Chemistry II: Introduction to Molecular Spectroscopy
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Lecture – 18
Rotational and Vibrational Line Intensities

Welcome back to the lectures on molecular spectroscopy and introductory chemistry. In this short lecture let us look at the rotational and vibrational line intensities from an elementary point of view using the Maxwell Boltzmann statistics. It was mentioned to you some lectures ago that there are three parameters which are of importance in any study using spectroscopy namely the line positions which are dealt with by quantum mechanics.

The line intensities which require both quantum mechanics and also statistical mechanics since we deal with populations of molecular systems in different energy levels and the third was the line width we shall not consider the line width in this course, but let us look at the line intensities a little more closely and particularly for the rotational microwave and infrared frequencies and transitions ok.

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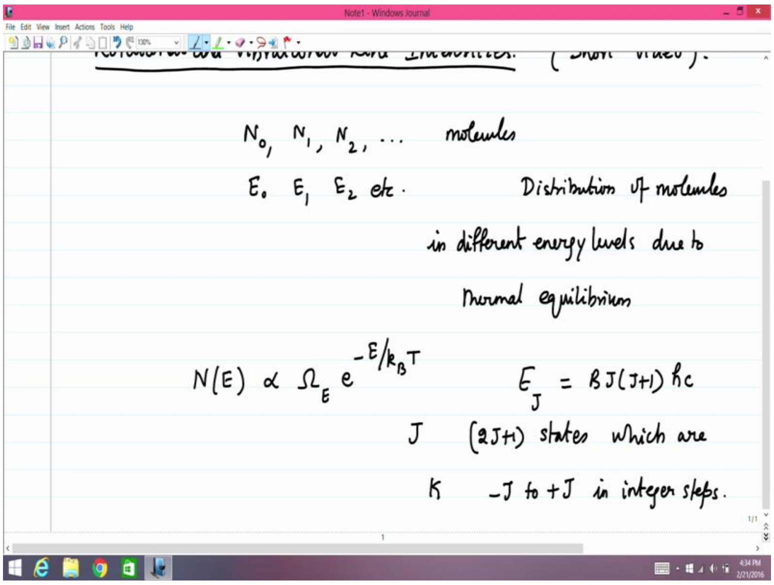

$N_0, N_1, N_2, \ldots$ molecules

$E_0 \; E_1 \; E_2$ etc. Distribution of molecules in different energy levels due to thermal equilibrium

$N(E) \propto \Omega_E \, e^{-E/k_B T}$

$E_J = BJ(J+1)\, hc$

J $(2J+1)$ states which are

K $-J$ to $+J$ in integer steps.

Now, the basic formula or the basic prescription that you should remember is that molecules the number of molecules in any energy state means assume that we have N 0, N 1, N 2 etcetera molecules in different energy levels E 0, E 1, E 2 etcetera there is distribution in thermal equilibrium; distribution of molecules in different energy levels due to thermal equilibrium what we need to know is the Boltzmann formula which was also mentioned to you earlier in the course.

The Boltzmann's formula tells you that the number of molecules N at any given energy level E is approximately proportional to the degeneracy of that energy often it is written using omega of E and to the Boltzmann factor which tells you the waiting for that number for that given energy E by k B T. In the case of rotational spectroscopy the molecular energy levels for the simple system of a diatomic they are proportional to the J in to they are basically J into J plus 1. You recall the energy level formula for rotation for a given quantum number J it is B J into J plus 1 times h c. The quantum number J corresponds to 2 J plus 1 state which are given by different values of the projection of J on the molecular axis and these are called the K quantum numbers and they go from minus J to plus J in integer steps.

In the case of diatomic molecule we have the symmetry axis which is the axis of the molecule about which there is no moment of inertia. Therefore, there is no rotational degree of freedom which would show up in that for that motion. The other two axis which are perpendicular to the molecular axis the moment of inertia above both of those axis are identical therefore, there is one moment of inertia and the moment of inertia is built in this constant B as h by 8 pi square I c you have already solved such problems.

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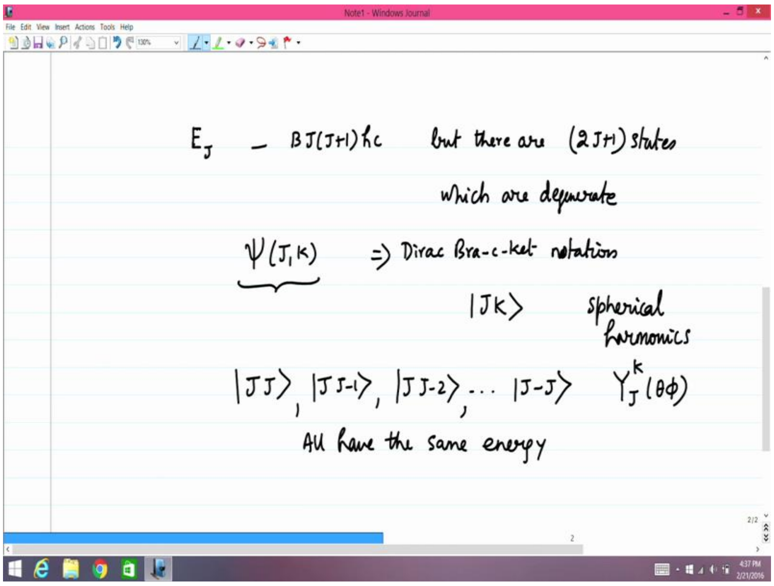

E_J – $BJ(J+1)hc$ but there are $(2J+1)$ states

which are degenerate

$\underbrace{\psi(J,K)}$ ⇒ Dirac Bra-c-ket notation

$|JK\rangle$ spherical harmonics

$|JJ\rangle, |J\,J-1\rangle, |J\,J-2\rangle, \ldots |J-J\rangle$ $Y_J^K(\theta\phi)$

All have the same energy

Therefore what you have is there is only one energy level in the sense one energy value for a given J. So, if you write E J it is B J into J plus 1 h c, but there are 2 J plus 1 states which are degenerate because they all have the same value and these are indicated by the wave function the 2 quantum numbers J and K and the wave functions are usually written as using the dirac notation ket notation is called the bracket notation what you see is that the states are represented as the states J K and for molecular systems where the rotational quantum numbers are integers these J K states can be identified with specific representations through spherical harmonics.

Y J K of theta phi which you had come across in the case of hydrogen atom as contributing to the angular distribution of the wave function therefore, the molecular wave functions for the rotational states or 2 J plus 1 fold degenerate because all the states starting from K is equal to J to J J minus 1, J J minus 2 and all the way down to J minus J all have the same energy; in the absence of any external field or in the absence any other consideration like moments of inertia being different and so on.

For a diatomic molecule the two moments of inertia are equal, the third moment of inertia is 0 therefore, we have all the energy levels for a given J B degenerate.

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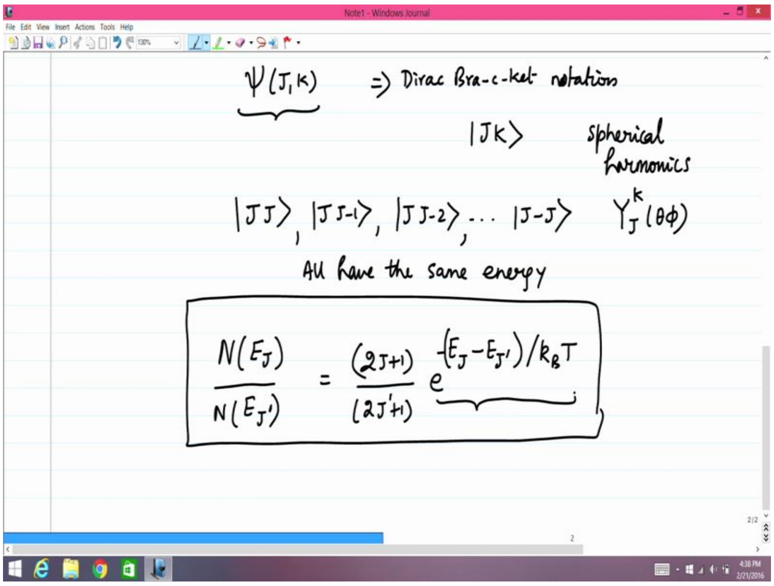

$\underbrace{\psi(J,K)}$ $\Rightarrow$ Dirac Bra-c-ket notation

$|JK\rangle$ Spherical harmonics

$|JJ\rangle, |J\,J-1\rangle, |J\,J-2\rangle, \ldots |J-J\rangle$ $Y_J^K(\theta\phi)$

All have the same energy

$$\boxed{\frac{N(E_J)}{N(E_{J'})} = \frac{(2J+1)}{(2J'+1)} e^{\underbrace{-(E_J - E_{J'})/k_B T}}}$$

Therefore, what does this tell you; this tells you that if you are calculating the molecules the number of molecules in a given energy state corresponding to the quantum number J energy value corresponding to the quantum number J and the number of molecules in another energy corresponding to a different value J prime this tells you that is ratio is 2 J plus 1 by 2 J prime plus 1 and then you have e to the exponential to the minus the energy corresponding to the quantum number J and the energy corresponding to the quantum number J prime the difference between the two divided by the Boltzmann's constant k B T.

So, this is the formula this is what is called the fundamental formula for the calculation of elementary form of microwave intensity without other considerations like reactions and i mean the interaction between rotations and vibrations and all those things not being considered pure microwave transitions of a rigid diatomic molecule that number of molecules in any given energy state J to the number of molecules in another energy state J prime is given by the ratio of the degeneracies and the exponential or the Boltzmann factor given by the energy difference.

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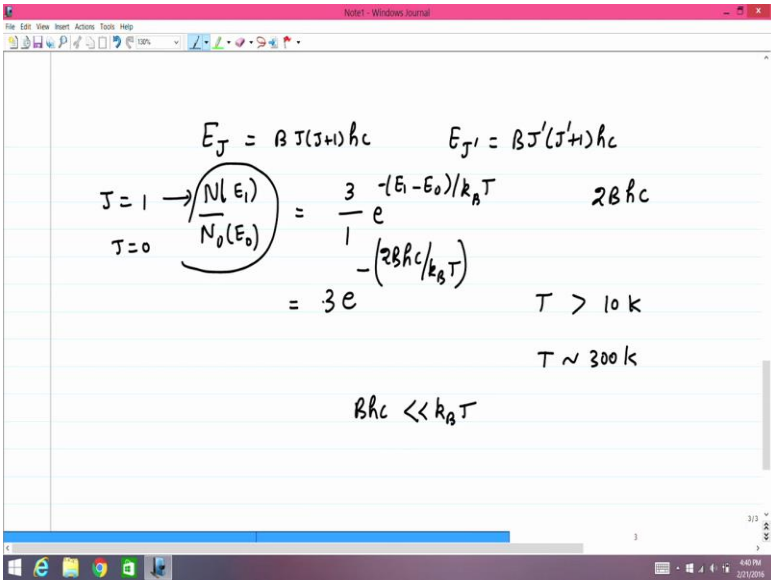

$E_J = BJ(J+1)hc$ $\quad$ $E_{J'} = BJ'(J'+1)hc$

$J = 1 \rightarrow$ $J = 0$

$$\boxed{\frac{N(E_1)}{N_0(E_0)}} = \frac{3}{1} e^{-(E_1 - E_0)/k_B T}$$

$2Bhc$

$$= 3e^{-\left(2Bhc/k_B T\right)}$$

$T > 10\,k$

$T \sim 300\,k$

$Bhc \ll k_B T$

So, what is this; if you write that you recall that E J is B J into J plus 1 h c and E J prime is B J prime into J prime plus 1 h c and if you calculate for example, N 1 by N 0; N 1 meaning E 1 with J is equal to 1 versus E with J is equal to 0; E 0 the grounds rotational state if you do that then this is 3 the 2 J plus 1 here is corresponding to the value J is equal to 1 and this is J is equal to 0 therefore, the degeneracy is here is 3 by 1 and what you have is the energy between E, E 1 with the difference minus E 1 minus E 0 by k B T and that you know is 2 B h c. Therefore, what you have is 3 exponential minus 2 B h c by k B T.

Now, this energy 2 B h c is very small compared to the factor k B T the thermal energy for any temperatures like greater than say 10 Kelvin and suddenly T 300 Kelvin this energy B h c is much smaller than k B T; therefore, you see that the number of molecules in the higher energy state to the number of molecules in the energy state in this particular case is actually that ratio is greater than 1 or N E 1 divided by N E 0 this factor is almost equal to 1 or very close to 1; therefore, it is greater than 1.

So, what you see in the microwave transition is since the degeneracy increases as J increases there is this accommodation of the higher energy state of the system into many more levels all of which are degenerate versus the accommodation of the rotational states into that lower J where the degeneracies are slightly lower.

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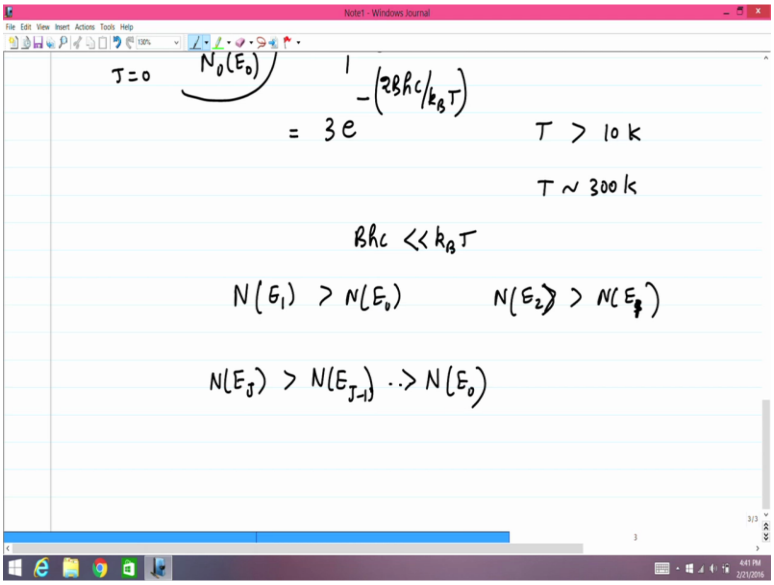

$J=0$ $N_0(E_0)$

$= 3e^{-(2Bhc/k_BT)}$

$T > 10k$

$T \sim 300k$

$Bhc << k_BT$

$N(E_1) > N(E_0)$ $N(E_2) > N(E_1)$

$N(E_J) > N(E_{J-1}) \cdot\cdot > N(E_0)$

Therefore what you see is that the number of molecules in E 1 is usually greater than the number of molecules in the energy state E 0 and the number of molecules in the energy state E 2 is again greater than the number of molecules in the energy state E 1 and so on. So, you can say N E J is greater than N E J minus 1 and so on, until greater than N E 0. Does is go on like that is forever? No, it does not because you see the rotational energy levels also increase very, very fast.

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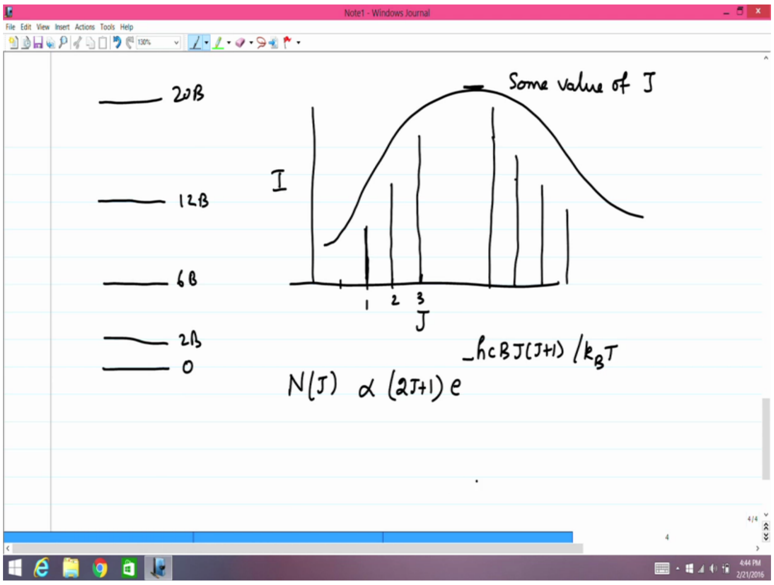

$$N(J) \propto (2J+1)\, e^{-hcBJ(J+1)/k_BT}$$

Because you see the lowest energy level is 0, the next one is 2 B the next one is actually 6 B and the third is 12 B and this one is 20 B and so on. Therefore, the energy gap between successive rotational quantum numbers the states of; states with successive rotational quantum numbers the gap increases therefore, at some point of time the numbers start decreasing therefore, if you plot the microwave rotational intensity as a function of J you start seeing for J is equal to say 0, 1, 2, 3 etcetera you start seeing that well let us keep the 0 out of picture start with 1 with respect to 0 this is some number 2 increases, 3; the J 3 increases and so on. But after some J when it reaches some maximum it comes down to it starts becoming less and less and so on.

So, what you see is that the microwave intensities are like an envelope bit increasing and there is a maximum for a some value of J and that can be easily calculated because if you write the number density or the number for that particular J being in proportional to 2 J plus 1 times exponential minus h c B J into J plus 1 by k B T because this is energy and the correct unit is the h c times the B which is only a wave number unit.

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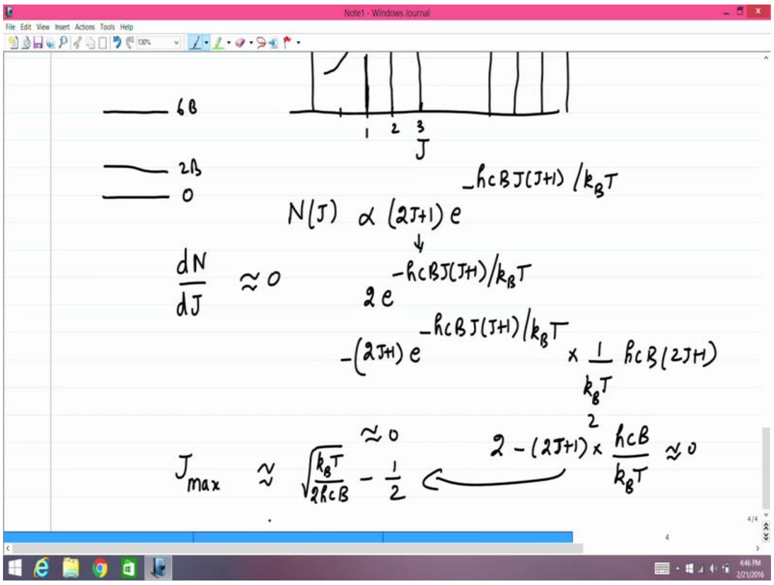

$$N(J) \propto (2J+1)\, e^{-hcBJ(J+1)/k_BT}$$

$$\frac{dN}{dJ} \approx 0 \qquad 2e^{-hcBJ(J+1)/k_BT} - (2J+1)\, e^{-hcBJ(J+1)/k_BT} \times \frac{1}{k_BT} hcB(2J+1)$$

$$J_{max} \approx \sqrt{\frac{k_BT}{2hcB}} - \frac{1}{2} \longleftarrow 2 - (2J+1)^2 \times \frac{hcB}{k_BT} \approx 0$$

So, if you have this you want to find out what is the value of J for which the number is maximum you can do a simple calculus by taking the derivative of the numbers with respect to J and then set that equal to 0; you know it is also approximate calculation J is not continuous therefore, you know to take the derivative does not make much sense, but to get a feel for this the energy levels gaps of still very small compared to thermal energies therefore, if you take a derivative like this you can see that immediately this gives you the following that the number density gives you the derivatives you take the derivatives of this it is 2 times e to the minus h c B J into J plus 1 by k B T; that is the first term of the derivative the second is the derivative of this term which if you take it is minus 2 J plus 1 and this will give you the expression e to the minus h c B J into J plus 1 by k B T times this derivative which is 1 by k B T and the minus sign is already here it will give you h c B into 2 J plus 1. This is what you will get and if you set that equal to 0; it is easy to show that the J max is approximately square root of k B T by 2 h c B minus 1 half. We call that this is a; if you set this equal to 0; the exponential factor goes away. So, it is you can see immediately that it is 2 minus 2 J plus 1 whole square into h c B by k B T that is equal to 0 and that gives you the solution; that is the J max the corresponding value of J is the J max and you can see that this is the ratio.

Therefore microwave intensities actually peak for some middle value of J versus the starting from J is equal to 0 to some other value J. What about the infrared intensity for a diatomic molecule; there is no problem because all vibrational states are non degenerate single vibrational states.

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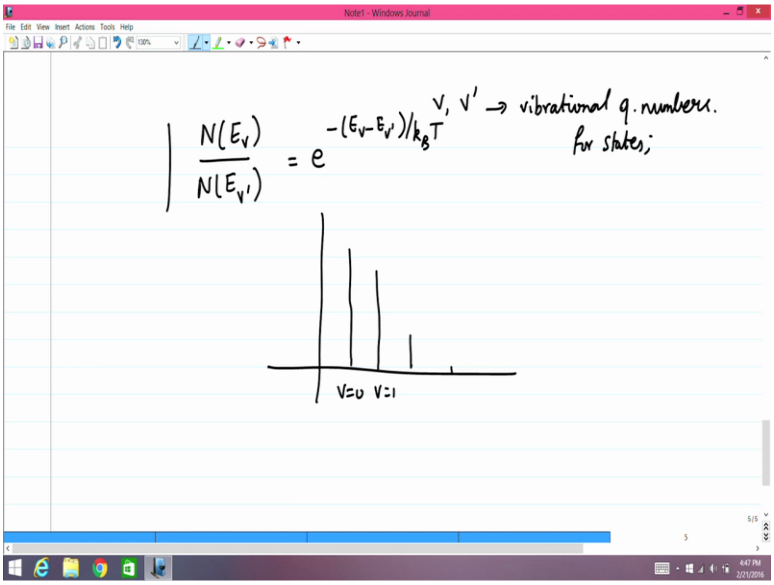

$$\frac{N(E_v)}{N(E_{v'})} = e^{-(E_v - E_{v'})/k_B T}$$

$v, v' \rightarrow$ vibrational q. numbers. for states;

The degeneracy is one; therefore in the case of vibrational motion if you write just N v for N v prime where v and v prime are the vibrational quantum numbers for two different states and then you can see that this is nothing other than simply exponential minus E v minus E v prime by k B T. Therefore, there is no factor in front of the exponential which counters the decrease of the exponential; you can see that vibrational intensities usually or maximum for the v is equal to 0 to 1 transition or the v is equal to 0 state it itself and then it is slightly lower and so on.

Secondly, with respect to microwaves and rotation spectroscopy the energy gap is very small compared to the thermal energy whereas, in the case of vibrational states the energy gap is comparable or even more than thermal energy therefore, the number of molecules even in the first excited vibrational state is going to be a lots smaller fraction of the number of molecules in the ground state. This is not so in the case of rotations. In the case of rotations; a large number of J values are populated fairly well whereas, in the case of vibration unless the vibrational energies are very close to each other most molecules will be at any given temperature in the ground state and few were in the first exited state and even few were in the second exited state. Therefore, you can see the drop in the intensity very very directly.

So, these are things that you have to keep in mind in observing the intensities and also some of the spectra that I will show in one of these lectures or through the lecture notes. We will continue this with the spectroscopy of the microwave spectroscopy of polyatomic molecules in the next lecture until then.

Thank you very much.