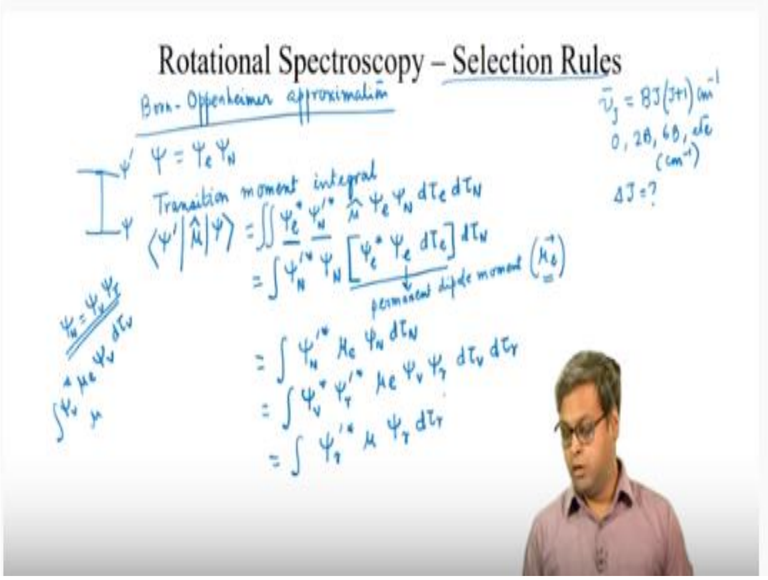
# Fundamentals of Spectroscopy

**Prof. Dr. Sayan Bagchi,**
**Physical and Materials Chemistry Division,**
**National Chemical Laboratory - Pune**

**Prof. Dr. Anirban Hazra,**
**Department of Chemistry,**
**Indian Institute of Science Education and Research – Pune**

## Lecture-14
## Rotational Spectroscopy: Selection Rules and Rotational Spectrum

**(Refer Slide Time: 00:16)**



Rotational Spectroscopy – Selection Rules

Born-Oppenheimer approximation

$\Psi'$

$\Psi$

$\Psi = \Psi_e \Psi_N$

Transition moment integral

$\langle \Psi' | \hat{\mu} | \Psi \rangle = \iint \Psi_e^* \Psi_N'^* \hat{\mu} \Psi_e \Psi_N \, d\tau_e \, d\tau_N$

$= \int \Psi_N'^* \Psi_N \left[ \Psi_e^* \Psi_e \, d\tau_e \right] d\tau_N$

permanent dipole moment $(\vec{\mu}_0)$

$= \int \Psi_N'^* \mu_e \Psi_N \, d\tau_N$

$= \int \Psi_v^* \Psi_r'^* \mu_e \Psi_v \Psi_r \, d\tau_v \, d\tau_r$

$= \int \Psi_r'^* \mu \Psi_r \, d\tau_r$

$\Psi_N = \Psi_v \Psi_r$

$\int \Psi_v \hat{\mu}_e \Psi_v \, d\tau_v$

$\mu$

$\bar{\nu}_J = BJ(J+1) \text{ cm}^{-1}$

0, 2B, 6B, etc
(cm$^{-1}$)

$\Delta J = ?$

In the last lecture, we obtained a physical understanding of the origin of rotational spectroscopy. We saw that the energy of the J level that is, nu bar J can be expressed as B times J times J + 1 centimeter inverse, where B is the rotational constant, and J is the rotational quantum number. We can write the energies of the different rotational levels as 0, 2B, 6B, etcetera and these again are in wave numbers.

So, now, as we have discussed, we can only get a rotational spectrum when a transition happens, we have to ask the question between which levels can the transition take place? In other words, the question is what change in rotational quantum number is allowed for a rotational transition or what is the allowed value of delta J? To answer this, we need to know the selection rules of rotational spectroscopy.

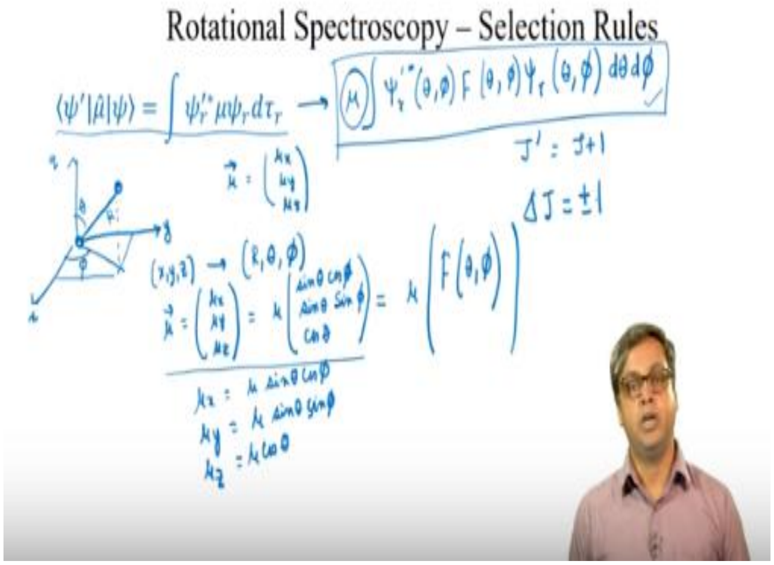
So, according to Born Oppenheimer approximation so, we can write the wave function of the molecule that is psi as products of the electronic wave function that is psi e and the nuclear wave function that is psi N and so, for a rotational transition, the electronic state does not change thus if the initial state is psi and the transition happens to a final state that is psi prime we are interested in the Transition moment integral which can be written as psi prime the dipole moment operator  psi and if we expand this integral.

We can write as psi e star psi N prime star dipole moment integral psi e psi N d tau e d tau N. So, we should remember as in the rotational transition, the electronic state does not change. So, we write this as psi e star. However, because the nuclear state changes we right psi N prime star. So, we can further write this integral as psi N prime star psi N and then bracket will write psi e star psi e d tau e d tau N.

So, the quantity in the bracket is the permanent dipole moment or mu e corresponding to the electronic state psi e since both psi e and the dipole moment operated depend on the nuclear configuration the dipole moment vector mu e depends also on the nuclear configuration. So, now, we can write the nuclear wave function as the products of the vibrational and rotational wave function. So, we can write psi N = psi v psi r.

So, if we write that, so, first of all here, because this is that permanent dipole moment, we can write this expression as psi N prime star mu e psi N d tau N. So now, we will write Psi N as a product of psi v and psi r. So we will write psi v star psi r prime star mu e psi v psi r d tau v d tau r. So the integral over the vibrational coordinates that is integration of psi v star mu e psi v d tau v this integral is the permanent dipole moment mu in that particular vibrational state. So, we can further right expression as psi r prime start mu psi r d tau r.

**(Refer Slide Time: 06:41)**



Rotational Spectroscopy – Selection Rules

$$\langle\psi'|\hat{\mu}|\psi\rangle = \int \psi_r'^{*}\mu\psi_r d\tau_r \rightarrow \boxed{\textcircled{\mu}\int \psi_r'^{*}(\theta,\phi)F(\theta,\phi)\psi_r(\theta,\phi)\,d\theta\, d\phi}$$

$$J' : J+1$$

$$\Delta J = \pm 1$$

$$\vec{\mu} = \begin{pmatrix}\mu_x\\ \mu_y\\ \mu_z\end{pmatrix}$$

$$(x,y,z) \rightarrow (R,\theta,\phi)$$

$$\vec{\mu} = \begin{pmatrix}\mu_x\\ \mu_y\\ \mu_z\end{pmatrix} = \mu\begin{pmatrix}\sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta\end{pmatrix} = \mu\begin{pmatrix}F(\theta,\phi)\end{pmatrix}$$

$$\mu_x = \mu\sin\theta\cos\phi$$
$$\mu_y = \mu\sin\theta\sin\phi$$
$$\mu_z = \mu\cos\theta$$

So, now, we have this transition moment integral in this form that is integration of psi r prime star mu psi r d tau r. So, let us now draw this diatomic molecule in the xyz axis. So, this is our x axis, this is our y axis and this is our z axis. So, due to symmetry, the dipole moment is oriented along the inter nuclear distance R.

So, we can write this factor mu as mu x, mu y, mu z. If we change the coordinate access from Cartesian coordinates to polar coordinates, that is from x y, z to R theta phi where this angle is theta and if we take a projection this angle is phi and the internal distance is R. So, if you make this axis transformation and solve the angular integral, we can write that mu vector = mu x mu y mu z, we can write this as mu times sin theta cos phi sin theta sin phi and cos theta.

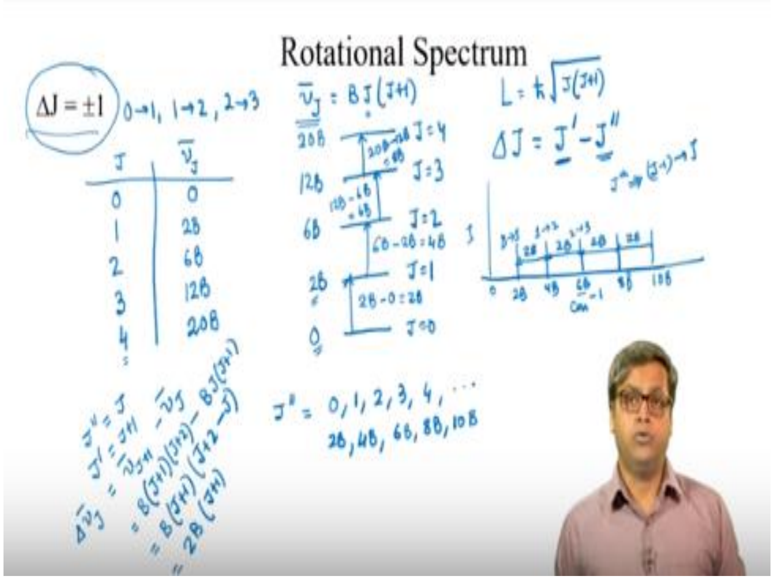
In other words, mu x = mu sin theta cos phi mu y = mu sin theta sin phi and mu z = cos theta. So, the magnitude of mu depends on the inter nuclear distance R and because we can write this way on in other words, we can also write like mu, then some function of theta and phi. So, this integral now becomes a mu integration of psi r prime star which is a function of theta and phi. Then we have this function of theta

And phi that is the angular part of the dipole moment psi r the function of theta and phi d theta d phi. So, this is the final form that we obtained. The molecule has a rotational spectrum only if this integral is nonzero, thus the grace selection rule for obtaining a rotational spectrum is that the molecule must have a permanent dipole moment. Because, if this mu becomes 0, then the whole integral becomes 0.

So, they should have or the molecule should have a permanent dipole moment to emit or absorb radiation in making a transition between different states of rotation. This is expected as we saw before our rotating dipole produces an oscillating electric field that can interact with the oscillating field of the light wave thus mononuclear diatomic molecules which do not have a permanent dipole moment, do not show rotational spectrum.

The dipole moment as we know is oriented along the inter nuclear axis of the diatomic molecule. It can be shown that in absence of an external electric or magnetic field, the integral is only nonzero if J prime = J + 1 where J prime is the rotational number associated with the final quantum state and J is the rotational number associated with the initial state does the selection rule for changes in rotational quantum numbers for a diatomic molecule is delta J = plus minus 1.

**(Refer Slide Time: 12: 20)**



Rotational Spectrum

| $J$ | $\bar{\nu}_J$ |
|---|---|
| 0 | 0 |
| 1 | 2B |
| 2 | 6B |
| 3 | 12B |
| 4 | 20B |

So, now, let us look into the transitions observed in the rotational spectrum of a diatomic rigid rotor with a permanent dipole moment. Since, the selection rule is delta J = plus or minus 1 transitions like 0 to 1, 1 to 2, 2 to 3 and so on and so 4th are allowed. So, first let us look again into the energies of the different rotational energy levels. So, we know that nu bar J = B J times J + 1. So now, let us make a table for the energies associated with different values of J.

So let us make a table where we are putting J in 1 column and nu bar J the other column. So let us say J = 0 1 2 3 4. So nu bar J is 0. For J = 1 this is 2B for J = 2. If I put the value of J = 3 was to in this equation, we will get 6 B for J = 3, we get 12B for J = 4, we get 20B. So if you want to visualize this, in terms of an energy level diagram, we can show let us draw this energy levels so this is J = 0.

This is J = 1, J = 2, J = 3 J = 4 and let us write the energies so this is 0. This is 2B for J = 2 it is 6 B for J = 3 is 12B and for J = 4 it is 20 B so we are only drawing up to J = 4 but we can have J = 5 6 7 8 so on and so. So for J = 0, we have the energy to be 0 or we can say that the molecule is not rotating at all. This is because the angular momentum which is given by L = H cross route over J times J + 1.

That angular momentum for J = 0 is 0. For J = 1, the energy is 2B, and a rotating molecule has its lowest angular momentum, or the molecule is rotating with the lowest angular velocity. As transitions happen from one energy level to another, we can think that a rotational transition will happen from an energy level with an associated quantum number J to another level with an associated quantum number J + 1.

So this is due to the selection rule, delta J = plus or minus 1 thus the spectral line correspond to energy difference of any to 2 adjacent rotational energy levels involved in the transition. So, conventionally, delta J is referred to J prime minus J double prime, but J prime is the quantum number of the upper state or the state with higher energy or the final state. And J double prime is the quantum number associated to the lower state or the state with less energy.

So now, we consider differences between that adjacent levels in order to discuss the rotational spectrum. So, if we imagine the molecule to be in J = 0 level, we can let the incident light to be absorbed to raise it to the J = 1 level. So the energy absorbed in wave numbers will be for this transition J = 0 to 1, the energy absorbed will be 2B - 0, that is 2B wave numbers. If now the molecule is raised from J = 1 to J = 2B absorption of more energy, we see that the energy of the incident light absorbed is 6B - 2B that is, 4B.

So in general, for a rotational transition from J double prime = J to J prime = J+1, we can right delta nu bar J this is given by nu bar J+ 1 - nu bar J that is B J + 1 times J +2 - B J times J+1. So, this is if we take B and J + 1 common, we have J + 2 - J that is 2B times J +1. So, this is the general formula we have for rotational transition. So, if we have let us say, J double prime equals 0 1 2 3 4 …. The absorption of radiation will happen.

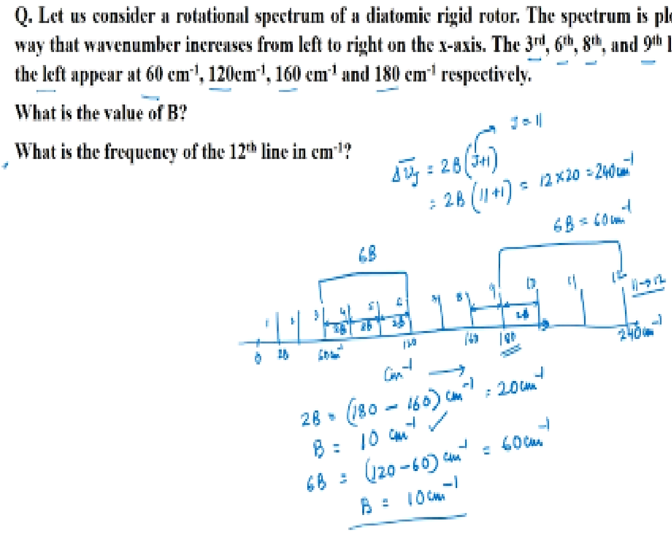
At 2B, 4B, 6B, 8B, 10B and so on. So if we now try to plot a rotational spectrum, what we will have will have centimeter inverse and the x axis. So, we are plotting, so we have some intensity on the y axis. So let us say this is 0. So we have 1st transition at 2B the 2nd transition 4B the 3rd transition of 6B the 4th transition at 8B the 5th transition at 10B and so on. So, this 1st transition comes from 0 to 1 transition, the 2nd line comes from 1 to 2. 3rd line comes from 2 to 3.

So, we can see, the jet line comes from the jet line in the spectrum comes from the transition of J minus 1 to J. In other words, a step wise rising of the rotational energy levels results in an absorption spectrum of lines at 2B, 4B, 6B, 8B etc. centimeter inverse. This can also be shown in the diagram. So, we have only shown up to 1 2, J = 1 to J = 2. Now, if you think about the transition from J = 2 to J = 3. The energy difference is 12B – 6 B this is 6 B.

So, we have the 3rd line at 6B, the 4th line, the energy difference is 20B - 12B that is 8B. So thus we should observe successive lines in the rotational spectrum, which are given by 2B, 4B, 6B does there is a series of lines spaced by a constant amount and the constant separation is equal to 2B. So, you can see 4B - 2B is 2B, 6B – 4B is 2B, 8B – 6B is 2B, 10B – 8B is 2B so the constant separation is 2B centimeter inverse.

That is from a rotational spectrum, we can find the value of B and from B we can estimate the value of the bond length or inter nuclear distance using the relation between moment of inertia I and that bond length R. So, let us look into a few problems to understand this concept.

**(Refer Slide Time: 22:20)**



Q. Let us consider a rotational spectrum of a diatomic rigid rotor. The spectrum is plotted in a way that wavenumber increases from left to right on the x-axis. The 3rd, 6th, 8th, and 9th lines from the left appear at 60 cm$^{-1}$, 120cm$^{-1}$, 160 cm$^{-1}$ and 180 cm$^{-1}$ respectively.

What is the value of B?

What is the frequency of the 12th line in cm$^{-1}$?

$$\Delta\bar{\nu}_J = 2B(\overset{J=11}{J+1})$$
$$= 2B(11+1) = 12\times20 = 240\,cm^{-1}$$

$6B = 60\,cm^{-1}$

$$2B = (180-160)\,cm^{-1} = 20\,cm^{-1}$$
$$B = 10\,cm^{-1}\ ✓$$
$$6B = (120-60)\,cm^{-1} = 60\,cm^{-1}$$
$$\underline{B = 10\,cm^{-1}}$$

So, we have the first problem here, let us consider a rotational spectrum of a diatomic rigid rotor. The spectrum is plotted in a way that wave number increases from left to right on the x axis. So, from left to right, the wave number increases. The question says the 3rd, the 6th, the 8th and the 9th lines from the left appear at 60,120,160 and180 wave numbers respectively. So, let us say this is our 0. So, our 1st line is a 2B. So we have 2nd line. This is 1st this is 2nd to this my 3rd line, my 4th line. This is my 5th line, 6th line, 7th, 8th, and 9th line.

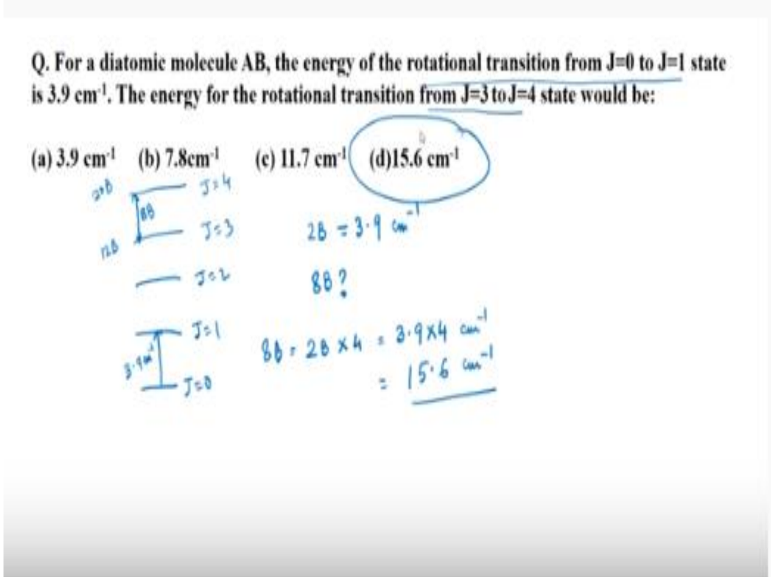
So the 3rd line appears at 60 wave numbers, the 6th line at 120 wave numbers, the 8th line at 160 wave numbers and the 9th line as at 180 wave numbers. So the 1st question we should solve is what is the value of B. So we know that any consecutive lines they are separated by 2B so we know that we have some data for these 2 consecutive lines. That is the 8th line and the 9th line. So we can write, 2B =180 – 160 wave numbers, that is 20 wave numbers. So B is 10 wave numbers.

So if you want to cross check this answer, let us say, 3rd to 4th line is separated by 2B, 4 to 5th by 2B, and 5th to 6 by 2B. So the separation between the 3rd and the 6th line is 6B. So we can also put 6B = 120 – 60 wave numbers, that is 60 wave numbers. So if you solve this again, we get B = 10 wave numbers. So we can just make sure our earlier result was right. And the value of the rotational constant B that we need to find out is 10 wave numbers.

So, the 2nd question is, what is the frequency of the 12th line in wave numbers? So, let us draw the 12th line. So, we have 9th line then the 10th 11th 12th. So, because everything is separated by 2B, so from 9 to 12, it is separated by 6B or 60, wave numbers. So we can say, if 9th line is 180 wave numbers, then the 12th line will be 240wave numbers. So we can also get this answered in a different way.

So we have seen that the delta nu bar J is 2B times J +1. That 12th line comes from the transition from the 11th to 12th level. So here, J = 11 this delta nu bar J = 2B times 11 + 1 that is 12 times 20. That is 240 wave numbers. So now let us look into another problem.

**(Refer Slide Time: 26:47)**



Q. For a diatomic molecule AB, the energy of the rotational transition from J=0 to J=1 state is 3.9 $cm^{-1}$. The energy for the rotational transition from J=3 to J=4 state would be:

(a) 3.9 $cm^{-1}$ (b) 7.8 $cm^{-1}$ (c) 11.7 $cm^{-1}$ [✓ (d) 15.6 $cm^{-1}$]

$2B = 3.9\ cm^{-1}$

$8B$?

$8B = 2B \times 4 = 3.9 \times 4\ cm^{-1}$

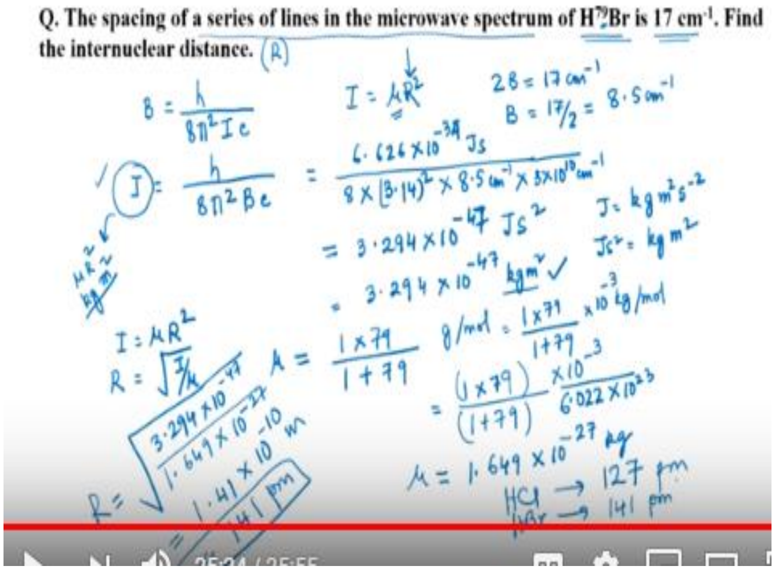
$= \underline{15.6\ cm^{-1}}$

So the next question that we have is for a diatomic molecule, AB the energy of the rotational transition from J = 0 to J = 1 state is 3.9 wave numbers. The energy of the rotational transition from J = 3 to J = 4 would be. So this is a multiple choice questions, we have 4 options. So let us look into the problem again. So J = 0. This draw the energy levels J = 1, J = 2, J = 3, J = 4. So what is given is from J = 0 to J = 1 the energy for the rotational transition, so this is 3.9 wave numbers.

So we know this J = 0 to 1, this is given by 2B so 2B = 3.95 wave number. So for J = 3, the energy is 12B, and for J = 4, the energy is 20 B. So the energy required for this transition is 8 B. So we have to find the energy for the rotational transition from 3 to 4. That means, we have to find what is the value of 8B is. So if 2B = 3.9 very easily we can say 2B times for that is 8B =

3.9 times 4 this is in wave numbers, that is 15.6 wave numbers. So, this is our answer and this matches with the option D. So, let us look into another problem.

**(Refer Slide Time: (29:02))**



Q. The spacing of a series of lines in the microwave spectrum of $H^{79}Br$ is 17 $cm^{-1}$. Find the internuclear distance. (R)

$$B = \frac{h}{8\pi^2 I c} \qquad I = \mu R^2 \qquad 2B = 17\ cm^{-1} \qquad B = 17/2 = 8.5\ cm^{-1}$$

$$I = \frac{h}{8\pi^2 B c} = \frac{6.626\times10^{-34}\ Js}{8\times(3.14)^2\times 8.5\ cm^{-1}\times 3\times10^{10}\ cm^{-1}}$$

$$= 3.294\times10^{-47}\ Js^2 \qquad J = kg\,m^2 s^{-2}$$

$$= 3.294\times10^{-47}\ kg\,m^2 ✓ \qquad Js^2 = kg\,m^2$$

$$\mu R^2 \quad kg\,m^2$$

$$\mu = \frac{1\times79}{1+79}\ g/mol = \frac{1\times79}{1+79}\times10^{-3}\ kg/mol = \frac{(1\times79)}{(1+79)}\ \frac{\times10^{-3}}{6.022\times10^{23}}$$

$$\mu = 1.649\times10^{-27}\ kg$$

$$I = \mu R^2 \qquad R = \sqrt{I/\mu}$$

$$R = \sqrt{\frac{3.294\times10^{-47}}{1.649\times10^{-27}}} = 1.41\times10^{-10}\ m = \boxed{141\ pm}$$

HCl → 127 pm
HBr → 141 pm

This problem says the spacing of a series of lines in the microwave spectrum of H Br is 17 wave numbers. So, we have to find the inter nuclear distance R so, as we already know by now, we can read B = h divided by 8 pi square I c, we also know for a diatomic molecule we can right I = mu r square, when mu with the reduce mass. So, we have to find the interdictor distance R and all we know is the spacing between a series of lines.

So we know the spacing is given by 2B, so 2B = 17 wave numbers, or B = 17 divided by 2 = 8.5 wave numbers. So we know the value of B. So we can right I = h divided by 8 pi square B times C. So if we put the value h is 6.626 times 10 to the power - 34 joule second divided by 8 times 3.14 square, and then we put the value of B that is 8.5 centimeter inverse and the value of C as 3 times 10 to the power 10 centimeter inverse. So, this becomes 3.294 times 10 to the power – 47 joule, second square.

So, because joule is kilogram meter square secondary power - 2, then joule second square equals kilogram meter square. So we can write this as 3.294 times 10 to the power - 47 kilogram meter square and this unit is right because we are finding out the value of I, I is moment of inertia, that is mu r square. So if you look into the unit, this is kg. This is an RS distance kilogram meter square. So, we found the right unit.

Now, we have found the value of I. So, because I = mu R square, so we can rate R equals root over I / mu. So, we know the value of I, but we do not know the value of mu. So, let us find out the value of mu. So, mu = 1 times 79 divided by 1 + 79, the unit is kilogram per mole. So we can write this as 1 time 79 divided by 1 + 79 10 to the power - 3 kilograms per mole. And because in 1 mole there Avogadro's number of molecules.

So we can write this as 1 times 79 divided by 1 + 79 times 10 to the power -3 divided by the Avogadro number that is 6.022 times 10 to the power 23. So if we do this calculation what we will get is 1.649 times 10 to the power - 27 kg. So, we now know the value of mu. So, we can write R that we need to find out is root over 3.294 times 10 to the power - 47 divided by 1.649 times 10 to the power - 27 so this becomes 1.41 times 10 to the power -10 meter so, that is 141 Pico meter.

So, the answer is R = 141 Pico meters. So, we should remember one thing in the last class, we found out the bond length of each CL and that was 127 Pico meter. Today we found out the bond length HB R and the bond length is 141 Pico meter. So from the rotational data, we can find out accurate bond length and we can see the bond length of HB R as expected is larger than the bond length of it CL.