Quantum Mechanics and Molecular Spectroscopy

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Lecture No -28
Rotational Selection Rules

Hello, welcome to lecture number 28 of the course quantum mechanics and molecular spectroscopy. In the last class, we are looking at the transient moment integral for the rotational transitions.

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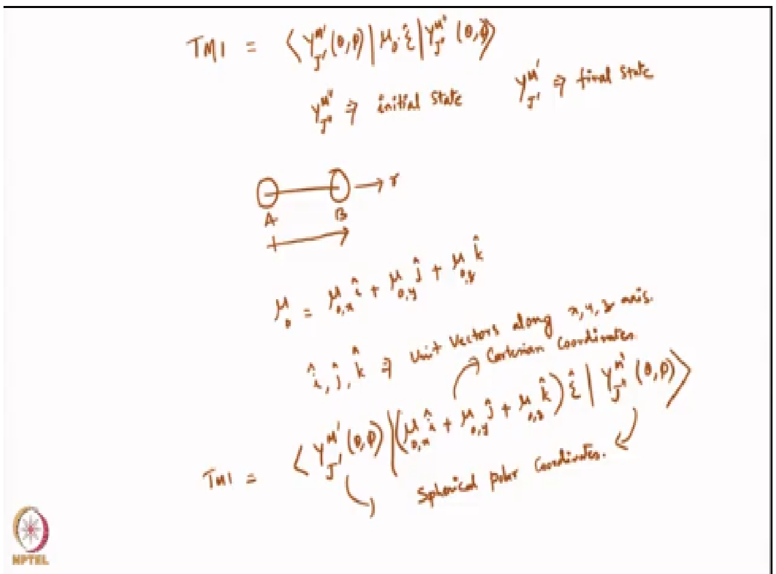

So T M I was equal to Y J prime M prime theta phi mu0 and, mu it is Y J double prime M double prime theta and phi. Now I told you that Y J prime M double prime, the double prime will belong to the initial state and Y J prime M prime will belong to final state. So single prime represents a final state and double prime represents a initial state. Now, of course if you consider the molecule A B and this is some direction r, then it could be, r could be pointing in any direction along x, y, z.

So your mu0 will be equal to mu0 along x axis into i vector which is a unit vector along x axis + mu0 into y along y axis where j is the unit vector + mu0 z to k vector that is the unit vector. So this i, j, k are unit vectors along x, y, z axis. Now, so your TMI will now become Y J M theta phi mu0 xi + mu0 Y J + mu0 z k along the electric field vector Y J double prime M double prime theta and phi.

Now the problem here is these are in Ys, these are in spherical polar coordinates and these are in Cartesian coordinates. So one has to express your mu0 in terms of Cartesian, spherical polar coordinates.

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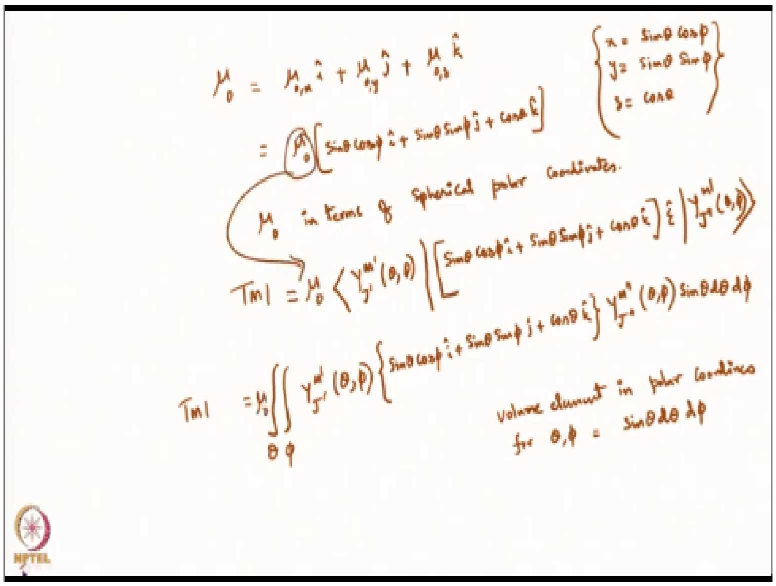

Therefore one can write mu0 is equal to mu0 into xi + mu0 YJ + mu0 z k will be equal to mu0 into, x is nothing but sin theta cos phi in spherical polar coordinates x is equal to sin theta cos phi, y is equal to sin theta sin phi and z is equal to cos theta, so this is from the conversion of spherical polar coordinates into Cartesian coordinates, cos phi into i + sin theta sin phi j + cos theta k. Now this is the modified mu0, mu0 in terms of spherical polar coordinates.

Now therefore your T M I can now be written as YJ prime M prime theta phi. So your mu0 is now sin theta cos phi + sin theta sin phi j + cos theta k, whole thing along the epsilon Y J prime M prime theta and phi. So that is your transition moment integral. Now, but this integral has to be integrated over spherical polar coordinates. So if I write the integral, this will become integral, actually double integral one over theta and one over phi.

YJ prime M prime theta and phi of theta and phi deployed by sin theta cos phi i + sin theta sin phi j + cos theta k Y J double prime M double prime theta and phi sin theta d theta d phi. Because the volume element in polar coordinates for theta and phi will be volume element in polar for theta, phi will be equal to sin theta d theta d phi. So we have these transition momentum integral will look like this.

So this transient moment integral of course you know depending on whether your dipole moment is along x axis or y axis or z axis and the electric field could be along x axis, y axis, z axis, you will get 3 integrals.

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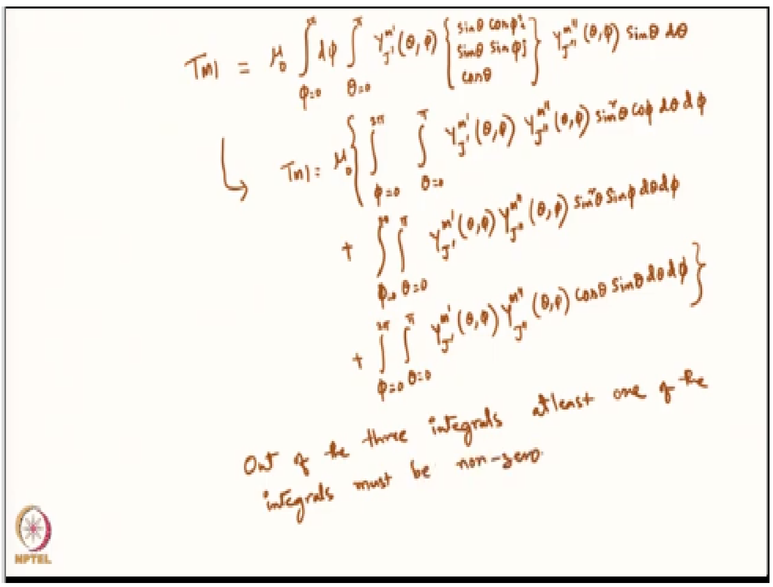

So, TMI will be now be equal to, i will take mu0 as common, by the way there is a mu0, there is a mu0 that I forgot because you know everything this multiplier, so mu0, so this will be equal to mu0 into integral phi d phi integral theta, phi will go from 0 to 2 pi, theta will go from 0 to pi, Y J prime M prime theta and phi will have 3 integrals, one will be sin theta cos phi, there is an i but i is inconsequential;

sin theta sin phi j and cos theta whole thing multiplied by Y J M double prime sin theta d theta. Now what I am going to do is that, I am going to rewrite this as 3 separate integrals so that will be equal to TMI mu0 equals to phi 0 to 2 pi, theta is equal to 0 to pi Y J prime M prime theta phi Y J double prime M double prime theta phi, this sin theta that then theta will be sin square theta, cos phi d theta d phi. So that is one integral + mu0 will be phi theta 0 to pi 0 to 2 pi Y J prime M prime theta phi YJ double prime M double prime theta phi.

This is sin theta, that sin theta, again sin square theta, sin phi d theta d phi + the third integral phi is equal to 0 to 2 pi, theta is equal to 0 to pi, Y J prime M prime theta phi Y J double prime M double prime theta phi, this is cos theta, that is sin theta, so cos theta sin theta d theta d phi. So you will have 3 integrals. Now the for the transient moment integral to become non zero or have a selection rule, any one of the integrals must be non zero. Out of the 3 integrals at least 1 of the integrals must be non zero.

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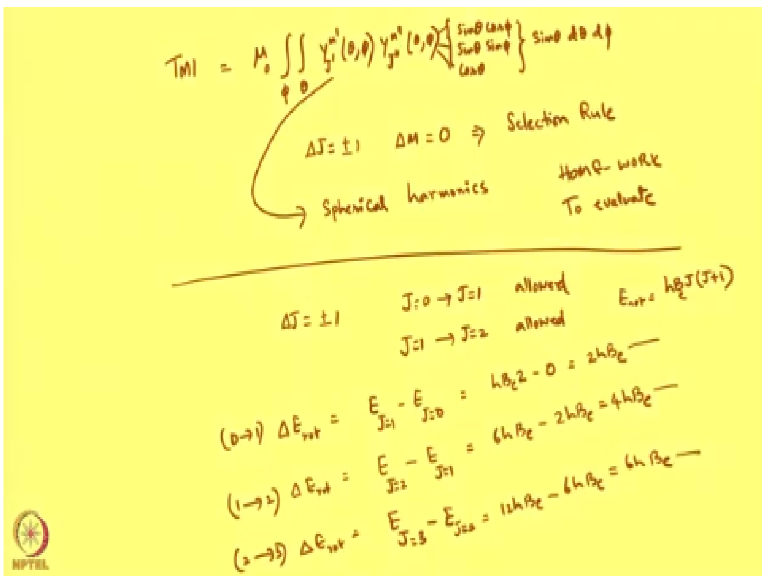

Now when you evaluate these integrals in terms of spherical harmonics, so your transient moment integral TMI in a compact form will be mu0 integral over phi integral over theta YJ prime M prime theta, phi YJ double prime M double prime theta, phi multiplied by sin theta cos phi sin theta sin phi cos theta into sin theta d theta d phi. Now one of this integral must be non, so there are 3 integrals 1, 2 and 3 and one of them must be non zero;

And when you evaluate what appears is you get delta J is equal to +- 1 and delta M is equal to 0. So that is the selection rule. So essentially one has to put the in a wave functions or these YJM are nothing but your spherical harmonics and once you plug in the spherical harmonics one can evaluate this integral. Evaluation of this integral is tedious but not, it is possible to evaluate, it will take about no an hour or so to evaluate each of these integrals.

So which is a, which you can do it as a homework. Let us just look at 1 integral, 2 integrals. So at the end when you have that, when you have the selection, so what you will get is delta J is equal to +-1, that means transition from J is equal to 0 to J is equal to 1 will be allowed. Similarly from J is equal to 1 to J is equal to 2 will be allowed etcetera and your delta E rotation will be equal to, what was our delta E? E rotation, E rotation was nothing but h B J into J+1.

You can go back and check or we call it as B equilibrium. So this will be now equal to E J is equal to 1 –E J equal to 0. So if I do that, this will be h Be, when J is equal to 1 you will get 1 into 1+1 2, so this will be 2 -, when J is equal to 0, this will go to 0, so that will be 0, that will be nothing but 2h B e. So similarly if you have delta E rotation is equal to E J is equal to 2 – E J is equal to 1. So this will be equal to, when J is equal to 2, this will be 2+1 3, 3 into 2, 6, so this will be 6h B e -2h B e, so this is equal to 4h B e.

Similarly when you have delta rotation E J is equal to 3 – E J is equal to 2, I am looking for, so this is from 0 to 1, this is from 1 to 2 and this is from 2 to 3, so when you have 3, this will be 3+1 4, 4 into 3; 12, so this will be 12h B e -, this is when is equal 2 is a 6h B e, so the 6h B e, so this will be nothing but 6h B e. Now you can see a geometric progression. This is 2h B e, this is 4h Be, so this is 6h B e.

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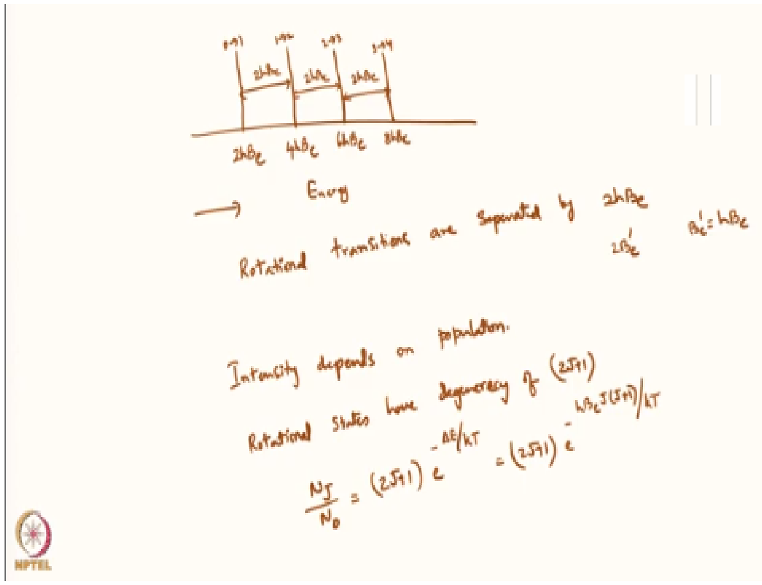

So what appears is that, so when you have this one, so the first line will come at 2h B e, the second line will come at 4h B e and third line will come at 6h B e. Now we will see the difference between these lines and it is also possible to show that it is the fourth line will come at 8h B e. So this is nothing but the energy. So this is will be from 0 to 1, this will be from 1 to 2, this will be from 2 to 3 and this will from 3 to 4, value of J s.

Now if you have this, now this will again be, this is 2h B e, this also 2h B e, this also 2h B e. So the rotational transitions are separated by 2h B e. By the way in some text books, this also written as this h is absorbed into B e and then you can also you also get as 2 B e, let us say B e prime, where B e prime is equal to h B e. So they are equally spaced rotational lines and each of them will be a geometric progression.

Now when you have such rotational spectrum, so you will think that you will get a rotational spectrum which is like this, but unfortunately the rotational spectrum does not look like this. What it looks is slightly different. Now this rotational spectrum will also, the intensity of the transition will also depend on the population. Now you know rotational states have a degeneracy of 2 J+1. So the zeroth state, that is J is equal to 0 state has degeneracy of 1 is non degenerate while J is equal to 1 state has a degeneracy of 3 and so on, that 2 J+1.

So now what happens is that your N J by N 0 will be equal to population, will be equal to 2 J+1 multiply e to the power of -delta E by K T. So this is nothing but 2 J+1, delta E, now if I want to go from J into J+1, J is or 0 to J to the power of –h Be J into J+1 divided by K T, where T is your absolute temperature and K is the Boltzmann constant.

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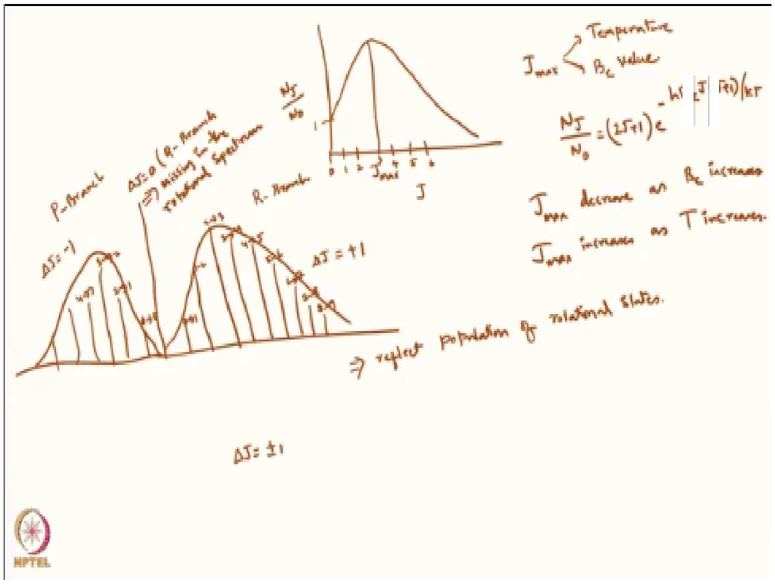

So in that scenario, now if I plot N J by N 0 as a function of J, then this will look something like this. So this is 1 and this value I will call it as J max, so this will be 0, 1, 2, in this case 3 could be J max, 4, 5, 6. 3 happens to be J max but this J max will depend on two things. So J max will depend on one temperature and two rotational constant or value of B e. N J by N 0 is given by 2 J+1 into e to the power of -h B e J into J+1 by K T.

Now you see this is e to the power of –B e, so as B e increases, this decreases and as so J max decreases as B e increases. Also J max increases as T increases. So depending on the molecule and the temperature the J max will keep changing because for different values of temperature and the rotational constant B e will have different J max. Therefore the rotational spectrum will look like, something like that.

So it will have intensities which will go up and come down something very similar to this. So this is 1, 0 to 1, 1 to 2, 2 to 3, 3 to 4, 4 to 5, 5 to 6, 6 to 7, 7 to 8, 8 to 9. So this profile will reflect population of rotational states. Now there is one more thing, we have to say that delta J is equal to +-1. So this is all will reflect to delta J is equal to +1, so increasing. But there is a another set of lines which is, which will have a mirror image, will go like that, will come to have delta J is equal to -1.

So this will be from 1 to 0, 2 to 1, 3 to 2, 4 to 3 etcetera. So there will be a mirror image. So this is called P branch, this is called R branch. And there is something right in the middle called Q branch where is delta J is equal to 0 is called Q branch. But this line is missing in the rotational spectrum. So that is 0 to 0, 1 to 1, 2 to 2, so those transitions are not allowed. So they will be missing. So your rotation spectrum will look like this. We will stop it here and continue in the next lecture, thank you.