Rotor

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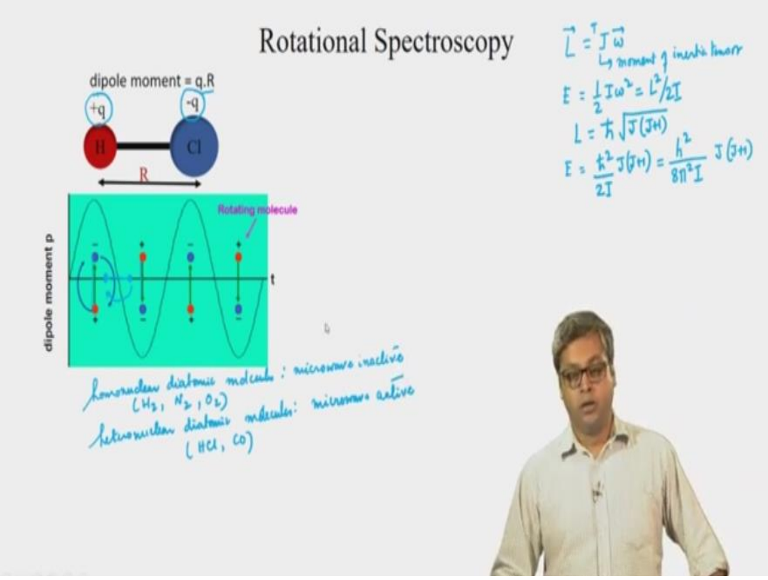

Rotational Spectroscopy

$\vec{L} = \overset{\leftrightarrow}{I}\vec{\omega}$

↳ moment of inertia tensor

$E = \frac{1}{2}I\omega^2 = L^2/2I$

$L = \hbar\sqrt{J(J+1)}$

$E = \frac{\hbar^2}{2I}J(J+1) = \frac{h^2}{8\pi^2 I}J(J+1)$

homonuclear diatomic molecule : microwave inactive
(H_2, N_2, O_2)

heteronuclear diatomic molecules: microwave active
(HCl, CO)

In the last lecture, we learned about the correspondence between linear and rotational motion. So, we have derived some important expressions related to rotation, we saw that L or the angular momentum which is a vector can be expressed as I omega and omega is a vector which is angular velocity and I is a tensor. So, I is known as the moment of inertia tensor. Also, we saw that energy can be expressed as half I omega square, or in terms of angular momentum, as L square / 2I.

So, we talked about the expression of energy. And we also mentioned that L is quantized and given by h cross root over J times J + 1. So the energy expression that we obtained for a diatomic rigid rotor is E = h cross square / 2I J times J + 1. That is h square / 8 pi square I J times J + 1, where J is the rotational quantum number. So, before we go into details of the rotational spectrum for a diatomic rigid rotor, let us get a physical understanding of the origin of this form of spectroscopy.

The primary condition for obtaining a rotational spectrum is the diatomic molecule should have a permanent dipole moment. So, let us consider a diatomic molecule for example, hydrogen chloride or HCL, which has a permanent dipole moment. So, here we have this HCL molecule and there is some partial positive charge on the hydrogen atom and some partial negative charge on the chlorine atom. And this hydrogen atom and the chlorine atom are separated by the inter nuclear distance which is given by R so, the dipole moment is given by this q.R.

So, we see that when this molecule rotates, and if the dipole moment is measured in a particular direction, let us say we are measuring the vertical component of the dipole moment, then this dipole moment or the vertical component of that dipole moment changes in a sinusoidal wave pattern. So, in other words, initially the HCL molecule was like this, then the rotation happens and the HCL molecules becomes parallel to the x axis, then it further rotates and it becomes again vertical.

So, we see, as the molecule rotates, the dipole moment is going through consecutive maxima and minima. So, because there is a wave pattern there is a frequency associated to it. So, if you remember, when we are discussing light or the electromagnetic wave, we defined wavelength and we defined frequency as the number of full wavelengths, but unit time. So, now, when we shine light or electromagnetic wave on this rotating molecule, the frequency of the light which resonates with the frequency of rotation is absorbed.

So, we can think this to be a form of resonance spectroscopy. The energy difference corresponding to the rotating frequency is equal to the energy gap between the rotational quantum levels. So, thus we can see that only hetro nuclear diatomic molecules like HCL because they are permanent dipole moment, they will have change of dipole during rotation. Hence, light matter interaction will take place.

On the other hand, if we think about homo nuclear diatomic molecules like hydrogen, nitrogen, oxygen, Etc. that do not have a permanent dipole moment. So, there is no change in dipole moment during the rotation. Hence, no light matter interaction happens, thus we can say that this homo nuclear diatomic molecules like hydrogen, nitrogen, oxygen, etc. These are microwaves inactive. On the other hand the hetro nuclear diatomic molecules like HCL carbon monoxide, they are microwave active.

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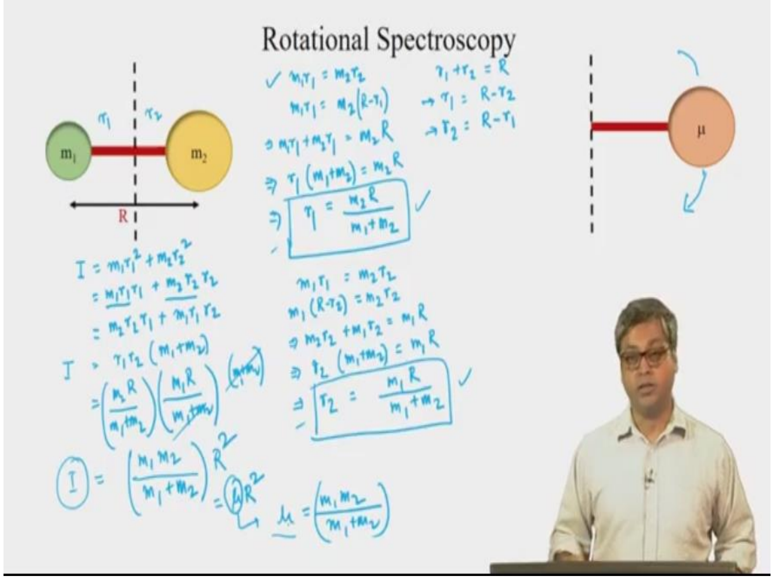

Rotational Spectroscopy

$\checkmark\ m_1 r_1 = m_2 r_2$

$m_1 r_1 = m_2 (R - r_1)$

$\Rightarrow m_1 r_1 + m_2 r_1 = m_2 R$

$\Rightarrow r_1 (m_1 + m_2) = m_2 R$

$\Rightarrow \boxed{r_1 = \frac{m_2 R}{m_1 + m_2}}\ \checkmark$

$r_1 + r_2 = R$

$\rightarrow r_1 = R - r_2$

$\rightarrow r_2 = R - r_1$

$m_1 r_1 = m_2 r_2$

$m_1 (R - r_2) = m_2 r_2$

$\Rightarrow m_2 r_2 + m_1 r_2 = m_1 R$

$\Rightarrow r_2 (m_1 + m_2) = m_1 R$

$\Rightarrow \boxed{r_2 = \frac{m_1 R}{m_1 + m_2}}\ \checkmark$

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

$= m_1 r_1 r_1 + m_2 r_2 r_2$

$= m_2 r_2 r_1 + m_1 r_1 r_2$

$I = r_1 r_2 (m_1 + m_2)$

$= \left(\frac{m_2 R}{m_1 + m_2}\right)\left(\frac{m_1 R}{\cancel{m_1 + m_2}}\right)\cancel{(m_1 + m_2)}$

$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) R^2 = \mu R^2$

$\mu = \left(\frac{m_1 m_2}{m_1 + m_2}\right)$

So, now going back to diatomic rigid rotor, so, where we have 2 masses m 1 and m 2 separated by the inter nuclear distance R such that the mass m 1 is r 1 distance away from the center of mass, and the mass m 2 is r 2 distance away from the center of mass. We saw in the last lecture that the moment of inertia I can be written as m 1 r 1 square + m 2 r 2 square. So, this molecule HCL or any other diatomic rigid rotor rotates end over end about the center of mass. And because it is rotating about the center of mass, we can write m 1 r 1 = m 2 r 2.

And also we can see from this figure that r 1 + r 2 = R. So, we can write r 1 = R - r 2 also, r 2 = R - r 1. So, now let us look into this equation m 1 r 1 = m 2 r 2. So you can write m 1 r 1 = m 2, so instead of r 2, we can use this expression for r 2, that is R - r 1. So if you accumulate all the terms, which has r 1, on the left hand side, we have m 1 r 1 + m 2 r 1 = m 2 R. So if you take r 1 common, I have m 1 + m 2 = m 2 R. Again, write r 1 = m 2 R / m 1 + m 2.

So this expression tells us we can express r 1 in terms of the masses m 1 and m 2, and the inter nuclear distance R. So similarly, let us start with the same equation m 1 r 1 = m 2 r 2. So now instead of putting r 2 = R - r 1, we will put r 1 = R - r 2. So I can write m 1 times R - r 2 = m 2 times r 2. So again, I can write m 2 r 2 + m 1 r 2 = m 1 R. So this will give us r 2 times m 1 + m 2 = m 1 R or r 2 = m 1 R / m 1 + m 2.

So now, we have obtained a similar expression for r 2 in terms of m 1 m 2 and R so why are we doing this? So we will see this. Now if we will go back to this expression for moment of inertia, I = m 1 r 1 square + m 2 r 2 square. So I can write this as m 1 r 1 times r 1 + m 2 r 2 times r 2 so we know that m 1 r 1 is m 2 r 2. So let us put this m 2 r 2 times r 1 + now here is the m 2 r 2 let us put m 1 r 1 that is m 1 r 1 times r 2.

So, we can write, I = if we take r 1 r 2 common m 1 + m 2. So, now, I have already derived expressions for r 1 and r 2. So let us put back this expression here. So r 1 I can write m 2 R / m 1 + m 2 for r 2 I will write m 1 R / m 1 + m 2 times m1 + m 2 so this will cancel out. So I will write I = m 1 m 2 / m 1 + m 2 times R square, which will write as mu R square, but this mu is the reduced mass of the system and mu is expressed as mu = m 1 m 2 / m 1 + m 2.

So, thus we can see, thus the system rotating around the center of mass is equivalent to the rotation of a single particle of mass mu, which is the reduced parts of the system. So, this single particle of mass mu is rotating around the center of mass. Why is this because when we are looking at this single particle rotation, we saw I or moment of inertia is given by m r square. So, here for a dynamic molecule the moment of inertia is given by mu r square, where mu is a reduced mass of the system.

So we can think as if the there is a single particle of mass mu is rotating around the center of mass with a radius the radius of this rotation is the inter nuclear distance or bond length that is given by R. So now, because we have found the relation between the moment of inertia and the reduce mass.

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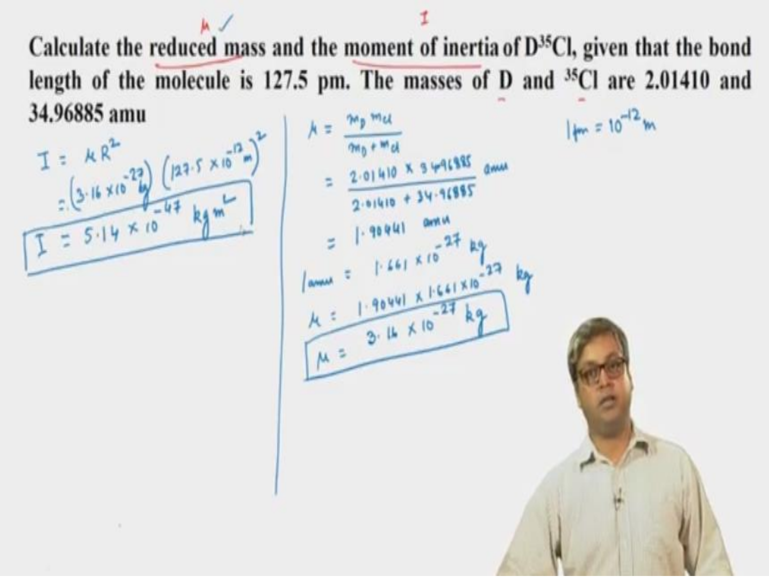

μ ✓ I

Calculate the reduced mass and the moment of inertia of $D^{35}Cl$, given that the bond length of the molecule is 127.5 pm. The masses of D and ^{35}Cl are 2.01410 and 34.96885 amu

$$I = \mu R^2$$
$$= (3.16 \times 10^{-27}\,kg)\,(127.5 \times 10^{-12}\,m)^2$$
$$\boxed{I = 5.14 \times 10^{-47}\ kg\,m^2}$$

$$\mu = \frac{m_D\, m_{Cl}}{m_D + m_{Cl}}$$
$$= \frac{2.01410 \times 34.96885}{2.01410 + 34.96885}\ amu$$
$$= 1.90441\ amu$$
$$1\,amu = 1.661 \times 10^{-27}\ kg$$
$$\mu = 1.90441 \times 1.661 \times 10^{-27}\ kg$$
$$\boxed{\mu = 3.16 \times 10^{-27}\ kg}$$

$$1\,pm = 10^{-12}\,m$$

Let us look into a problem where you need to calculate the reduced mass and the moment of inertia of a diatomic molecule. So, the problem is calculate the reduced mass that is mu. And the moment of inertia that is I of DCL. So given the bond length of the molecule is 127.5 Pico meter, the masses of D and CL are also given. So, first, let us find out the reduced mass, you know, mu = mass of D, and mass of CL / mass of D + mass of CL.

So let us put the values that is 2.01410 times 34.96885 divided by 2.01410 + 34.96885. So, this is in amu. So, if you do this calculation, the answer you will get is 1.90441 amu. And also, 1 amu = 1.661 times 10 to the power - 27 kilogram. So we can write mu = 1.90441 times 1.661 times 10 to the power - 27 kilograms 3.16 times 10 to the power - 27 kilogram. So, this is the answer to the first part where we needed to calculate the reduced mass so now, let us looking to the second part where we need to calculate, I or the moment of inertia which is given by mu R square.

So we have already calculated the mu that is 3.16 times 10 to the power - 27. This is in kg and R is 127.5 Pico meter. So we know 1 Pico meter equals 10 to the power - 12 meter to write 127.5 times 10 to the power - 12 meter square. And if you do this calculation, what you get is 5.14 times 10 to the power - 47 kilo gram meter square. So, now, we have found out the reduce mass and the moment of inertia of our diatomic molecule that is DCL. So, going back to the energy expression we saw for this diatomic rigid rotor.

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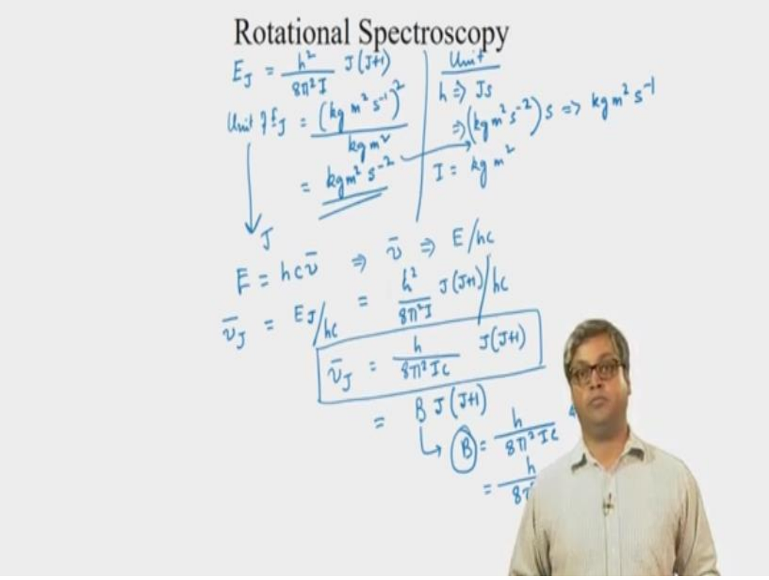

Rotational Spectroscopy

$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$

Unit

$h \Rightarrow Js$

$\Rightarrow (kg\,m^2 s^{-2}) s \Rightarrow kg\,m^2 s^{-1}$

$I = kg\,m^2$

Unit ? $E_J = \frac{(kg\,m^2 s^{-1})^2}{kg\,m^2}$

$= \underline{\underline{kg\,m^2 s^{-2}}}$

$\downarrow J$

$E = hc\bar{\nu} \Rightarrow \bar{\nu} \Rightarrow E/hc$

$\bar{\nu}_J = E_J/hc = \frac{h^2}{8\pi^2 I} J(J+1)/hc$

$$\boxed{\bar{\nu}_J = \frac{h}{8\pi^2 Ic} J(J+1)}$$

$= B J(J+1)$

$\hookrightarrow B = \frac{h}{8\pi^2 Ic}$

We can write E J for the J is rotation level = h square / 8 pi square I J times J + 1. So the unit of energy here is injured. So let us see how do get this unit. So the unit of h is Joule second, so, 1 joule is given by kilogram meter square s to the power - 2. So, unit of h is kilogram meter square s to the power - 2 times seconds, that is kilogram meter square s to the power - 1 and also the unit of I, as we saw in the last problem is kilogram meter square.

So, this J is a rotational quantum number, it has no unit and all the other things by an either constant, so, the unit of E J is kilogram meters square s to the power - 1 square divided by kilo gram meter square. So, this you will see it will be kilogram meter square s to the power - 2. So, this is the same as this. So, the unit of energy here is a joule. So, now, we have already discussed in module 1, that it is more convenient to express energies related to rotational spectroscopy in wave number units or centimeter inverse.

So, we know that E = h c nu bar therefore, from this we can write nu bar = E / hc. So, we already have the energy expression in joule. Now, if you want the energy expression in wave number that is nu bar J, I can write this equals EJ / hc, that is h square / 8 pi square I J times j + 1 divided by hc. And that is nu bar J is h / 8 pi square I c J times J + 1. So, this expression we got for the energy in wave number units.

This can also be written as B times j times J+1 where B = h / 8 pi square I c and as we expand I has mu r square I can write h / 8 pi square mu r square c. So, B is known as the rotational constant and the unit of B is centimeter inverse or wave numbers. So, we can see that B is inversely proportional to I and also I is proportional to the square of the bond length. Thus determination of B from the spectroscopy experiments will result in the determination of inter nuclear distances.

That is R or the bond length and thus, rotational spectroscopy represents a very powerful structure technique. So, as bond length or inter nuclear distance can be determined with high precision from microwave spectroscopy let us illustrate this using an example.

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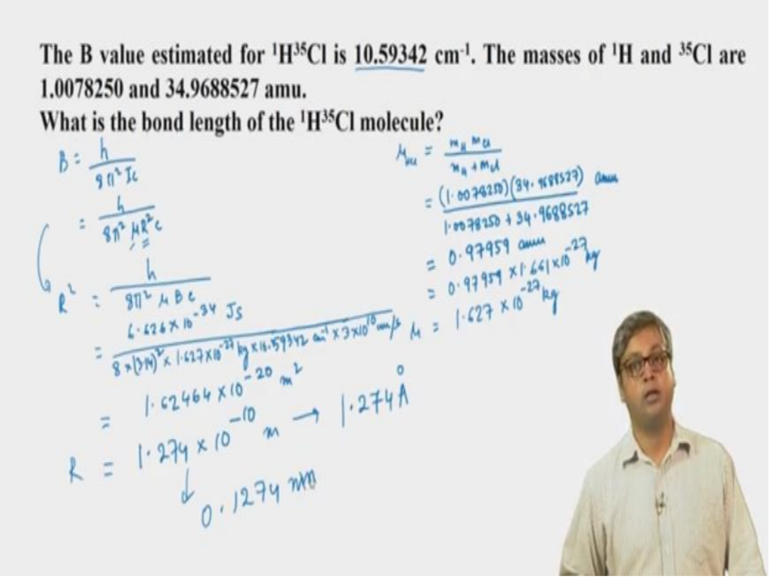

The B value estimated for $^{1}H^{35}Cl$ is 10.59342 cm^{-1}. The masses of ^{1}H and ^{35}Cl are 1.0078250 and 34.9688527 amu.
What is the bond length of the $^{1}H^{35}Cl$ molecule?

$$B = \frac{h}{8\pi^2 I c}$$

$$= \frac{h}{8\pi^2 \mu R^2 c}$$

$$R^2 = \frac{h}{8\pi^2 \mu B c}$$

$$= \frac{6.626\times10^{-34}\ Js}{8\times(3.14)^2\times1.627\times10^{-27}\ kg\times10.59342\ cm^{-1}\times3\times10^{10}\ cm/s}$$

$$= 1.62464\times10^{-20}\ m^2$$

$$R = 1.274\times10^{-10}\ m \rightarrow 1.274\ \mathring{A}$$

$$\downarrow$$

$$0.1274\ nm$$

$$\mu_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$$

$$= \frac{(1.0078250)(34.9688527)}{1.0078250 + 34.9688527}\ amu$$

$$= 0.97959\ amu$$

$$= 0.97959\times1.661\times10^{-27}\ kg$$

$$\mu = 1.627\times10^{-27}\ kg$$

So, the question we have is the B value estimated for HCL is 10.59342 and here again the masses of hydrogen and chlorine are given in atomic mass units or amu. So, we have to find out the bond length of this diatomic molecule HCL. So, first we see that B = h / 8 pi square I c. Or in other words, equals h / 8 pi square mu R square c so, in this particular problem, we have to find this r are the bond length of the HCL molecule.

So, for this, we need to find the reduced mass. And we already know the value of B so from there, we can get the value of R so, let us try to find the reduced mass here. So, mu of HCL is given by m H m cl divided by m H + m cl. So this is 1.0078250 times 34.9688527 divided by 1.0078250 + 34.9688527. This is an atomic mass units and if you do this, you get the answer in that is 0.97959 amu, and in kgs we can write this is 0.97959 times 1.661 times 10 to the power - 27 kilograms.

So that is 1.627 Times 10 to the power - 27 kilograms so this is our reduced mass. So from this, I can write R square equals 8 / 8 pi square mu B times c. So let us put the values, the value of h is 6.626 times 10 to the power - 34 joule seconds divided by 8 times 3.14 square, times reduce mass, it is 1.627 times 10 to the power - 27 kilo gram the value of B is given that is 10.59342 centimeter inverse and we can write C as 3 times 10 to the power 10 centimeter per second.

So, if you do this the value of R square that you will get is 1.62464 times 10 to the power - 20 meter square. And if you take the square root of this then R becomes 1.274 times 10 to the power - 10 meter. So, you can either expresses as 1.274 angstroms or we can say this is 0.1274 nanometers. So once we know about the energy expression, we can put different values of J to find the energies of this different energy levels. So first when J = 0, we know the energy 0, so we can say the molecule is not rotating at all.

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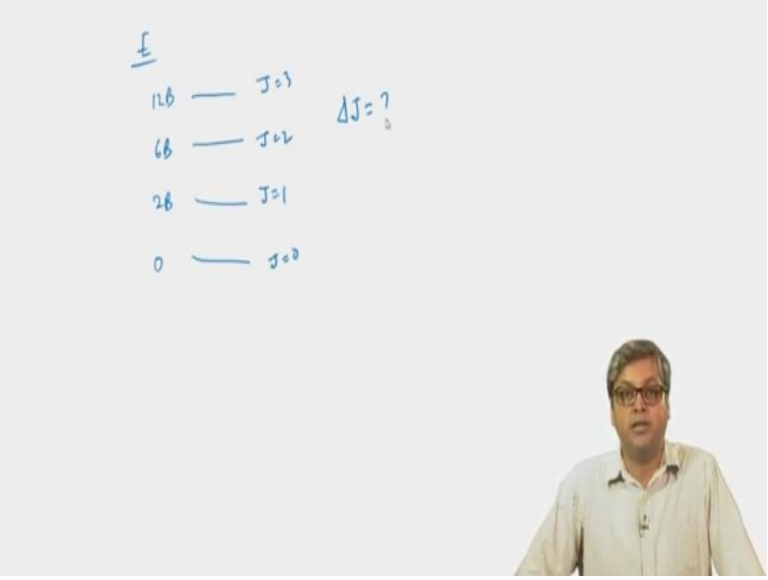

The other energies, for example, when J = 1, J = 2, J = 3. So the energies for J = 0 it was 0. When J = 1 its 2B J = 2 its 6B, and J = 3 its 12B, and so on and so 4th. So we can continue to calculate energies with increasing J values and in principle there is no limit to that rotational energy the molecule can have at normal temperatures. So, so far, we have learned about the expression of energy in joules and centimeter inverse.

We have also learned about the energy associated with each rotational level in order to obtain a rotational spectrum transitions should happen from one energy level to another. So, we have to ask the question now, between which levels can the transition take place, can we get peaks corresponding to transitions between any 2 J levels? So, in other words, the question is what change in rotational quantum number J is allowed for a rotational spectrum. In other words, what should be the allowed value of delta J.

So because we know the energies of each level, if we know what delta J is allowed for a diatomic rigid rotor with permanent dipole moment. We would have an idea about the rotational spectrum. To answer this, we need to know the selectional rules of rotational spectroscopy. So in the next lecture, we will discuss in details about the selectional rules of rotational spectroscopy.