Fundamentals of Spectroscopy

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Lecture-17
Intensities of Rotational Lines

Hello everyone, in the last lecture we discussed about the space quantization. We saw that the diatomic molecule cannot arbitrarily orient itself with respect to the reference axis. But the molecule can only orient itself in certain directions.

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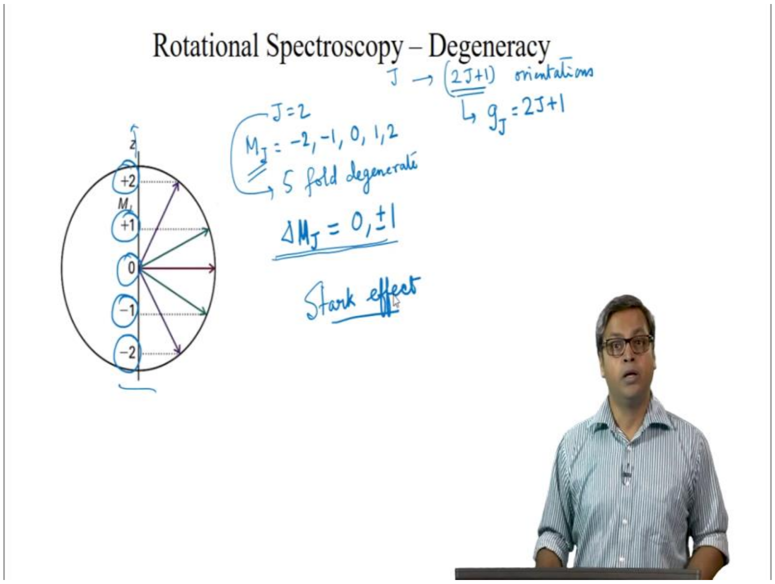

Rotational Spectroscopy – Degeneracy

$J \rightarrow (2J+1)$ orientations

$\hookrightarrow g_J = 2J+1$

$J=2$

$M_J = -2, -1, 0, 1, 2$

$\rightarrow$ 5 fold degenerate

$\Delta M_J = 0, \pm 1$

Stark effect

If one molecule is in the jth quantum level, so, let us say the molecule is in the jth level then there are two J + 1 possible orientations so 2 J + 1 possible orientations and these orientations all have the same rotation and energy. So, for example when J equals 2 we know MJ equals -2 - 1, 0, 1 & 2. So, we can see in this figure so MJ can take values of + 2, + 1, 0 - 1 and - 2. So, we can say that J equals 2 is 5 fold degenerate.

So the Jth level is 2J + 1 degenerate or we can write the degeneracy GJ equals 2J + 1 because we have looked into space quantization in the last lecture. Today we will start by looking into the consequences of space quantization. There is an additional selection rule associated with MJ. And this additional selection rule associated with MJ is given by Delta MJ equals 0 + - 1. That means the change in the MJ quantum number must be equal to 0 or + - 1.

However as the energy of the rotational level does not depend on the quantum number MJ, this selection rule Delta M J equals 0 or + - 1 has no effect on the rotational spectrum, as the molecule does not know what the z axis or this arbitrary axis or the reference axis. Now, the question is when can we have an exception of this. We can have an exception if the molecule is not in an isotropically event spatial environment.

If somehow the molecule knows what the reference axis is the result would be different. But how can the molecule know the direction of the reference axis? This can only happen if an electric or magnetic field is applied externally in a particular direction. If an electric field is applied in a particular direction, there will be an interaction between the electric field and the dipole moment. This interaction will depend on the spatial orientation of the molecule.

So, the energy of the system will now depend on the MJ quantum number and the selection rule with regard to MJ that is Delta MJ equals + - one will affect the rotational spectrum. Thus the degeneracy will be lifted and this lifting of degeneracy in the presence of an externally applied electric field is known as start effect.

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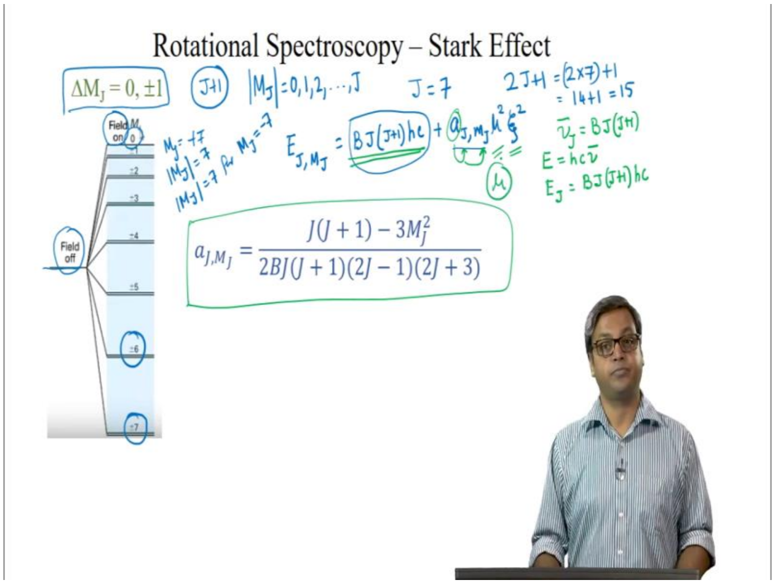

Rotational Spectroscopy – Stark Effect

$\boxed{\Delta M_J = 0, \pm 1}$ $(J+1)$ $|M_J| = 0, 1, 2, \dots, J$ $J = 7$ $2J+1 = (2\times7)+1 = 14+1 = 15$

$M_J = +7$
$|M_J| = 7$
$|M_J| = 7$ for $M_J = -7$

$E_{J,M_J} = \boxed{BJ(J+1)hc} + a_{J,M_J}\mu^2\xi^2$

μ

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

$$\boxed{a_{J,M_J} = \frac{J(J+1) - 3M_J^2}{2BJ(J+1)(2J-1)(2J+3)}}$$

So let us say J equals 7. So, there will be 2 J +1, that is, 2 times 7 + 1 that is 14 + 1 or 15 possible levels, which will all be degenerate in the absence of the externally applied electric field. In the presence of the electric field, the degeneracy is partially lifted. And the selection rule Delta MJ equals 0 or + - 1 becomes important. Each level now splits into J + 1 components such that the absolute value of MJ can be either 0, 1, 2 or integral values up to J. so, we can see this in this figure when the field is off the states are degenerate.

However when we turn on the field, or we apply the external electric field then the degeneracy is partially lifted and we can say that for + 7 or mg equals + 7 mod MJ equals 7 also mod M J equals 7 for MJ equals - 7. So, when the molecule is at MJ equals + - 7 it is here these are the levels 4 + - 6 and the highest level is for MJ equals 0. The energy of any level now is given by E which is now a function of both the j quantum number and the MJ quantum number.

And this is given by B times J times J +1 hc + a which is a function of J quantum number and the MJ quantum number, the dipole moment mu squared and the electric field squared. So, this a term has some complex dependence. But before we go there we see that the first term that we have this first term is actually the term when the field is not present. This is because we know Mu bar g is given by B times J times J +1.

So, we also know the energy if we express the energy in Joule then E equals hc nu bar in other words I can write EJ equals B times J times J + 1 which is Mu bar J times hc. So, this first term was already there in the absence of the field. So, we have an additional term here which depends on the electric field strength on the dipole moment. And another parameter which itself depends on the quantum numbers J and MJ and the dependence as we can see here, the term depends on J and M J in a complex manner.

But we do not need to care about this complex form of dependence but as the energy depends on the dipole moment of the molecule, this is a useful way to measure the dipole moment of the molecule. We should remember that spectroscopy is done just not to obtain a spectrum, but to use the spectrum to determine something about the molecule. The start effect can be used to precisely determine the dipole moment Mu of the molecule.

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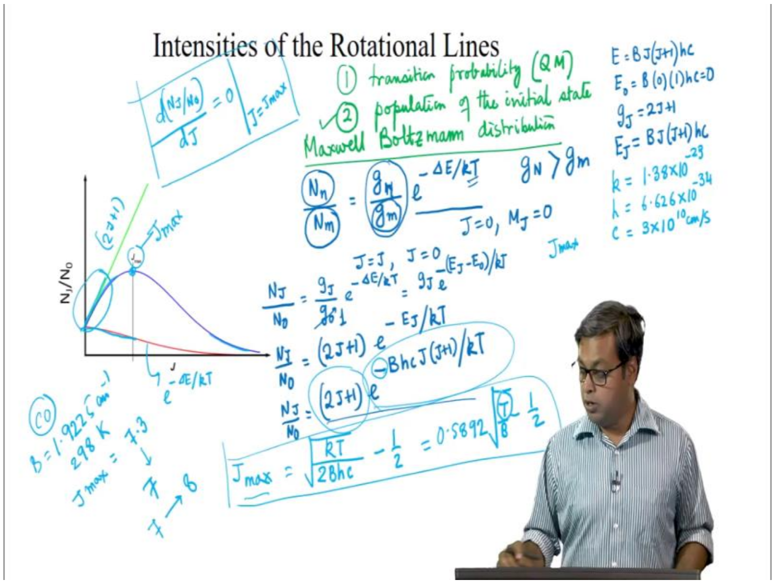

Intensities of the Rotational Lines

So, now we will focus on the intensities of the rotational lines. The spectral line intensity is controlled by two things: Number one is the transition probability which can be estimated from quantum mechanics. And the other is the population of the initial state that is the population of the initial state from which the transition will take place. The 2j + one degeneracy is going to affect the second thing that is it is going to affect the population of the initial State.

If degeneracy is more for a particular level the molecule has more chances to have that energy. So therefore, more molecules are in that level if we calculate the transition probability for a rotational system from quantum mechanics we will see that the intrinsic probabilities of transition between any two adjacent rotational levels are identical. And here we are talking about adjacent rotational levels because we know in the absence of any externally applied electric field the selection rule says Delta J equals + - 1.

So we can largely ignore the quantum mechanical effect of change in probability so, the intensities of the spectral lines will be directly proportional to the number of molecules in each rotational level. So, we can imagine that as the spectrum is recorded over an ensemble of molecules, the molecules are distributed over different energy levels. Or we can think the molecules are distributed over different values of J. The populations of these levels are governed by Maxwell Boltzmann distribution.

So, from Maxwell Boltzmann distribution, we can write the population of the inner state divided by the population of the MH state equals degeneracy of the state n divided by degeneracy of the state m there is a ratio of the degeneracy's times an exponential term e to the power - Delta e by K T. so, here G is the degeneracy and this expression relates the number of molecules in the two states, the state M and the state N.

So, the ratio of the number of molecules in the two states depends on the ratio of the degeneracy's of the two states. So, if G n is greater than G M more molecules will be in the end state. In addition the ratio of degeneracy is multiplied by an exponential term e to the power - Delta e by K T where Delta e is the energy difference between the N and the M state and the KT is the amount of thermal energy available to excite the molecules in any of the excited States.

So, let us see how degeneracy is going to affect the population of the distribution. It makes sense to refer the population of any state to the ground state. So, here instead of referencing the population of the N F state to the population of the M F State we can think about referencing the population of the N F state to the population of the ground state or J equals 0. This is because at J equals 0 MJ can only take the value of 0. That means J equals 0 is more degenerate.

So as J equals zero is not degenerate the degeneracy of the denominator that is G M disappears. So, let us consider two states one state is J equals J and the other is J equals zero. So, we can write NJ by N0 equals GJ by G0. e to the power - Delta e by K T. so, we can write this as G J what G 0 is 1. So, we can write GJ e to the power - of e j - e0 in brackets by K T. so, we will also know that the energy is given by B times J times J + 1 hc.

So for J equals 0 is 0 equals B times 0 times 1 times hc that is 0. So, e 0 equals 0 and we also know G of J equals to J + 1. So, we can write this as NJ by N0 equals 2J + 1 times e to the power - EJ by K T. Again EJ equals B times J times J + 1 hc. So, we will write NJ by N0 equals to J + 1 e to the power - b hc J times J + 1 divided by KT. So, now if you carefully look into the right hand side, we have to consider two terms. One is that of this 2J + 1 and the other is this exponential term.

As J increases to J + 1 increases or the degeneracy increases. But on the other hand the exponential term decreases, because of the negative sign. So, we have two competing terms. In other words DJ indicates more molecules in the high J level, but the exponential term indicates fewer molecules as J increases. So, there will be a balance between these two terms at some value of J, we will have a maximum population denoted by J max.

So, if you look into this figure, here, we are plotting 2J + 1 and we can see the steady increase of 2 J + 1 as the J increases. And this red curve shows the plotting of this exponential term e to the power - Delta e by K T which also decreases. And because there is this competition we find a balance or at some value of J,that is J max there is a maximum so that 2J + 1 factor increases with J whereas the exponential term rapidly decreases.

So, we can see the 2 J + 1 increases the exponential term rapidly decreases so we can see the 2 J + 1 factor increases with increasing J and the exponential term decreases with increasing J. so, at low J the 2 J + 1 term makes this increase in this blue curve. But until at higher J the exponential factor wins and NJ by N0 approaches 0. So, we can appreciate this by doing some simple calculus we can simply differentiate the expression with respect to J.

So, when the expression or D NJ by N0 or 0, dj this is the gradient and this gradient equals 0 at the maximum or at J equals J max. So, the population therefore shows a maximum at a value of J equals J max which corresponds to D NJ by n 0 of D J equals 0 at J equals J max. So, if we solve this if we solve this particular equation, we can get the value of J max. And we can see J max equals root over K T by 2 B hc - half.

Now if we put the values, for example, if we put the Boltzmann constant k equals 1.38 times 10 to the power - 23 in the SI units and we put h equals 6.62 10 to the power - 34 in the SI unit and the value of C if we put 3 into 10 to the power 10 centimeter per second, then, what we will get, will get this expression we can simplify as 0.5892 root over T by B - ½.

The J max in the expression is a non integer. But it has to be an integer because J max is some value of J and J can only take integral values. So, this non integer value of J max happens because when we differentiate we assume J is continuous. But this is not true as J is always an integer or in other words these levels are quantized. The maximum line intensity should be the nearest J value or the nearest integral J value obtained from the above equation.

I mean this particular equation that we have solved here. So, for example, for carbon monoxide CO, the value of B is 1.9225 centimeter inverse. And this value is at 298 Kelvin. So, if we solve this expression, we will find J max equals 7.3. so, the nearest integral value of J Max or the nearest integral value of 7.3 is 7. Thus we can say the transition from G equals 7 to J equals eight will show the maximum intensity. But more importantly G max depends on temperature.

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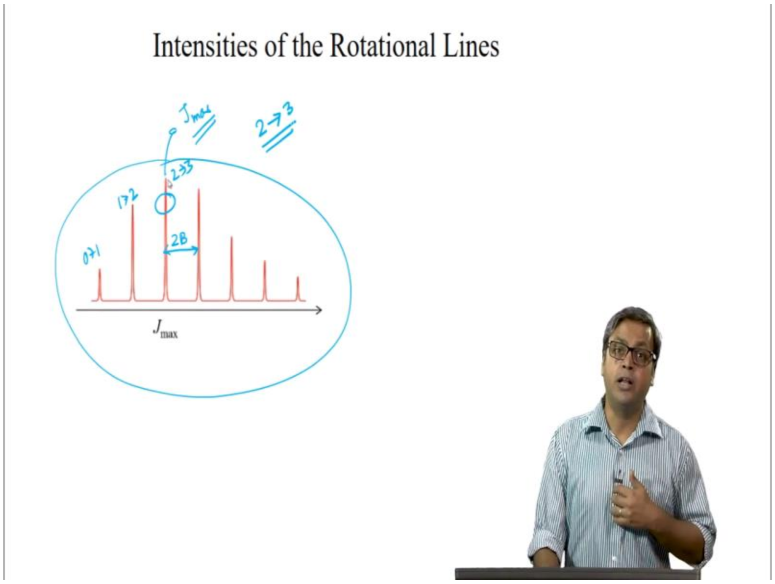

Intensities of the Rotational Lines

So, now let us have a closer look in the intensities or how will a rotational spectrum look like. so here, in this figure, we have a rotational spectrum. So, if we know the value of B from the spacing between the spectral lines because the spectral lines are spaced out by 2b. so, if we know the value of B from the spacing and also can identify the line which has the maximum intensity, that is, this is the J max line or at this value, the population or the spectrum has maximum intensity. So, if you can use this information to determine the temperature of the sample.

So, in this particular figure we see we have transitions 0 to 1, 1 to 2, 2 to 3. So, we can see J equals 2 gives the most intense line in the spectrum and that means the transition which is most intense is coming from 2 to 3 transitions. So, we can use this to determine the temperature. But we can think in the lab it is not helpful as we can measure the temperature in a much easier way, we can just use a thermometer. But what if the molecule is in that misfile or even further away in space.

In that case these intensities of the spectral lines can be extremely useful to determine the temperature. So, now we will look into a couple of problems before we end this lecture.

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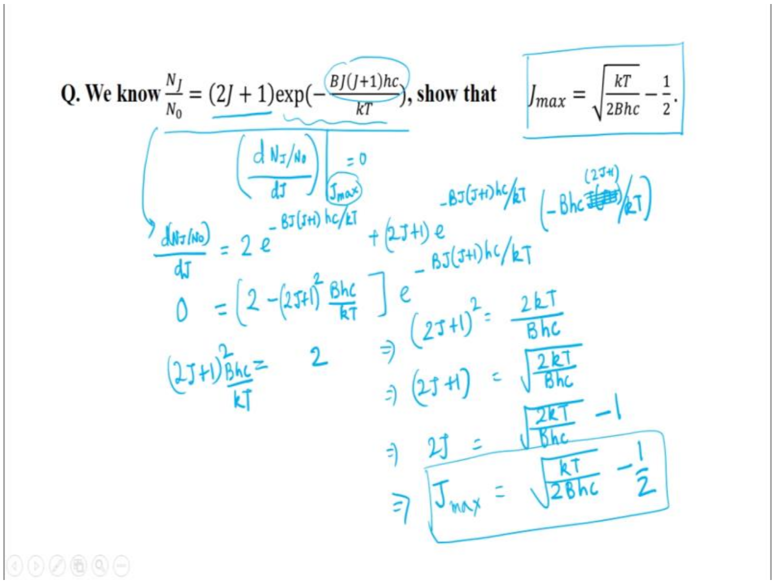

Q. We know $\frac{N_J}{N_0} = (2J+1)\exp(-\frac{BJ(J+1)hc}{kT})$, show that $J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$.

$$\left(\frac{d\, N_J/N_0}{dJ}\right)\Bigg|_{J_{max}} = 0$$

$$\frac{d(N_J/N_0)}{dJ} = 2e^{-BJ(J+1)hc/kT} + (2J+1)e^{-BJ(J+1)hc/kT}\left(-Bhc\overset{(2J+1)}{\cancel{}}/kT\right)$$

$$0 = \left[2 - (2J+1)^2\frac{Bhc}{kT}\right]e^{-BJ(J+1)hc/kT}$$

$$(2J+1)^2\frac{Bhc}{kT} = 2$$

$$\Rightarrow (2J+1)^2 = \frac{2kT}{Bhc}$$

$$\Rightarrow (2J+1) = \sqrt{\frac{2kT}{Bhc}}$$

$$\Rightarrow 2J = \sqrt{\frac{2kT}{Bhc}} - 1$$

$$\Rightarrow \boxed{J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}}$$

So, the first problem we have, so we have actually discussed a part of it during the lecture but we did not do the entire derivation. So, we know in J by n 0 is given by 2 J + 1 exponential - B times J times J + 1 hc by KT. So, we have to show or we have to get to the final expression that we discussed in the lecture. So, we know that d NJ by N0 by dJ at J max equals zero. So, let us try to evaluate from this expression. d NJ by N0 divided by dJ.

So, for this we have to get that the derivative first term that is 2 times e as the exponential term - B J times J + 1 hc by KT and then we have to keep this term constant. That is 2 J + 1 and take the derivative of the next term so that we have exponential - B J times J + 1 hc by KT and then we have J here you have to take the derivative of this so that is x - b hc J times J + 1 divided by KT. so, this the left hand side we know equals 0 so 0 equals 2.

We can take the exponential part common that is e to the power - B times J and this J + 1 hc by KT, so we have 2 - 2 J + 1. So, here we have to take the derivative. So, this will be 2 J + 1. So, we have 2 J + 1 squared b hc by KT. So, we can write 2 J + 1 squared times B hc by KT equals 2. Or we can write 2 J + 1 squared equals to KT by bhc or 2j + one equals root over 2 KT by b hc or 2 j equals root over 2 KT by HC - 1.

So from this we can get J and because we are solving this at J equals J max, so we can write JM x equals root over here KT by 2 b hc - half. So, we have come to the expression that we needed to derive. So, now let us look into the next question.

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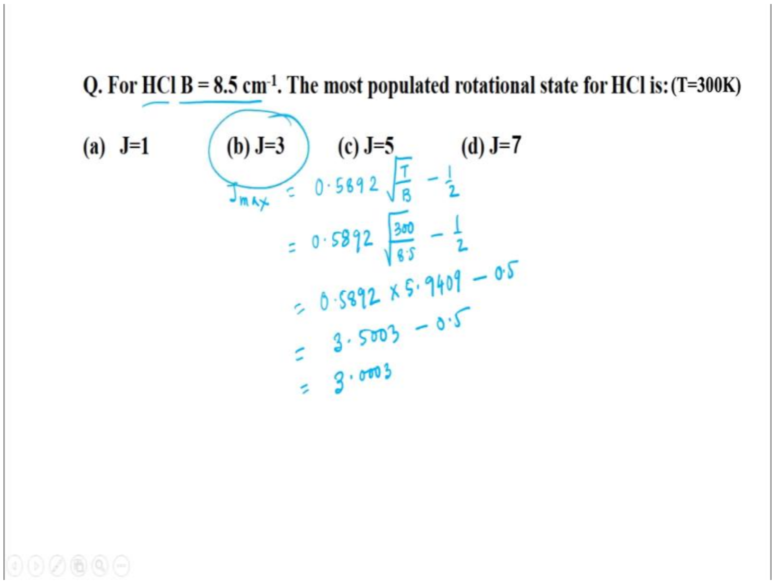

Q. For HCl $B = 8.5\ cm^{-1}$. The most populated rotational state for HCl is: (T=300K)

(a) J=1 [✓ (b) J=3] (c) J=5 (d) J=7

$$J_{max} = 0.5892\sqrt{\frac{T}{B}} - \frac{1}{2}$$
$$= 0.5892\sqrt{\frac{300}{8.5}} - \frac{1}{2}$$
$$= 0.5892 \times 5.9409 - 0.5$$
$$= 3.5003 - 0.5$$
$$= 3.0003$$

So for HCl here, the value of B is given the B is 8.5 wave numbers. So, the question is the most populated rotational state for HCl we have four options. J equals 1, J equals 3, J equals 5 and J equals 7. So, we know that J max that is exactly what we need to find out here is 0.589 to root over T by B - 1/2 so, we can write 0.5892 root over temperature. The temperature here is 300 so, 300 by B that is 8.5 - 1/2 so that becomes 0.5892 times 5.9409 - 0.5 so this becomes 3.5003 - 0.5. So, this is 3.0003 so the answer which is the nearest integer that is J equals 3.