# Atomic and Molecular Physics
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## Lecture – 44
## Rotation of a molecule (Contd.)

So, we are studying basically the rotation of a molecule. So, we have chosen diatomic molecule, linear molecule and we have taken model that is rigid rotator model. So, when this molecule rotates, there will not be change of the bond length. So, considering these model; so we have calculated the energy.

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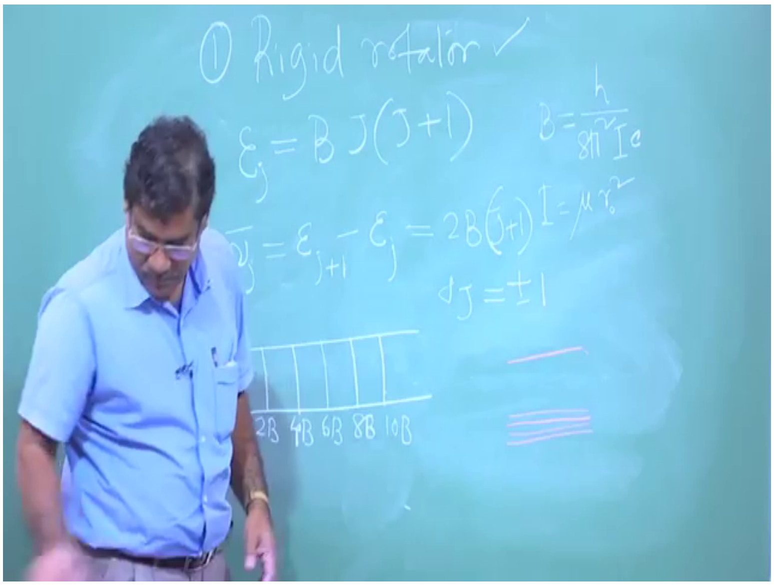

In terms of wave number E j equal to I think B J J plus 1, J is the rotational quantum number, J is rotational quantum number, and B is the rotational this constant. So, B it has B equal to I think h by 8 pi square I think Ic and I is moment of inertia, its mu r 0 square right. So, that we have, we have seen and we have seen also that if I calculate nu J bar, nu J bar. So, that is basically this, this transition from one rotational state to another rotational state. So, transition from between this j plus 1 to j. So, the between these two energy level if these transition is there.

So, will get the radiation that is in microwave range and their radiation wave length or wave number will be what we got; that is I think 2 B 2 B J plus 1 yes. So, that is what we got and using the selection rule d J equal to plus minus 1. We have seen that we have seen that this will get spectral lines will get spectral lines they are equispaced. So, this energy of the spectral lines, it will be, this is 2 B 4 B 6 B 8 B 10 B right.

So, these, the spectra will see from linear molecules if it is rigid, rigid rotator, if it is rigid enough so that they are bond length, is not changing leaving the rotation so. So, now, what is the use of these spectra, what is the use of the spectra, what is the use of the study? So, that is the basically microwave spectroscopy, some from microwave spectroscopy one can get some information. So, one example I will give you so, this Gilliam et al, Gilliam et al, basically Gilliam et al, so he majored.

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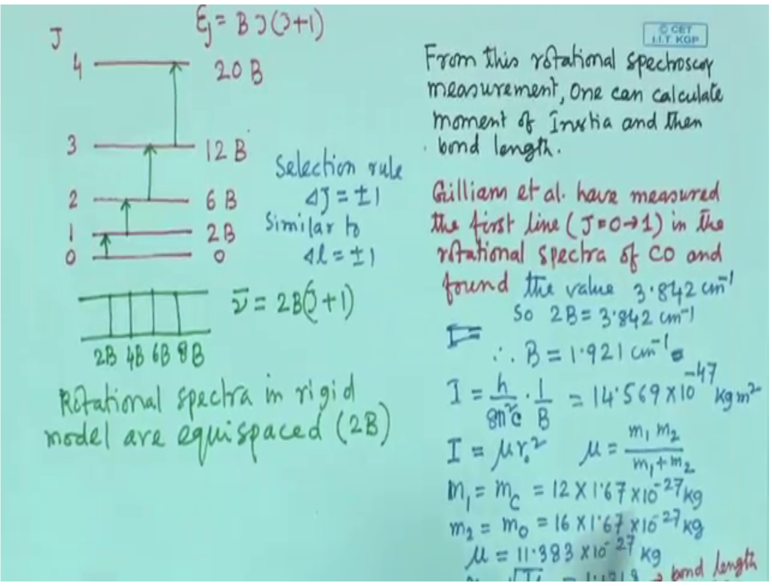

$E_J = BJ(J+1)$

Selection rule
$\Delta J = \pm 1$
Similar to
$\Delta l = \pm 1$

$\bar{\nu} = 2B(J+1)$

Rotational spectra in rigid model are equispaced (2B)

From this rotational spectroscopy measurement, one can calculate moment of Inertia and then bond length.

Gilliam et al. have measured the first line ($J = 0 \rightarrow 1$) in the rotational spectra of CO and found the value $3.842\ cm^{-1}$

So $2B = 3.842\ cm^{-1}$

$\therefore B = 1.921\ cm^{-1}$

$I = \frac{h}{8\pi^2 c} \cdot \frac{1}{B} = 14.569 \times 10^{-47}\ kg\,m^2$

$I = \mu r_0^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

$m_1 = m_C = 12 \times 1.67 \times 10^{-27}\ kg$

$m_2 = m_O = 16 \times 1.67 \times 10^{-27}\ kg$

$\mu = 11.383 \times 10^{-27}\ kg$

bond length

So, he majored this, this wave number of this first spectral lines for which molecule cobalt monoxide molecule, and he majored this spectroscopically. So, that is the spectroscopically, I can major the wave number or wave length or energy of this spectral lines. So, Gilliam et al he majored the first line, means transition from 0 to 1 in the rotational spectra of cobalt monoxide, and he found the value of this spectral lines is 3.842 centimeter inverse ok. From theory we have seen this that is nothing, but is equal to 2 B. So, you can write 2 B equal to 3.842 centimeter inverse.

So, B equal to 1.921 centimeter inverse. Now B equal to this B, what is B. So, B if, as I as I have written B equal to this. So, from here I can write I equal to h by 8 pi square BC that what I have written I equal to h by 8 pi square BC lucky. So, C; so that is 1 by B. So, I have written separate, I have written separate this 1 by B, because B value I know from experiment. So, if I put B value and other is constant, you see C, this velocity of light pi and h, these are constants if I put this value of constant. So, I moment of inertia I will get this, this value 14.569 into 10 to the power minus 47 kg meter square ok. So, I was able to calculate this moment of inertia. So, moment of inertia I equal to mu r 0 square. So, mu equal to m 1 m 2 by m 1 plus m 2. So, m 1 is, if it is mass of carbon then m 2 is mass of oxygen, so mass of carbon.

So, this, the mass of mass of carbon so, this I think yeah mass lambda is 12 for carbon and this for oxygen it is 16. So, 12 and then this, the mass of hydrogen, now 1.67 into 10 to the power minus 27 multiplied with these. Then we will get the mass of this weight of this, basically weight this mass in terms of kg will get for carbon and for oxygen.

So, now, mu you can find out from this mu equal to m 1 m 2 by m 1 plus m 2. So, mu is the, this 11.383 into 10 to the power minus 27 kg. So, now, mu you know. So, r 0 you mu you know and I also, you know I also you know this is value is available. So, r 0 will be square root of I by mu. So, if you put this mu value, it is coming 1.131 angstroms and r 0 is nothing, but bond length. It is nothing, but bond length of cobalt monoxide.

So, this very nice experiment so, just from rotational spectroscopy one can or this also called microwave spectroscopy, one can measure the energy of the spectral lines. So, first spectral lines or second, third, fourth, but first one is the in tensed one, other one is difficult to see that I will discuss. So, why he measured the first one so that I will discuss intensity of all these spectral lines is not same.

So, only this, first one is very bright and other one is with higher order. So, second, third, fourth, they are very weak. So, but measuring the first one is, if you find out then we have seen that using the theory rigid, rigid rotator model. So, using whatever from this theory, whatever the expression we got of energy of these spectral lines.

So, if we equate this theoretical energy of spectral lines with the calculated or experimental energy of the spectral line, then from their one can calculate or find out the bond length of molecule. So, this is the nice way to measure the bond length of molecule. So, this is one nice example of application of this, for this studying of the rotational spectroscopy of molecules. So, next I can so if basically, as I mentioned that all molecules, all spectral lines intensity of spectral lines first line, second, third, fourth line they are not intensity are not same. So, why they are not same that we want to find out?

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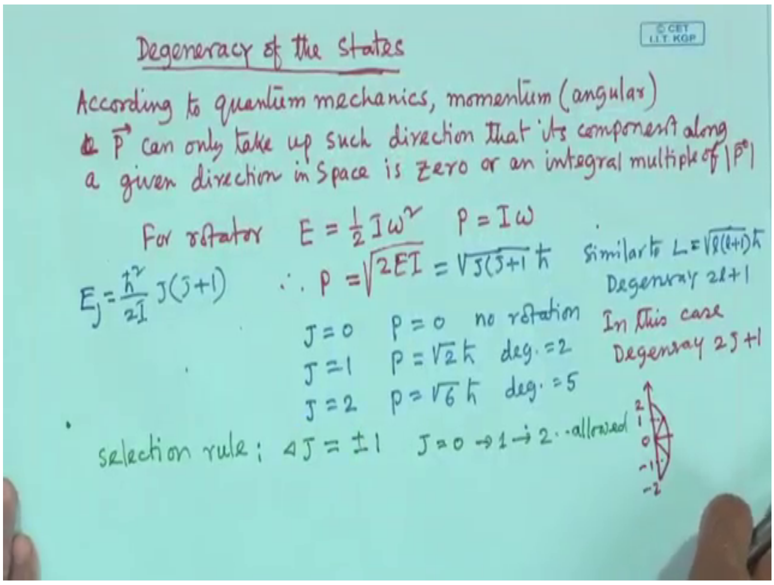

Degeneracy of the States

According to quantum mechanics, momentum (angular) $\vec{P}$ can only take up such direction that its component along a given direction in Space is zero or an integral multiple of $|P^{\circ}|$

For rotator $E = \frac{1}{2} I\omega^2$ $P = I\omega$

$E_J = \frac{\hbar^2}{2I} J(J+1)$ $\therefore P = \sqrt{2EI} = \sqrt{J(J+1)}\,\hbar$

Similar to $L = \sqrt{l(l+1)}\,\hbar$

Degenray $2l+1$

In this case

Degenray $2J+1$

$J = 0$ $P = 0$ no rotation

$J = 1$ $P = \sqrt{2}\,\hbar$ deg. $= 2$

$J = 2$ $P = \sqrt{6}\,\hbar$ deg. $= 5$

selection rule; $\Delta J = \pm 1$ $J = 0 \rightarrow 1 \rightarrow 2$ .. allowed

So, before that we should know this, there is a degeneracy of the states so, what you got. We got this different energy level of the rotator rigid rotator or of a molecule rotating molecule. So, different energy level means they have so defined, so they; so these energy levels are allowed, means these are the energy allowed for the rotating molecules. So, but it is in which state, it is in which state. It can be in one of them. So, there are many states energy levels. So, each energy levels means if the energy of the rotating molecule, if it can be one of them. So, then we tell if it is at the lowest energy state J equal to 0, then we tell this molecule is in down state. If it is in J equal to 1.

So, this is the fast first excited state, second excited state, third excited state. So, these the, this, in rotational excited state, this rotational energies spectra is like this, and then this molecule due, its rotation, it can be in one of this states ok. Now, each of the states whether it, whether it is non degenerate or degenerate. So, in case of hydrogen atom, we have seen that for n equal to 1, then n equal to 0 to m minus 1. Now, for each l, again for each l, again about a fixed direction so, there is a quantum number that is m or ml, we tell right or m whatever.

So, how many, how many states as possible; that is basically the space quantization with respect to this fixed direction. So, how many, how many this allowed value. So, that is basically minus m l to plus m l. So, total this quantum number is basically 2 l plus 1. So, then we tell if energy depends on m and l that if does not depends on m l. So, then we tell the, this, this, this, this has 2 l plus 1 times degeneracy ok. So, that is why 2 l plus 1 number of states having the same energy. So, that is the degeneracy. So, here as I told that this rotation rotating, whatever this we are saying that is equivalent to the angular motion, angular momentum.

So, J whatever we have constant that is the equivalent to l basically so, due to this, due to this rotation. So, this energy there are different energy levels and different energy levels is based on different value of J and there is a degeneracy of each level depending on the value of J. So, what is the number of degeneracy? So, it is basically as I mentioned, so is the similar to l. So, for l how many number of degeneracy we have seen; that is 2 l plus 1 2 l plus 1 so, here also in this case, degeneracy 2 J plus 1, so 2 l plus, so 1 2 J plus 1 ok. So, yeah here I have mentioned this for rotator, its energy E equal to half m B square kinetic energy half m B square half m B square.

So, m is replaced by I moment of inertia and is B is replaced by omega angular velocity. So, E equal to half I omega square and P equal to m B, so here I omega. So, this P one can from here, one can write P equal to square root of 2 E by I. So, and this p is a basically in this case here angular momentum P, have, which is not linear momentum; although I have written P, but its angular momentum. So, P angular momentum is the Eigen value, basically square root of J J plus one h, so l square. So, in case of quantum mechanism l is replaced by square root of l l plus 1 h square, so here, so J square root of J J plus 1, so that is why.

So, that is energy E P square by 2 m a cross squared by P squared by 2 n, in case of linear motion. So, here this it is. So, one can write P square by 2 m. So, P square by 2 m means P square by 2 I. So, p is I a cross minus I e cross del kind of things is there. So, from here also energy of this rotator, one can write h square by 2 I J J plus 1 ok. So, for just simple way also one can tell and. So, it has degeneracy each energy levels have degeneracy and that degeneracy is basically 2 J plus 1. So, now, what is the meaning of degeneracy. means I have energy levels, I have energy levels, I have energy levels.

So, each energy levels means state of the, this is the state of the, state of the molecules rotation rotating molecules energy state of the rotating molecules. Now here energy level and the states that is the difference in one energy level. So, there may be more than one state when we tell in terms of state. So, that basically state of it can be one of the degeneracy state, having the same energy. So, having the same energy it may have more than one state. So; that means, here its the one state it is the, all the energy, this energy are same, but it has many states number, few number of states more than one state ok.

So; that means, at just energy molecule have probability to stay that should be proportional to the degeneracy of the energy level, as well as energy of this level energy of this level. So, that is why if more; so this one can think other way. See I have taken say hcl molecule. So, 100 number of hcl molecule. So, each molecule have their own, their same energy have their same energy states configuration, but all molecules are not staying in, all molecules are not staying in at a particular energy states.

They can have in different states, because different states of different energy levels are there, each energy levels again has the degeneracy. Now if I have 100 molecules now. These 100 molecules where will stay, what is the probability to stay at J equal to 0 and J equal to 1, at J equal to 2, in which state they can stay ok. So, that should be the proportional of the number of states at a particular energy; that is 2 J plus 1. This population of the molecules means out of 100, how many will be there that is called population, population of this molecule or I have say N 0, wherever 100 I told.

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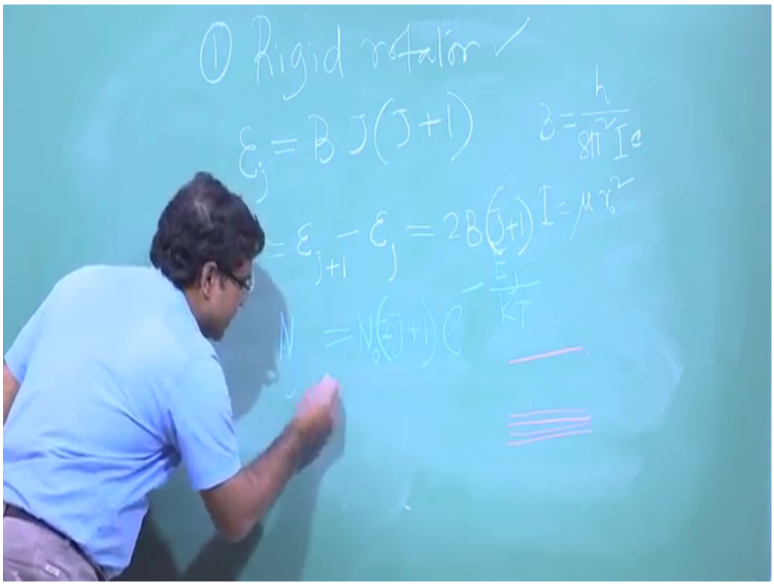

If I take that is N 0 out of N 0 molecules, out of 100 molecules; that is N 0, how many molecule will stay in jth state. So, N j; that is the number of molecule will stay at jth state, jth energy level. So, that is proportional to the, basically that is called population, how many will be there. So, that will be proportional to J J plus 1, no 2 J plus 1; that is the degeneracy proportional to the degeneracy, as well as it will be proportional to the Boltzmann factor, all the time this Boltzmann factor we use. So, if this system is at a particular temperature ok. So, then what is the distribution.

So, that is the Boltzmann distribution so, what is the Boltzmann factor? So, e to the power minus e energy by k T so, this will connect with the temperature of the system and energy of the system. So, e to the power minus Ej; in our case the energy of jth level is Ej by kT. So, these are the, here it is, it will tell you the population of the molecules at a particular energy level. So, one can show, one can show that at yes. So, so if I plot is this, this population if I plot, I think I can plot here, if I plot this population I think I can show also, here this yes.

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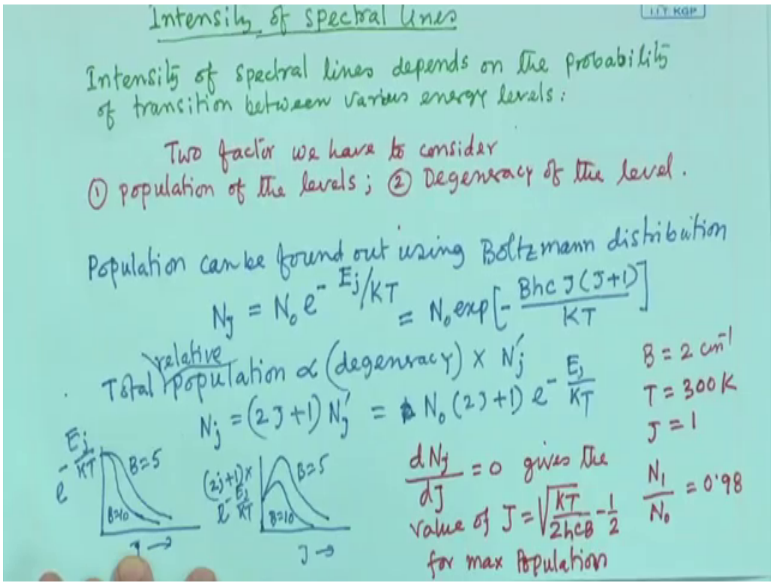

Intensity of spectral lines

Intensity of spectral lines depends on the probability of transition between various energy levels:

Two factor we have to consider
① population of the levels; ② Degeneracy of the level.

Population can be found out using Boltzmann distribution

$$N_J = N_0 e^{-E_j/KT} = N_0 \exp\left[-\frac{BhcJ(J+1)}{KT}\right]$$

Total relative population $\propto$ (degeneracy) × $N_j'$

$$N_j = (2J+1)N_J' = N_0(2J+1)e^{-\frac{E_j}{KT}}$$

$\frac{dN_J}{dJ} = 0$ gives the value of $J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$ for max Population

$B = 2\ cm^{-1}$
$T = 300K$
$J = 1$
$\frac{N_1}{N_0} = 0.98$

I can show here so, intensity then that the intensity of spectra will depend on the basically population of the rotating molecules in different energy levels. So intensity of spectral line depends on the probability of transition between various energy levels that is true. So, two factors we have to consider; one is population of the levels and another degeneracy of the level.

So, that is why N j, this is basically Boltzmann factors E j E j; if so I have written here that in terms of expression so, B J J plus 1. Now it was in wave number. So, that is why you have to multiply with hc, then it will be energy. So, B hc J J plus 1 by kT.

Now total population or relative population, actually it is a proportion of both factor. So, these, the basically N j equal to. So, here if I take this is as an Nj this Boltzmann factor so, then degeneracy into this Boltzmann factor in j dash. So, that is finally, we are writing N j. So, N j equals to this 2 J plus 1 N j dash Boltzmann factor, and equal to N 0 2 J plus 1 e to the power minus E j by kT. So, that is what I have shown if I plot. So, this Boltzmann factor is varies like this with J value, it will vary like this. So, it depends on B. So, we have considered B equal to 5 and B equal to 10. So, if higher the B so, exponential term it will be, it will take a fluster.

So, this will be the variation of Boltzmann factor. So, now, we have exponential term as well as the linear term 2 J plus 1; so how to plot. You know I have shown in case of hydrogen atom. So, this term is basically N j, it is basically varies like this. So, it will have maximum that a particular J value, it will have the maxima and it will depend on temperature of course. So, at which value one can get maxima that you can find out. So, that is the standard positude d Nj by dJ equal to 0 gives the value of J square root of kT by 2 hc B minus 1 so, just differentiated with respect to J equal to 0.

So, then you will find out the J value, where you will get the maximum population so, J value. So, maximum population will get at J equal to square root of kT by 2. So, it depend, maximum this population depends on temperature as well as depends on B, others are constant. So, this, this one can find out easily so, but just if you put, if you take 1 B value, if you take 1 B value, B equal to say 2 centimeter inverse and at room temperature what is the, what is the population at J equal to 1. So, J equal to 1. So, ratio you see N 1 by N 0. N 0 is basically at temperature 0 at 0 temperatures. So, what about the, all molecules will be at rotating molecules will be at J equal to 0 energy level.

So, now, yes now basically at; so at J equal to 1 what is the population? So, N 1 by N 0 it will come, if you take this value, this will come 0.98 ok. So, 0.98 means, so N 1. So, they are most of their 98 percent molecules out of 198 molecules will be at J equal to between these two level, you know J equal to. So, if initial is initial this N 0. So, for J equal to 1 N 1 J equal to 1 N 1. So, at N 1 level 98 molecules out of 198 molecules will be at J equal to 1. So, how many numbers will be at J equal to 2, how many numbers will be at J equal to 3 etcetera. So, you will see this, it will reduce drastically. So, most of the molecules will be at the lower level. So, that is why transition we are considering only from.

So, here transition del J equal to plus minus 1, it is allowing from J equal to 0 to J equal to 1 or J equal to 1 to J equal to 2, J equal to 2 to J equal to 3. So, I think there is a, here just slightly I think J equal to 1 I have taken. So, it should be, it should be the. So, then J value one can chose J equal to 1 2 3 4; that is the lowest energy level. So, in lowest energy level 98 percent molecules will be there, and two percent will be at the rest of the J equal to 2 3 4 5. So, from transition from J equal to 2 to J equal to 3. So, molecule in J equal to 2 is only 1 percent or less than 1 percent, even it is 2 percent and J equal to 1, it is 98 percent. So, J equal to 1 2 to. So, whatever the intensity I will get, if it is 90 percent this population.

So, I will get 90 percent this say intensity, so then 2 to 3 2 percent population. So, I will get the intensity compare to this first or it is just 2 percent of that first one. So, that is why I told this first line only will have the highest intensity, and this next onwards this intensity drastically reduce. So, that is why we get the intensity, bright intensity only for first line, in case of rigid rotator model and yeah measuring this first spectral lines one can, one can predict the.

Sorry this bond length of the molecule. So, that is why Gilliam as I showed you; this tell did this experiment on cobalt monoxide, and they measure only the first one. The reason is that this first one is very bright and thus very easy to measure. So, I will stop here I will continue in next class.

Thank you.