Fundamentals of Spectroscopy

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Lecture-18

Non Rigid Rotor

Hello all welcome to this lecture so far in all the lectures on rotational spectroscopy we have discussed or focused on diatomic molecule whose bond is rigid. But now we will relax that condition but the question is why would I need to relax that condition? This is because we know bonds are not rigid we know molecules vibrate for instance but what is going to happen to a molecule as it rotates faster and faster.

Intuitively we can say that the bond length will get longer and longer but why would the bond lengths get longer as the molecule rotates faster?

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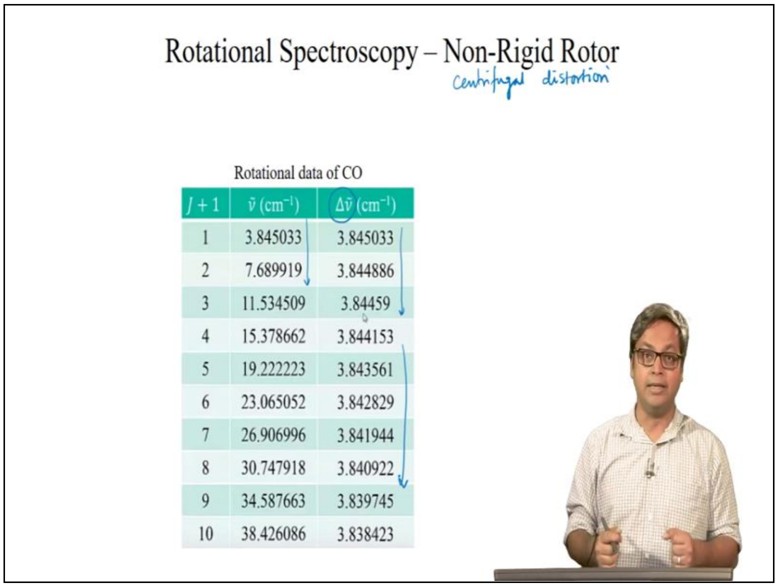

Rotational Spectroscopy – Non-Rigid Rotor

centrifugal distortion

Rotational data of CO

$J+1$	$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
1	3.845033	3.845033
2	7.689919	3.844886
3	11.534509	3.84459
4	15.378662	3.844153
5	19.222223	3.843561
6	23.065052	3.842829
7	26.906996	3.841944
8	30.747918	3.840922
9	34.587663	3.839745
10	38.426086	3.838423

This is due to centrifugal Distortion centrifugal distortion but does this centrifugal distortion going to affect the rotational spectrum? To answer this let us look into the real experimental data from carbon monoxide rotational spectrum here the frequencies of each lines are given and in this last column we have the frequency gap between that just in lines. We see that the gaps are steadily decreasing or rather we can say that the gaps are more rapidly decreasing as we go to higher and higher T. This happens because the bond length is changing.

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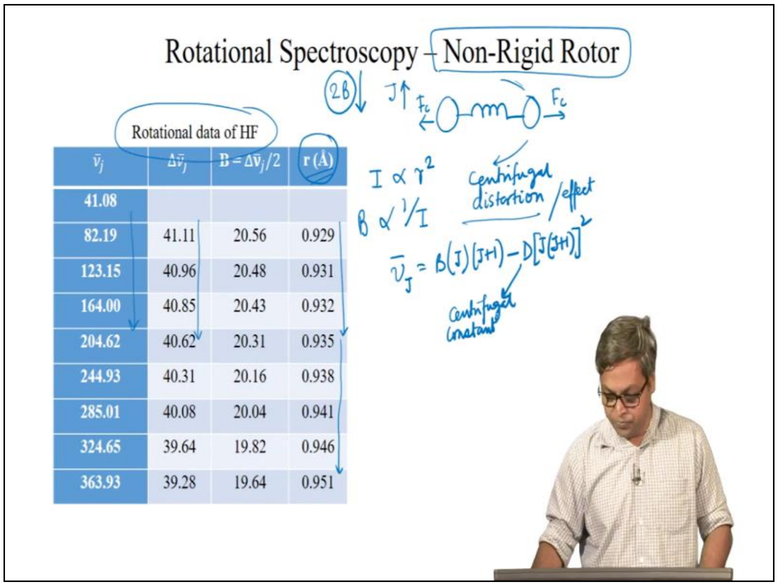

Rotational Spectroscopy – Non-Rigid Rotor

Rotational data of HF

$\bar{\nu}_j$	$\Delta\bar{\nu}_j$	$B = \Delta\bar{\nu}_j/2$	r (Å)
41.08			
82.19	41.11	20.56	0.929
123.15	40.96	20.48	0.931
164.00	40.85	20.43	0.932
204.62	40.62	20.31	0.935
244.93	40.31	20.16	0.938
285.01	40.08	20.04	0.941
324.65	39.64	19.82	0.946
363.93	39.28	19.64	0.951

$2B \downarrow \quad J \uparrow$

$I \propto r^2$

$B \propto 1/I$

Centrifugal distortion / effect

$$\bar{\nu}_J = B(J)(J+1) - D[J(J+1)]^2$$

Centrifugal constant

So, let us look into more details in another set of data obtained from the rotational spectrum of HF, here also we see the same trend in the frequencies and the frequency gaps between the all the lines. So, here we can see the separation between the successive lines change with change because the apparent separation between two lines is given by 2B. We can think that the rotational constant that is B is decreasing as J is increases or we can say the 2B or B is decreasing as J increases.

So why is the energy difference decreasing with increasing J we can get some hint if we look into the last column which shows the; inter nuclear distance. We can see a steady increase in the inter nuclear distance with increasing T. In other words we can say that the molecule is not strictly rigid as we can see that the bond length increasing or the bond length increases with increasing J. Thus our more accurate description of the diatomic molecules is to consider them as non rigid rotors.

Such that the atoms are connected by a spring as the molecule rotates the atoms experiences centrifugal force, so the atoms I am showing here that terms are experiencing centrifugal force.

And as the speed of the rotation increases that is as the value of J increases the nuclei are thrown outwards by a larger centrifugal force increase in the bond length at higher J levels due to the centrifugal force results in the decrease of B or the rotational constant.

Because we know that if the bond length is larger and we know the moment of inertia is proportional to the square of the internuclear distance. So, as the internuclear distance increases the moment of inertia increases and as the moment of inertia is inversely proportional to the rotational constant that means as I increases B becomes smaller. So, it is not surprising that the gap is getting smaller and smaller as J increases this effect is known as, as I said before this distortion is known as centrifugal distortion or centrifugal effect.

So, qualitatively we can think that the bond length depends on which rotational level the molecule is in this is because the chemical bond is elastic. The chemical bonds are not rigid as the J value increases the molecule rotates faster and faster the nuclear experiences the centrifugal force that stretches the bond. So, we can say the centrifugal forces distort the molecule stretching the bond length. So, we have to improve our model by taking into account this effect of centrifugal Distortion.

Thus for a non rigid rotor the energy expression that is nu bar G is given by B times J times J + 1 and we have an extra term that is - D times J times J + 1 squared where this D is called the centrifugal constant.

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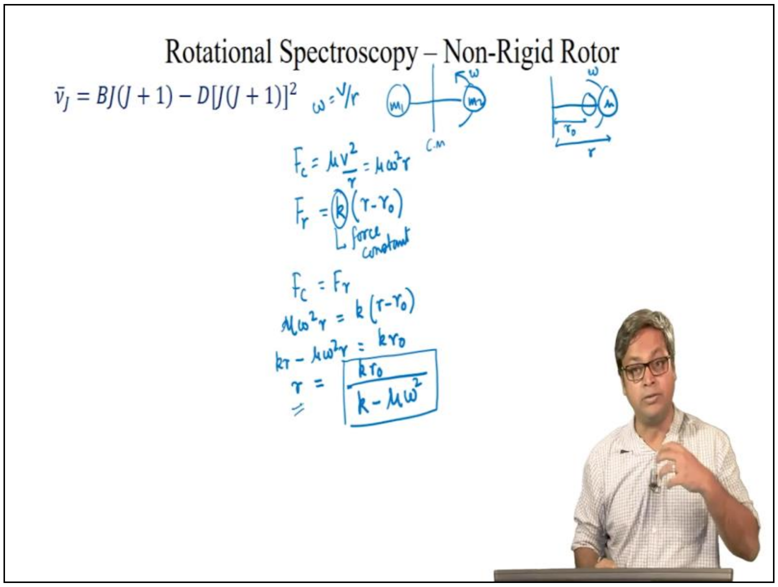

Rotational Spectroscopy – Non-Rigid Rotor

$\bar{\nu}_J = BJ(J+1) - D[J(J+1)]^2$

$\omega = v/r$

$F_c = \mu \frac{v^2}{r} = \mu \omega^2 r$

$F_r = \boxed{k}(r - r_0)$

└ force constant

$F_c = F_r$

$\mu \omega^2 r = k(r - r_0)$

$kr - \mu \omega^2 r = k r_0$

$r = \boxed{\frac{k r_0}{k - \mu \omega^2}}$

So, let us try to understand the origin of this equation using a simple approach on the basis of classical behavior. We have discussed before that we can consider a diatomic molecule let us say m1 and m2 rotating about the center of mass, so this is the center of mass and this Dietetic molecule is rotating. So we can consider this molecule rotating with an angular velocity Omega as single particle of reduced mass mu rotating with angular velocity Omega. So, let us assume that when there is no rotation the particle is at a distance say r0 from the center of mass.

And the distance increases to r when the particle rotates. So, the centrifugal force which is denoted by FC is given by mu v square by r and as we know that Omega equals v by r, so we can write FC as mu Omega squared r. So, this force the centrifugal force are FC is balanced by a restoring Force which will write as F r and this restoring force is given by K times r - r0, so here this K is not the Boltzmann constant but this is the force constant.

So this is the force constant of the bond or the spring connecting the 2 nuclei of the diatomic molecule so because Fc is counterbalanced by F r we can write Fc equals F r in other words we can write mu Omega square r equals K r - r0, so if we put all the terms which are on the left hand side we can write k r- mu Omega square r equals K r 0 or we can write r equals K r 0 divided by K - mu Omega square, so we can write r equals K r 0 divided by K - mu Omega square.

So we can see from this equation that as the angular velocity increases that means as the molecule goes to higher and higher J levels then K - mu Omega square decreases so this K - mu Omega squared is in the denominator, so the inter nuclear distance or r increases.

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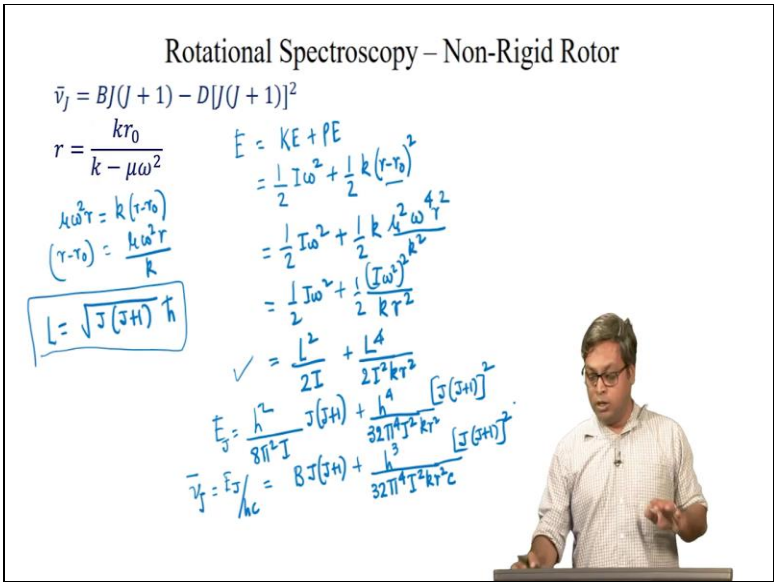

Rotational Spectroscopy – Non-Rigid Rotor

$$\bar{\nu}_J = BJ(J+1) - D[J(J+1)]^2$$

$$r = \frac{kr_0}{k - \mu\omega^2}$$

$$\mu\omega^2 r = k(r - r_0)$$

$$(r - r_0) = \frac{\mu\omega^2 r}{k}$$

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

$$E = KE + PE$$

$$= \frac{1}{2} I\omega^2 + \frac{1}{2} k (r - r_0)^2$$

$$= \frac{1}{2} I\omega^2 + \frac{1}{2} k \frac{\mu^2 \omega^4 r^2}{k^2}$$

$$= \frac{1}{2} I\omega^2 + \frac{1}{2} \frac{(I\omega^2)^2}{kr^2}$$

$$\checkmark = \frac{L^2}{2I} + \frac{L^4}{2I^2 kr^2}$$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) + \frac{h^4}{32\pi^4 I^2 kr^2} [J(J+1)]^2$$

$$\bar{\nu}_J = E_J/hc = BJ(J+1) + \frac{h^3}{32\pi^4 I^2 kr^2 c} [J(J+1)]^2$$

So, the total energy of the molecule is the sum we can write energy is the sum of the kinetic energy plus potential energy. So, the kinetic energy as we have discussed before is given by half I Omega squared where I is the moment of inertia and Omega is the angular velocity. Now the potential energy is given by half a r - r0 squared, so because we had mu Omega squared r equals K r - r0 we can actually write r - r 0 equals mu Omega square r divided by K.

So, if we replace the r - r 0 with mu Omega square r by K what we get you can write this as half I Omega squared + 1/2 K and r - r0 squared I can write as mu squared Omega to the power 4 r squared by K squared. So, we can even simplify this we can write this equals 1/2 I Omega squared and the next term we can simplify as 1/2 I Omega squared whole squared divided by K r squared. So, this I can write in terms of angular momentum as L squared divided by 2 I which you already know + L to the power 4 divided by 2 I squared K r squared.

So the quantum restriction that L is quantized that means L is given by root over J times J + 1 h cross so this quantum restriction will convert this classical result to a quantum mechanical result so if we replace L equals root over J times J + 1 h cross into this expression then we can write E equals h squared by 8 pi square I J times J + 1 so we know this part from previous lecture plus we can write h to the power 4 by 32 pi to the power 4 I squared K r squared J times J + 1 whole squared. So, this energy is in joules so if we press this E or EJ in terms of wave numbers we can write nu bar J equals EJ divided by HC.

So that becomes as you already know the first terms becomes B times J + J + 1 and the second term now becomes h cubed by 32 pi to the power 4 I squared K r squared C J times J + 1 whole squared.

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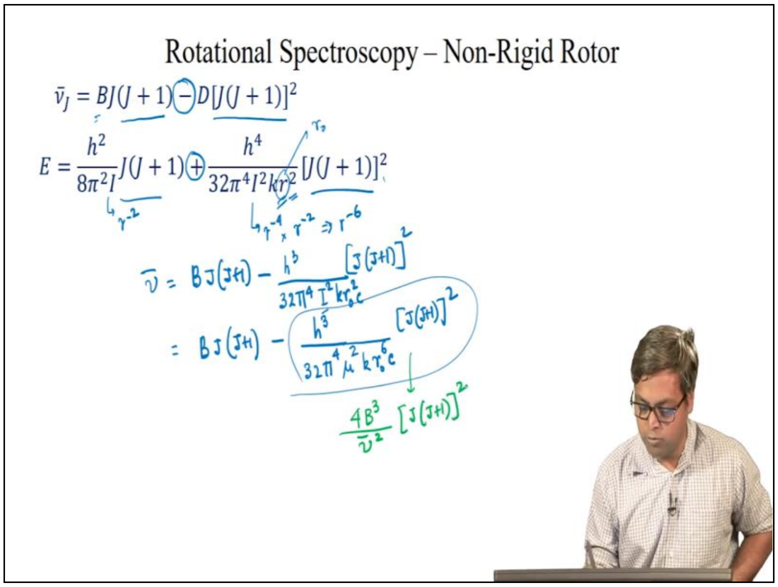

Rotational Spectroscopy – Non-Rigid Rotor

$$\bar{\nu}_J = BJ(J+1) \boxed{-} D[J(J+1)]^2$$

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \boxed{+} \frac{h^4}{32\pi^4 I^2 k r^2}[J(J+1)]^2$$

$$\bar{\nu} = BJ(J+1) - \frac{h^3}{32\pi^4 I^2 k r_0^2 c}[J(J+1)]^2$$

$$= BJ(J+1) - \frac{h^3}{32\pi^4 \mu^2 k r_0^6 c}[J(J+1)]^2$$

$$\frac{4B^3}{\bar{\nu}^2}[J(J+1)]^2$$

So, this expression apparently looks like the equation due to centrifugal Distortion. However there is a sign mismatch in the centrifugal distortion expression we have a negative sign though we have J into J + 1 and J times J + 1 whole squared terms here also we have similar terms but we have a positive sign. So, now we should remember that this r this r is the extended bond length due to the centrifugal force on the other hand we have obtained this B from the rigid rotor with bond length r 0 as r and r 0 are related we can express this equation in terms of r 0 instead of expressing it in terms of r.

And for this we will take another approximations so if we look carefully in this equation this first term because it is inversely proportional to I and we know that I is mu r squared so this is proportional to r to the power -2. The second term is proportional to here we have at I square so it's r to the power - 4 and here we have another r to the power - 2 term so it is proportional to back to the power – 6. So, as we have seen from the previous table that the centrifugal distortion changes the bond length only by a small amount.

So for the second term we'll just replace this r with r 0 so if we do all the mathematical steps what we get is nu bar equals B times J times J + 1 and the next term is the same just it becomes negative so it will be h cubed by 32 pi to the power 4 I squared K r0 square C J times J + 1 whole square. So, now we can even expand the moment of inertia so we will write this as B times J times J + 1 - h cubed and 32 pi to the power 4 then mu to the power two K r 0o to the power 6 C J times J + 1 whole squared.

So, this second term so the second term can be further simplified and this further simplification gives the second term as 4 b cubed by nu bar squared and we have the J times J + 1 whole squared.

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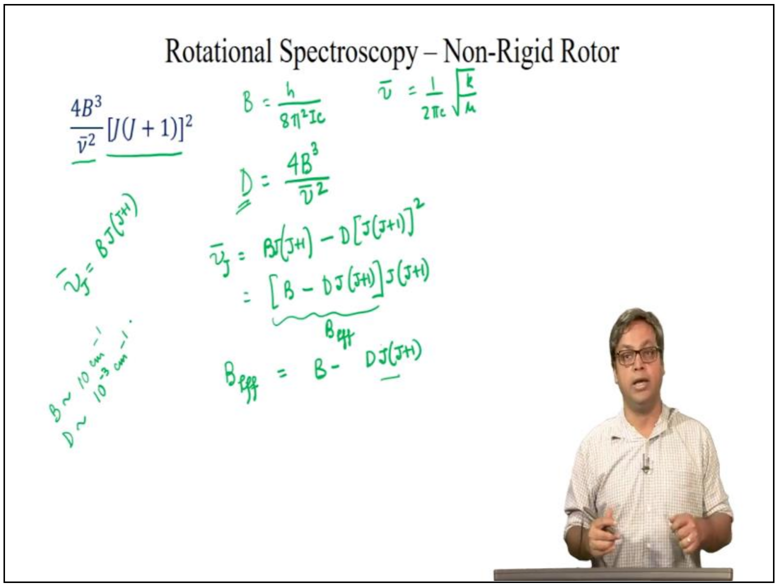

Rotational Spectroscopy – Non-Rigid Rotor

$$\underline{\frac{4B^3}{\bar{\nu}^2}}\underline{[J(J+1)]^2}$$

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

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\underline{D} = \frac{4B^3}{\bar{\nu}^2}$$

$$\bar{\nu}_J = BJ(J+1)$$

$$\bar{\nu}_J = BJ(J+1) - D[J(J+1)]^2$$

$$= \underbrace{[B - DJ(J+1)]}_{B_{eff}}J(J+1)$$

$$B_{eff} = B - \underline{D}J(J+1)$$

$B \sim 10\ cm^{-1}$

$D \sim 10^{-3}\ cm^{-1}$.

So we can write the second term as full B cubed by nu bar square times J times J + 1 whole squared here as we know B is given by h by 8 pi squared I C and nu bar is the vibrational term and that is given by 1 by 2 pi C root over K by mu where K is the force constant and mu is the reduced mass. So, we can see by comparing the non rigid rotor energy expression with the final expression that we have got we can write D equals 4 B cubed by nu bar squared.

So this D is always a positive number as all the terms related to D that is for B and nu bar are positive numbers. This says that with increase in J there is a decrease in the energy gap as we have seen earlier from the tables. Thus we can think about an effective B or we can write so let us say we wrote new bar J equals B times J times J + 1 - D times J times J + 1 whole squared. So, if I take J times J + 1 common what I have here is B - D times J times J + 1 so we can compare this with the rigid rotor where we have nu bar J equals B times J times J + 1.

So we can think this B - D times J times J + 1 as the effective B or we can write B effective equals B - D J times J + 1, so as be effective is a function of J be effective decreases as J increases the value of D is significantly less than the value of B for example we have already discussed the value of B is in the order of 10 wave numbers. So, the value of D is around 10 to the power - 3 wave numbers so that means this is orders of magnitude smaller. So, as this value of D is significantly less than the value of B thus the difference between the rigid. And non rigid rotor treatments can be expected to show up only when the value of J or the high value of J is involved.

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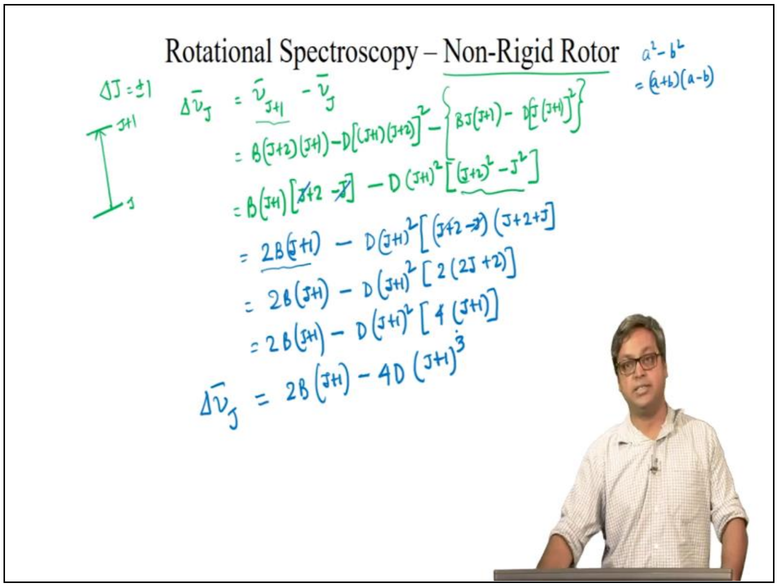

Rotational Spectroscopy – Non-Rigid Rotor

$\Delta J = \pm 1$

$$a^2 - b^2 = (a+b)(a-b)$$

$$\Delta\bar{\nu}_J = \underbrace{\bar{\nu}_{J+1}} - \bar{\nu}_J$$
$$= B(J+2)(J+1) - D[(J+1)(J+2)]^2 - \{BJ(J+1) - D[J(J+1)]^2\}$$
$$= B(J+1)[\cancel{J}+2-\cancel{J}] - D(J+1)^2[\underbrace{(J+2)^2 - J^2}]$$
$$= \underline{2B(J+1)} - D(J+1)^2[(\cancel{J}+2-\cancel{J})(J+2+J)]$$
$$= 2B(J+1) - D(J+1)^2[2(2J+2)]$$
$$= 2B(J+1) - D(J+1)^2[4(J+1)]$$
$$\Delta\bar{\nu}_J = 2B(J+1) - 4D(J+1)^3$$

So, we have talked about the energy expression, so the expression for the rotational transition based on the selection rule Delta J equals + - 1 we can write Delta and we are considering a transition from J to J + 1 so we can write this Delta nu bar J equals nu bar J + 1 - nu bar J and we will consider the non rigid rotor. So, we can write this as B times J + 2 times J + 1 - D times J + 1 times J + 2 squared. So, this is for nu bar J + 1 and for nu bar j as we already know we will write B times J times J + 1 - d times J times J + 1 whole squared.

So, if we put all the terms with B together what we have we have B and we will also take J + 1 common. So, we have J + 2 – J, so if we do the same for the terms with D what we have we have - D and here we will take J + 1 squared common so what we have here is J + 2 squared - J square so this is like A square - B squared. So, we know A squared - B squared equals A + B times A - B so we can write this as 2 because this J and J will cancel B times J + 1 and this is the part we already know from the rigid rotor and the other part is d times J + 1 squared and we have J + 2 - J and J+ 2 +J.

So, we can write this as 2 B times J + 1 - D J + 1 squared then I have 2 times 2 J + 2 so this is 2 B J + 1 - D J + 1 squared times 4 times J + 1. So, we can write this as the final form delta nu bar j equals to b times J + 1 this is for the rigid rotor and for the non rigid rotor we have an extra term that is - 4 D times J + 1 cube.

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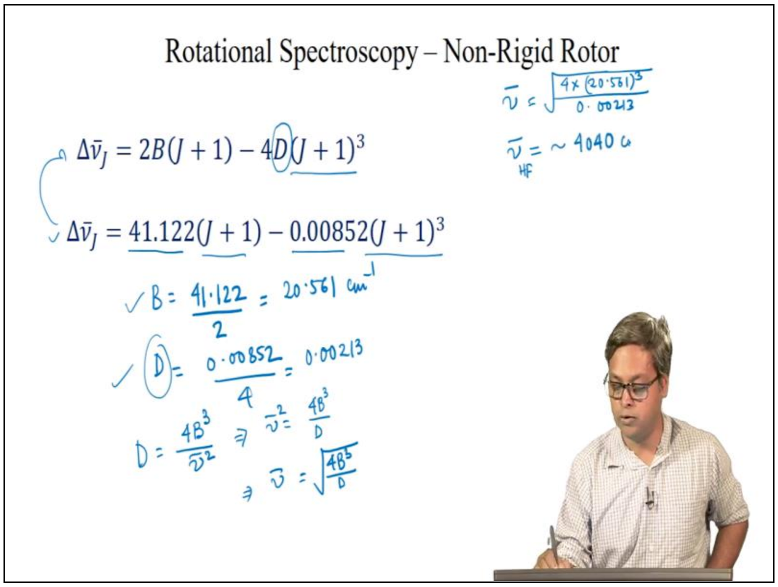

Rotational Spectroscopy – Non-Rigid Rotor

$$\Delta\bar{\nu}_J = 2B(J+1) - 4\boxed{D}\underline{(J+1)^3}$$

$$\Delta\bar{\nu}_J = \underline{41.122}\underline{(J+1)} - \underline{0.00852}\underline{(J+1)^3}$$

$$✓ B = \frac{41.122}{2} = 20.561\ cm^{-1}$$

$$✓ \boxed{D} = \frac{0.00852}{4} = 0.00213$$

$$D = \frac{4B^3}{\bar{\nu}^2} \Rightarrow \bar{\nu}^2 = \frac{4B^3}{D}$$

$$\Rightarrow \bar{\nu} = \sqrt{\frac{4B^5}{D}}$$

$$\bar{\nu} = \sqrt{\frac{4 \times (20.561)^3}{0.00213}}$$

$$\bar{\nu}_{HF} = \sim 4040\ c$$

So, we can see that the spectrum of the non rigid rotor is similar to that of the rigid rotor except each line is slightly displaced to a lower frequency and the displacement increases with J + 1 cubed. So, displacement actually increases as the value of J increases a knowledge of D gives two useful information first it allows us to determine the value of J of lines in the observed experimental spectrum we should not measure an isolated transition or an isolated line to determine which J value it arises from.

But we have to measure three consecutive lines to get these unique values of three variables B D and J. So, for example the data that we had shown for HF in the previous table can be fitted to some number times J + 1 and some other number times J + 1 cubed. So, if we compare this equation with this equation we can immediately write B equals 41.122 divided by 2 that is 20.561 wave numbers and D equals 0.00852 divided by 4 that is 0.00213. Now the second thing it gives is the knowledge of D enables us to very roughly estimate the vibrational frequency nu bar of the diatomic molecule.

Because we know D is given by 4 B cubed by nu bar squared so from here we can write nu bar squared equals 4 B cubed by D or in other words we can write nu bar equals 4 B cubed by the square root of the entire thing. So, now if you put the values that we have obtained for B and D in this expression we find new bar equals root over 4 times the value of B that is 20.561 cubed divided by the value of D that is 0.00213. And if we do this calculation we can estimate the nu bar of HF to be round 4040 wave numbers.