Atomic and Molecular Physics
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Lecture - 49
Vibration of a molecule (Contd.)

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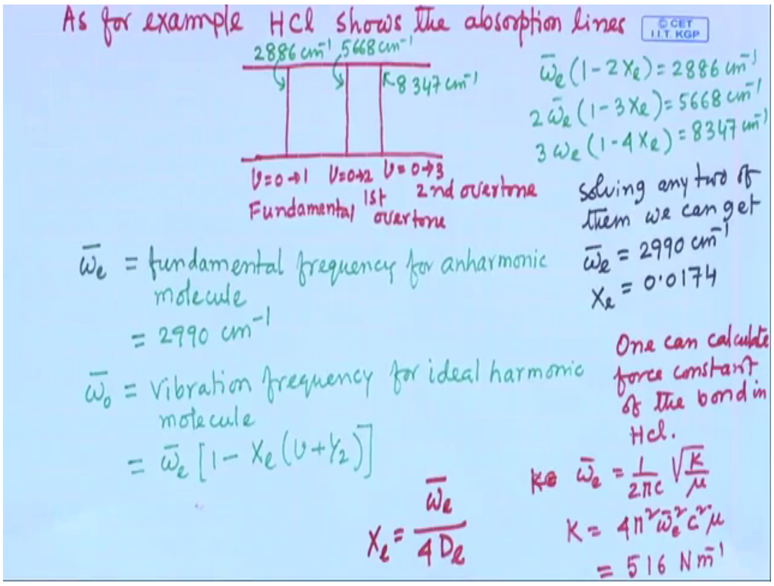

As for example HCl shows the absorption lines

$\bar{\omega}_e(1-2x_e) = 2886\ cm^{-1}$

$2\bar{\omega}_e(1-3x_e) = 5668\ cm^{-1}$

$3\omega_e(1-4x_e) = 8347\ cm^{-1}$

solving any two of them we can get

$\bar{\omega}_e = 2990\ cm^{-1}$

$x_e = 0{\cdot}0174$

$\bar{\omega}_e$ = fundamental frequency for anharmonic molecule $= 2990\ cm^{-1}$

$\bar{\omega}_0$ = Vibration frequency for ideal harmonic molecule $= \bar{\omega}_e\left[1 - x_e(v+\frac{1}{2})\right]$

$$x_e = \frac{\bar{\omega}_e}{4D_e}$$

One can calculate force constant of the bond in HCl.

~~Ke~~ $\bar{\omega}_e = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$

$K = 4\pi^2\bar{\omega}_e^2c^2\mu$

$= 516\ Nm^{-1}$

So, I was discussing that absorption lines of HCl. So, experimentally it is measured that in infrared spectrometer. So, it is seen that this frequency of these fundamental lines of band it is 2886 centimetre inverse. First overtone from the frequency is wave number is basically 5668 centimetre inverse; and second overtone this 8347 centimetre inverse. So, these are experimentally measured data for HCl molecules. Now, from this measurement what we can know what information we can get about the molecules that is the question ok.

So, experimentally we have measured these lines. And theoretically from the model, we have seen this fundamental spectral lines that is the energy is omega e 1 minus two X e that we have seen I have already shown you, so that will be equal to this one 2886. And this first overtone that is 2 omega e 1 minus 3 x e equal to 5668 centimetre inverse. And second overtone that is 3 omega e 1 minus 4 X e that will be equal to 8346 ok. So, here this you can take 1, 2, 3 this is the three relation or equation number 1, 2, 3 ok.

Now, here unknown is two omega e in this equation unknown is two omega e and X e ok. So, so two unknown to solve this to get the value of this unknown, we need minimum two equation. So, here I have three equation. Any two we can consider and solve them you will get you can find out the value of omega e and xe, so that is our just it is simple problem. If you just solve it then you will see this omega e bar equal to 2990 centimetre inverse; and X e this is anharmonicity constant that is equal to 0.0174 74 ok. So, from this measurement one can get an anharmonicity constant and anharmony and omega e and basically anharmonicity constant x e equal to I think it was omega e bar by 4, I think 4 D e as I as I showed you the relation is X e is equal to omega e bar by 4 d e.

So, you know omega e bar and X e from your experimental data. Now, if you put here, so you will get the value of dissociation, I have not calculated, but one can find the dissociation energy ok. And omega e bar it is related with the you remember this is related with the k value spring constant right yeah square root of k by mu the k value is there. So, omega here I have written here. So, so one can calculate from this data one can calculate dissociation energy of the molecule means to decouple the molecule in the atomic set what is the energy required so that is D e. So, one can calculate D e value, one can calculate D e value ok, also one can yeah force constant k because omega e bar equal to 1 by 2 pi c square root of pi k by mu ok.

So, yeah so earlier it was omega 0 bar, now just I replaced this omega e bar for anharmonicity. So, omega e bar you know. A nu for HCl one can calculate ok. So, basically your k is this higher from experimental value omega e bar square ok, you will get from here. If you put then k is 5 or 6 Newton meter square Newton per meter ok. So, if you know the force constant k, basically you can find out the bond length also r 0 you can find out. So, from this study of the infrared spectral infrared spectra of a molecule, you can get information of the molecule like is what is the what is the force constant, what is the bond length, what is the dissociation energy of the molecule. So, that is the that is the purpose that is the application of these of this spectrometer spectroscopy infrared or microwave spectroscopy.

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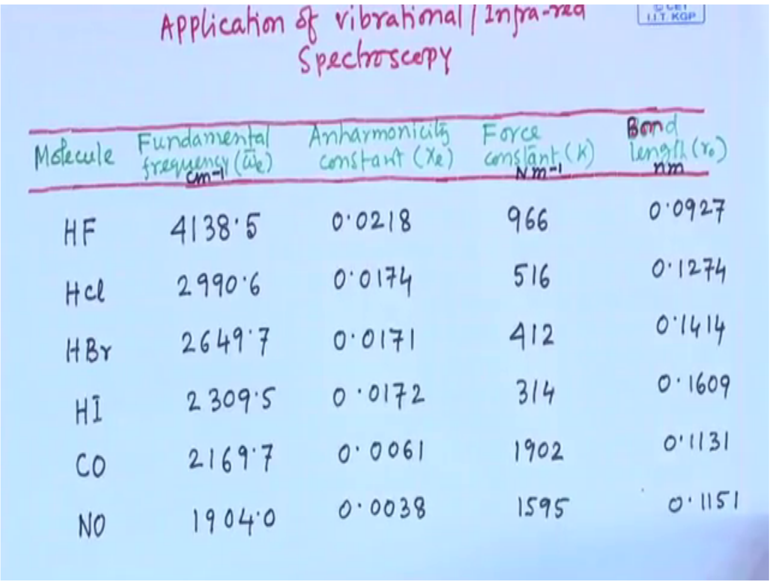

Application of vibrational / Infra-red Spectroscepy

Molecule	Fundamental frequency ($\bar{\omega}_e$) cm^{-1}	Anharmonicity constant (x_e)	Force constant (k) Nm^{-1}	Bond length (r_0) nm
HF	4138·5	0·0218	966	0·0927
Hcl	2990·6	0·0174	516	0·1274
HBr	2649·7	0·0171	412	0·1414
HI	2309·5	0·0172	314	0·1609
CO	2169·7	0·0061	1902	0·1131
NO	1904·0	0·0038	1595	0·1151

So, I will show you some other data just with his experiment it was measured and that is given. So, you can see here I have given a table. So, here I am showing these for different molecules these are from experimental value ok. So, from experimental value, so this for a HF molecule, for HCl, H hydrogen bromide, hydrogen iodide, coba carbon monoxide, nitrogen monoxide ok, so their fundamental frequency just here I have given fundamental frequency. But other frequency one can also I have not have noted down, but these are the fundamental experimenter it is from spectrometer it is measured of first overtone, second one that is also there. ah

So, then how to calculate anharmonicity constant that I have shown. So, these are the value of anharmonicity constant of different molecules ok. Then from there force constant and from there one can calculate bond length ok. So, these are the bond length for different molecules. So, these are the so that is why just here I have shown some data available in the in the literature ok.

So, these the utility what else we want to know from a from the from a molecule. We want to know what is the, what is the dissociation energy, what is the what is the bond length of the molecule and that is why these are simple case I have shown, but it is a, it is the simple molecule diatomic molecule, but for other polyatomic molecule and yeah. So, calculation is not slightly, for linear molecule, we are considering for non-linear molecule we are not studying here because this slightly complicated.

So, but it is very interesting that the spectrometer, the spectroscopy very useful to get the information about the about the molecule ok. So, studying their microwave or infrared radiation in terms of emission or absorption really absorption is more convenient one ok. And what is the meaning of absorption how it is done, so I try to explain within short time ok. So, so these are this it is whatever we are studying this very it is really effective to study because this study gives lot of information about the about the molecules ok.

So, a what we have learned so far what we have learned so far that basically we have considered the rotation and vibration of a molecule pure rotation or pure vibration of a molecule ok. So, for rotation of a molecule, we have considered the model, rigid rotator model or another non rigid rotator model ok. For vibration we have considered also two model; one is simple harmonic oscillator model, and another is anharmonic oscillator model ok.

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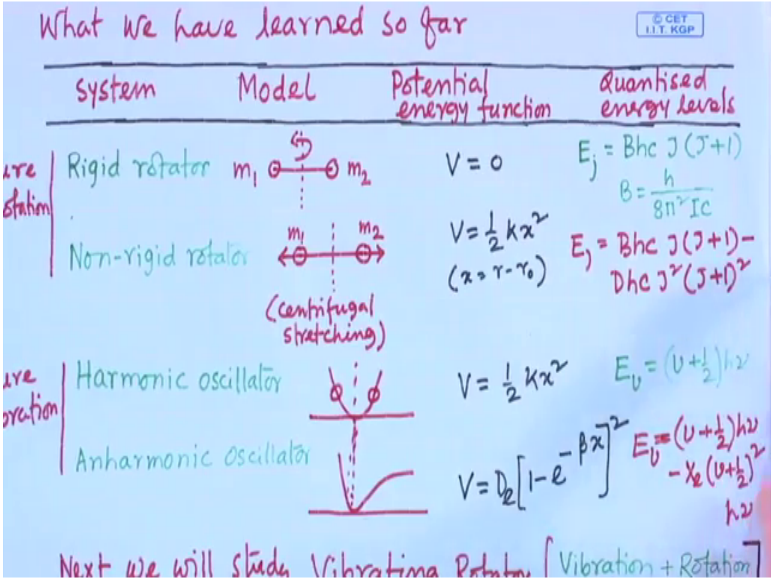

What we have learned so far

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	System	Model	Potential energy function	Quantised energy levels
ure otation	Rigid rotator	m_1 m_2	$V = 0$	$E_J = BhcJ(J+1)$ $B = \frac{h}{8\pi^2 Ic}$
	Non-rigid rotator	m_1 m_2 (centrifugal stretching)	$V = \frac{1}{2}kx^2$ $(x = r - r_0)$	$E_J = BhcJ(J+1) - DhcJ^2(J+1)^2$
ure ration	Harmonic oscillator		$V = \frac{1}{2}kx^2$	$E_v = (v+\frac{1}{2})h\nu$
	Anharmonic Oscillator		$V = D_e[1-e^{-\beta x}]^2$	$E_v = (v+\frac{1}{2})h\nu - x_e(v+\frac{1}{2})^2 h\nu$

Next we will study Vibrating Rotator [Vibration + Rotation]

So, so these are the either pure rotation or pure vibration and rigid rotator that I explained that that diatomic linear molecules. So, it is it is rotating and then in this case its potential energy basically in rigid rotor model potential energy zero and its energy E j equal to Bhc J J plus 1, and B equal to h by 8 pi square I C, I is moment of inertia, C is the light velocity ok. So, for non-rigid model, so there is a distortion spacing basically I try to explain in terms of vibration that is not basically vibration it is basically stretching when it is rotating with rapid with very high speed, then basically there will be stretching of these two molecules externally outside ok, so that is why it is called centrifugal stretching. So, due to this distortion during rotation, there is called non-rigid rotational model.

So, in this case this, it is its potential energy is half kx square x equal to r minus r 0 this as I told earlier. So, if you consider r minus r is equal to x, it will be potential energy will be v equal to half k x square. And this rotational energy E J now this term is there and then additional term this correction term is there. So, Dhc J square J plus 1 square there will be a higher term also, but we have kept up to J square term here. So, D is called distortion constant right. And so for this asymmetry will come in the in the in the in the spectra and so these are the these basically pure rotation ok.

Similarly, for pure vibration just we discuss harmonic oscillators this the energy and then anharmonic oscillator. So, here this asymmetry is there. And this potential energy is more function this D e 1 minus e to the minus beta x x is r minus r 0 is whole square. So, in that case energy is this minus this correction term ok, due to this asymmetry this the term that we just we have seen. So, here just I summarize that I summarized that so far we have considered the rotation of a molecule. We have considered the vibration of a molecule, but a molecule it can rotate, it can vibrate. So, there may be there may be some molecules which can which is microwave active, but it is not infrared active ok.

It may happen it may happen that some molecules. So, in that case, it is a purely rotational spectra will see. And it may happen that for some molecules which is microwave inactive, but infrared active ok. So, in this case, we will see only it is pure vibrational case, and we will see only vibrational spectra ok. But there are some molecules higher it can be microwave active as well as infrared active means it will have simultaneous motion rotational motion as well as vibrational motion ok. So, now, we will consider this case, and it is it is it is really call this diatomic vibrating rotator molecules, diatomic vibrating rotator molecules.

Vibrating rotator molecule means vibration and rotation both are present at a time. So, then what will be the what will be the energy levels or spectral lines for this vibrating rotator molecules ok, so that we will discuss now. So, diatomic vibrating rotator now vibration is there also rotation also there; and individually we have we have we know both cases for vibration what will be the energy state of the molecule for rotation what will be the energy states of the molecule. So, individually separately we know.

Now, if both are the there both are there, so there will be interaction for vibration and rotation there will be interaction you know ok. So, there will be so will get energy total energy will be should be total energy should be energy due to the vibration plus energy due to the rotation plus energy due to the interaction between vibration and rotation ok. So, so that should be the total energy. Now, if so then it is slightly complicated because one has to find out the interaction energy between rotation and vibration.

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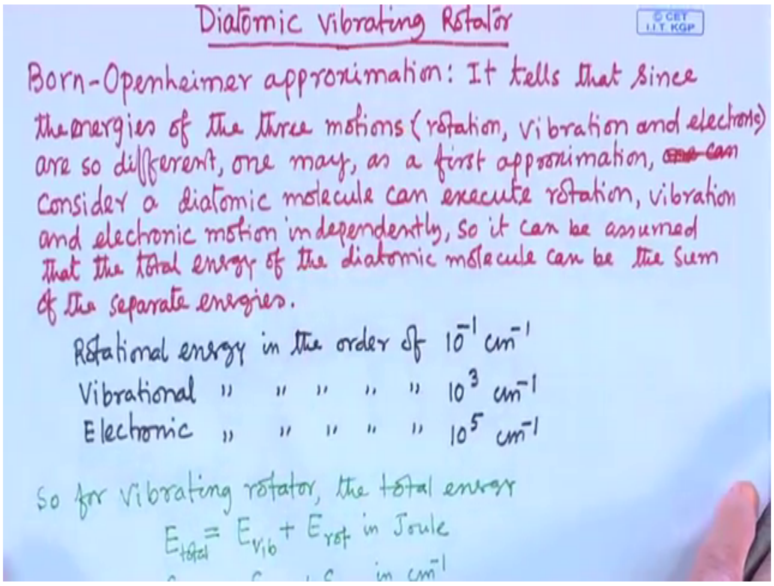

Diatomic Vibrating Rotator

Born-Openheimer approximation: It tells that since the energies of the three motions (rotation, vibration and electronic) are so different, one may, as a first approximation, ~~one~~ can consider a diatomic molecule can execute rotation, vibration and electronic motion independently, so it can be assumed that the total energy of the diatomic molecule can be the sum of the separate energies.

Rotational energy in the order of 10^{-1} cm^{-1}

Vibrational " " " " " 10^{3} cm^{-1}

Electronic " " " " " 10^{5} cm^{-1}

So for vibrating rotator, the total energy

$E_{total} = E_{vib} + E_{rot}$ in Joule

in cm^{-1}

But here Born-Openheimer approximation, what it is Born-Openheimer approximation. It tells that since the energies of the three motion, rotation, vibration and electronic motion. So, electric motion I have not taught you yet, but later on I will teach you. So, electronic this three type of motion in a molecule are there energy are so different means their energy range of energy order of the energy are different ok. It is they are not very close ok. So, they are so different one may as a first approximation, consider a diatomic molecule can execute rotation, vibration and electronic motion independently ok.

So, independently means as if there is no interaction among them ok. So, whatever I told that one has to (Refer Time: 18:19) direction term then things will be slightly complicated. But since the energy order of the energy for rotation, order of the energy for vibration, order of the energy for electronic motion ok, so these are so separate so different range of order are different. So, so this Born-Openheimer approximation is telling that just total energy we can take the just sum of these two or three energy independent individual energy ok. We do not need to consider the interaction energy because there will not be much interaction among them because their energy separation are quite large.

So, basically this rotation energy in the order of 10 to the power minus 1 centimetre inverse; vibrational energy in the order of 10 to the power 3 centimetre inverse, and electronic energy in the order of 10 to the 5 centimetre inverse. So, this is the order of the energy of rotation vibration and electronic. So, they are really quite there is quite separated. So, that is why this as for the Born-approximate Openheimer approximation the total energy can be considered the E total equal to E vibration plus E rotation.

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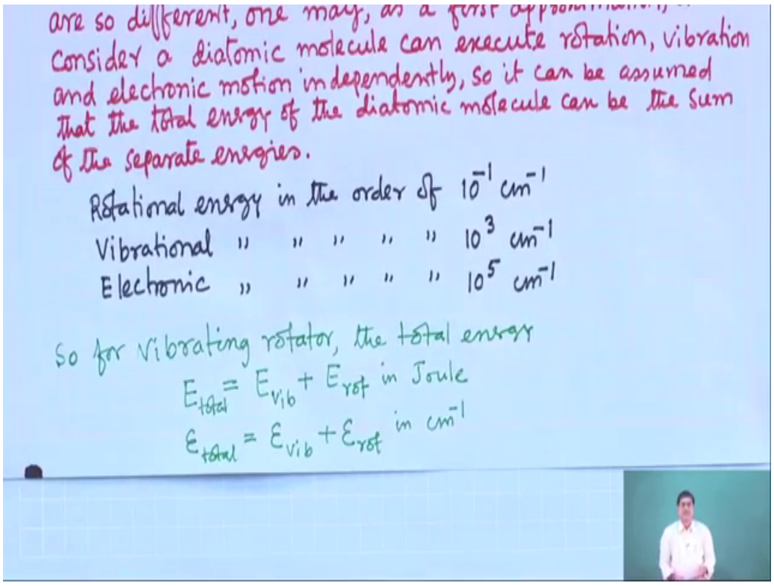

are so different, one may, as a first approximation, consider a diatomic molecule can execute rotation, vibration and electronic motion independently, so it can be assumed that the total energy of the diatomic molecule can be the sum of the separate energies.

Rotational energy in the order of 10^{-1} cm^{-1}
Vibrational " " " " " 10^{3} cm^{-1}
Electronic " " " " " 10^{5} cm^{-1}

So for vibrating rotator, the total energy

$$E_{total} = E_{vib} + E_{rot} \text{ in Joule}$$
$$\varepsilon_{total} = \varepsilon_{vib} + \varepsilon_{rot} \text{ in } cm^{-1}$$

In joule or this in centimetre inverse in wave number e total equal to e vibration plus e rotation ok. So, now, things are very life is easy due to this Born-Openheimer approximation. And this Born-Openheimer approximation is based on the consideration that the systems if they are if their energy separations for different event if for each event energy separations from the other event is quite large, then we can take them individually we can take the total energy of the system then the their summation of this individual energy ok. So, so now, for diatomic vibrating rotators what will be the energy.

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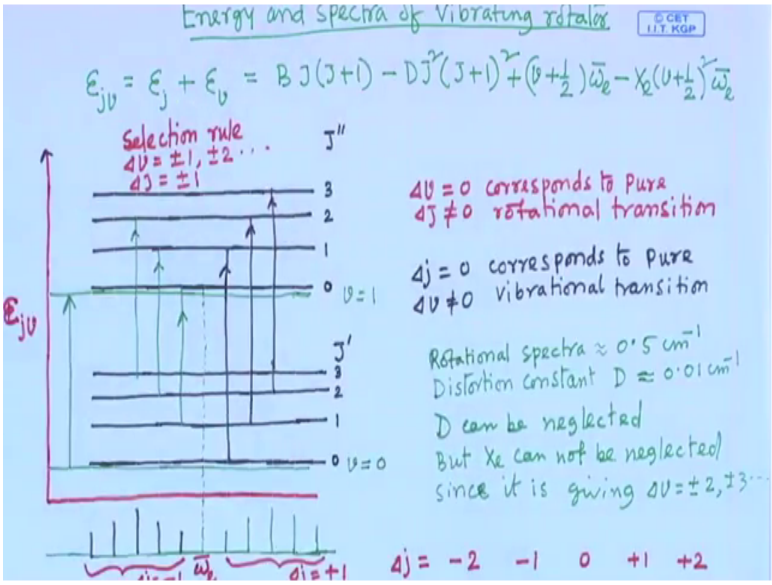

Energy and spectra of Vibrating rotator

$$\varepsilon_{jv} = \varepsilon_j + \varepsilon_v = BJ(J+1) - DJ^2(J+1)^2 + (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})^2\bar{\omega}_e$$

Selection rule
$\Delta v = \pm 1, \pm 2 \cdots$
$\Delta J = \pm 1$

$\Delta v = 0$ corresponds to Pure
$\Delta J \neq 0$ rotational transition

$\Delta j = 0$ corresponds to pure
$\Delta v \neq 0$ vibrational transition

Rotational spectra $\approx 0{\cdot}5\ \mathrm{cm}^{-1}$
Distortion constant $D \approx 0{\cdot}01\ \mathrm{cm}^{-1}$
D can be neglected
But X_e can not be neglected
since it is giving $\Delta v = \pm 2, \pm 3 \cdots$

$\Delta j =$ −2 −1 0 +1 +2

So, already we know the individual energy already we know the individual energy that is energy and spectra of vibrating rotator. Energy have seen this E j v, now j is for rotational and v is for vibration ok. So, E j v equal to E j plus E v rotational energy plus vibration energy. So, rotational energy plus vibration energy, rotational energy we know B J J plus 1 minus D J square J plus 1 whole square that is the rotational energy. And vibration is v plus half omega e bar minus x c v plus half square omega e bar ok. So,. So, these are now total energy for the vibrating rotator ok.

So, for vibrating rotators, I have now energy expression. Here if you want to see these spectral lines, so we have we have to draw the energy levels first and then we have to consider a selection rule. So, selection rule is same as we have considered for individual rotation and vibration. So, del v equal to plus minus 1, plus minus 2 right and del J equal to plus minus 1.

So, considering these transition rules now here this energy E j v. And if I draw the spectral lines, so for v equal to 0 this is the green line; and v equal to 1 this is the green line ok. So, if it is if it is just pure vibration there is no rotation, so I could get del v equal to plus minus 1, plus minus (Refer Time: 23:23), I could get this the just rotation v equal to 0 to v equal to 1.

So, these spectral lines I could get. This is nothing but the fundamental line right this is nothing but the fundamental lines ok. But as I told you that (Refer Time: 23:43) fundamental band any line that term we do not use its band. Why it is called band that now I think I will be able to explain you because it is not a one line, it is a it is composed of many lines. So, from where this other lines are coming ok, so that will understand from this transition.

Here you see I have used these black lines ok. So, these the vibration energy level v equal for v equal to 0. Now, for a for v equal to 0, if you put v equal to 0 here, v equal to 0 here. So, and for different value of J considering del J equal to plus minus 1, no these are for transition, but for different value of J, J equal to 0, J equal to 1, J equal to 2, J equal to 3, if we if you if you calculate, so you will see whatever the v equal to 0, whatever the energy value now some more value is added for different value of J ok.

So, you will get; so, this v equal to 0, J equal to 0, J equal to 0, I think this term are 0 J equal to 0 this term all this term are 0, J J ok. So, it is just v equal to 0 and J equal to 0. So, this is the same line. So, I have to just show separately I have just here shown separately slightly separation I kept, but it is basically same line ok, so that is for J equal to 0 already v equal to 0 I have put here.

Now, J equal to 0, J equal to 1, J equal to, J equal to 3 right so that is so in one vibrational energy level in one vibrational energy level in one vibrational energy level, so now, there are many rotational energy levels ok. And these rotational energy levels, so they are not there they are closely there because they are separation is 10 to the power in the order of 10 to the power minus 1 centimetre inverse right.

So, in one vibrational energy level, there are many rotational level are associated right. Similarly, for v equal to 1, for v equal to 1, now J equal to so put here v equal to 1 ok, so I will get this green line ok. Now, J equal to different value of J value, J equal to 0, 1, 2, 3 right. So, same way so whatever the value of for v equal to 1, now for different value of J, so energy will increase, but it is in the order of 10 to the power minus 1 centimetre inverse, it will increase ok. So, these rotational levels will be associated with the is close to the value of v equal to 1 ok.

So, here in case of vibrating rotator, so this each vibrational energy levels, each vibration energy level I have shown here just to vibration energy level. Each vibrational energy level are associated with the rotational energy levels ok. And now this transition if you consider the transition, so here I have shown that transition these lines, these lines basically from v equal to 0 to v equal to 1 ok, so that means, J equal to 0, this case and this case there they will coincide with the v equal to 0 and v equal to 1. So, here basically these lines transition between these line J equal to 0, but they J equal to del J equal to 0 is not allowed this transition is not allowed. So, as if this energy, this transition this original line whatever, so this one position will be here ok. If transition between these two 0, J equal to 0 to J equal so as we this position this wavelength will be here. I think I should like ensure ok.

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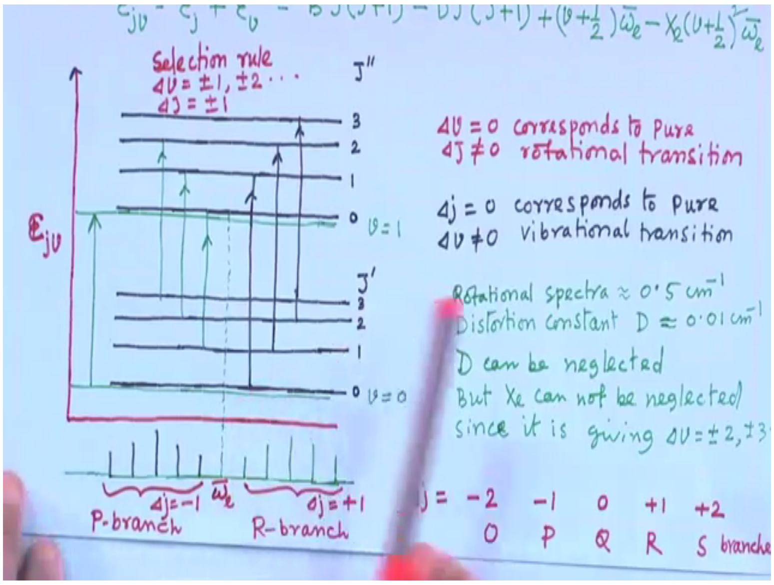

$\Delta v = 0$ corresponds to pure rotational transition
$\Delta J \neq 0$

$\Delta j = 0$ corresponds to pure vibrational transition
$\Delta v \neq 0$

Rotational spectra $\approx 0.5\ cm^{-1}$
Distortion constant $D \approx 0.01\ cm^{-1}$
D can be neglected
But X_e can not be neglected since it is giving $\Delta v = \pm 2, \pm 3$

So, transition will be here. So, it could be this frequency would be omega e bar ok. Now, you see if I consider so transition from this vibrational energy level to the this vibrational energy level, transition from the v equal to 0 to v equal to 1. So, this transition rule permit, now here there are many rotational energy levels. Now, following the transition selection rule del J equal to plus minus 1. So, here if I here I have considered this transition for the del J equal to minus 1 means from here J equal to 1 to here J equal to 0.

So, from final J equal to 0, this is the final quantum number, rotational quantum number minus the initial quantum number minus 1 0 minus 1, so minus 1. So, that way I have written the del J equal to minus 1. So, in that case 1 to 0, this transition; 2 to 1, 3 to 2, so this transition are allowed. And we will get the spectral lines, we will get the spectral lines left side this side ok. And other side for del J equal to plus 1 that means, 0 to 1, 1 to

2, 2 to 3, these spectral lines will get ok, these spectral lines will get in the for the transition rule del J equal to plus 1 ok.

So, as if there is both side of this original spectral lines, both side of the original spectral lines, we will get bunch of spectral lines ok. So, this is one just I have shown there are many transitions, there will be many transition and we will get a bunch of spectral lines for higher wave number side and lower wave number side ok. So, this side which follows the del J equal to minus 1, this bunch of spectral lines is called P-branch ok. And for del J equal to plus 1. So, this other side is called this R-branch ok. So, we will get bunch of spectral lines.

So, as if so as if here we are getting many spectral lines, but transition between two vibrational level ok, and this energy separation it is it is this separation is basically is very small, it is in the order of 10 to the minus 1 centimetre inverse compared to the energy separation of this vibrational energy that is in the order of 10 to the power 3 centimetre inverse.

So, these spectral lines basically whichever only for pure vibration energy only we can get one, but now we will get closely spaced many spectral lines, so that is why as I told this, this is the fundamental lines as if, but it is not a line it is a it is a bunch of spectral lines they are closely spaced so that is basically all band, so that is why I told earlier that it is not line it is a band and this is basically due to the rotation. So, I think I will stop here I will continue the discussion in next class.

Thank you.