Concepts of Chemistry for Engineering
Professor Anindya Dutta
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Lecture 42
Rotational spectroscopy

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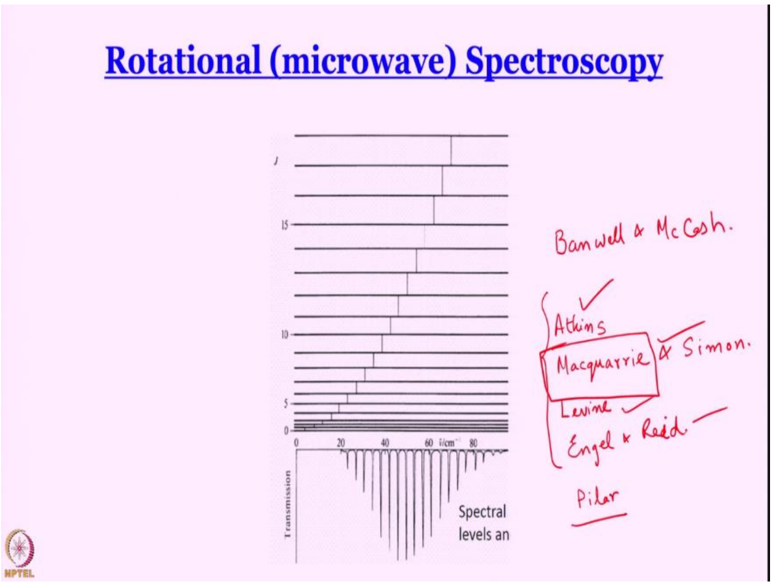

Rotational (microwave) Spectroscopy

Banwell & McCash.

Atkins

Macquarrie & Simon.

Levine

Engel & Reid.

Pilar

We are now ready to discuss rotational spectroscopy. And as we have said earlier, rotational spectroscopy is performed in the microwave regime. So, you want to use microwave radiations if you want to study the rotation of molecules. But before I begin, maybe it is time when I told you once again, something about textbooks.

So, most of the discussion that were performed on quantum chemistry so far are from Atkins physical chemistry. There are portions that we have taken from McQuarrie and Simon, forgive me if the spelling is wrong, I keep forgetting whether this a is there between m and c or not. And also, whether there are two R is or one because there is something some people call McQuarrie University.

Their spelling and this McQuarrie author spelling are not the same. Simon is easier. You can also study from Levine’s is book. And another book that is very nice for quantum chemistry is Engel and Reid at this level. If you want to learn quantum chemistry in a little further detail, then you should study the elementary quantum chemistry book by Pilar.

And there is another book by just McQuarrie on quantum chemistry, which is also excellent. And all these discussions that we are now doing on rotational vibrational spectroscopy. You will find them in all these books, Atkins, McQuarrie and Simon, Levine, Engel and Reid, or maybe not Pilar. And also, you could study spectroscopy from the book by Banwell and McCash.

This is the introductory book on spectroscopy that everybody studies at the beginning. And then if you are interested in spectroscopy, there are many more texts available, but we can talk about that later. That being said, let us talk about rotation of simple diatomic molecule HCl. Note, we are not talking about H_2, why, we will see why. So, what we need really is a diatomic molecule with permanent dipole moment.

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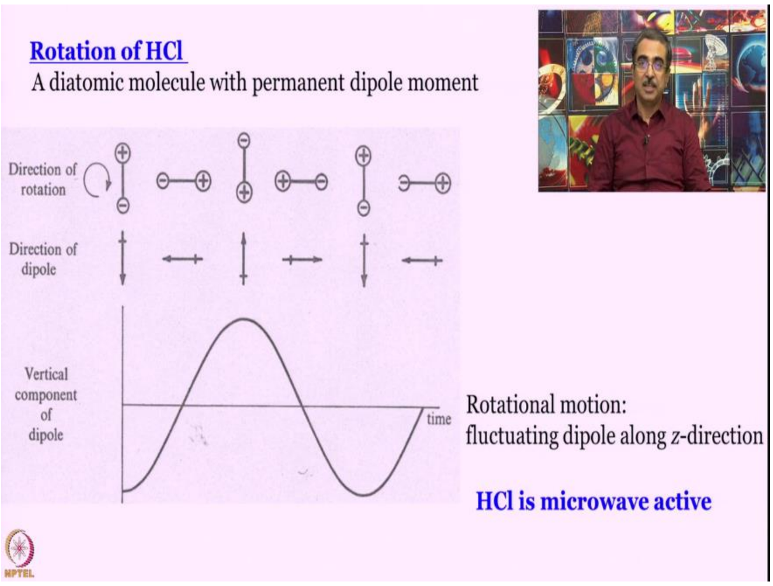

Rotation of HCl

A diatomic molecule with permanent dipole moment

Rotational motion: fluctuating dipole along *z*-direction

HCl is microwave active

And this is a figure that is taken from Banwell and McCash's is book, to be very honest, I do not like this too much, because it is always better to do the more rigorous treatment, unfortunately in this course, there is no scope for it. So, this should be good enough. So, you will understand why it is that rotation couples with radiation by thinking like this. Think of this HCl molecule which has a permanent dipole moment rotating. What happens, the direction of dipole keeps changing constantly.

And if you plot the vertical component of dipole, then what happens, here it is negative, here it is zero, here it is positive and maximum, then again it is zero, negative and maximum, zero and so on and so forth. It goes on like a negative cosine wave or something like that. What is light? Light is an electromagnetic radiation. So, it has electric field and magnetic field with the same frequency as the frequency of light.

So, now, you can think that this oscillating electric field produced by the rotating molecule can have constructive-destructive interference with the oscillating electric field of light and that is the origin of the emission of the of spectroscopy, interaction of radiation with matter. So, this is a very, very rudimentary hand waving kind of understanding that we may develop at the moment.

The important point that come out from here is that if this molecule better have a permanent dipole moment, in order to be microwave active, this rotation is not going to produce any oscillating electric field unless that dipole moment is there in the first place. And that is why we did not say hydrogen, H_2 is a nonpolar molecule. So, no matter how much H_2 might rotate, it is not going to interact with microwave.

Does that mean that we cannot study rotation rotational levels of H_2? No, it does not mean that, we can find it using something called Rotational Raman spectroscopy. Unfortunately, in this course, we are not going to get into Raman spectroscopy. Now, so that is the first condition, it requires a permanent dipole moment. And that immediately opens up several applications, at least one of which is perhaps very well known to each other happens in our household.

So, this is the essential condition and HCl is microwave active. Water is also microwave active because water can also be approximated as a dipole. It is a polar molecule. So, even rotation of water can give you microwave activity and that is an important point remember in our discussion of application that is going to come up soon. To build a quantum mechanical description, what we use commonly is a rigid rotor model.

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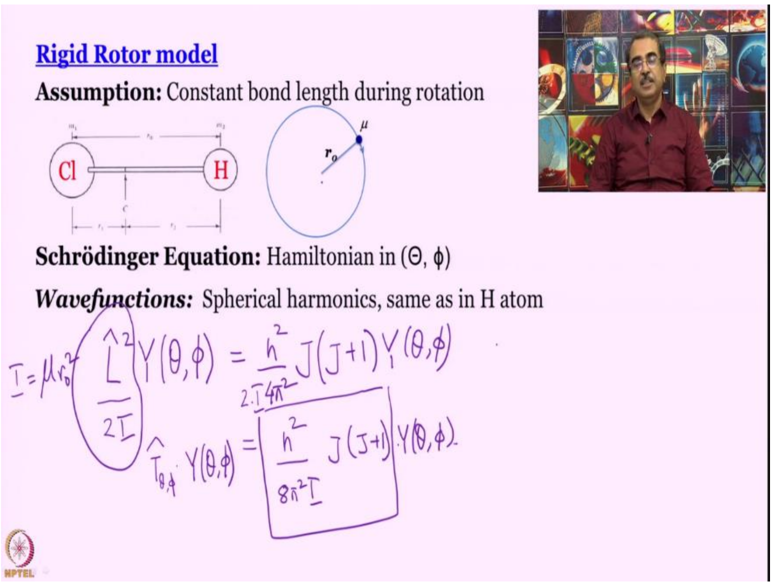


Rigid Rotor model

Assumption: Constant bond length during rotation

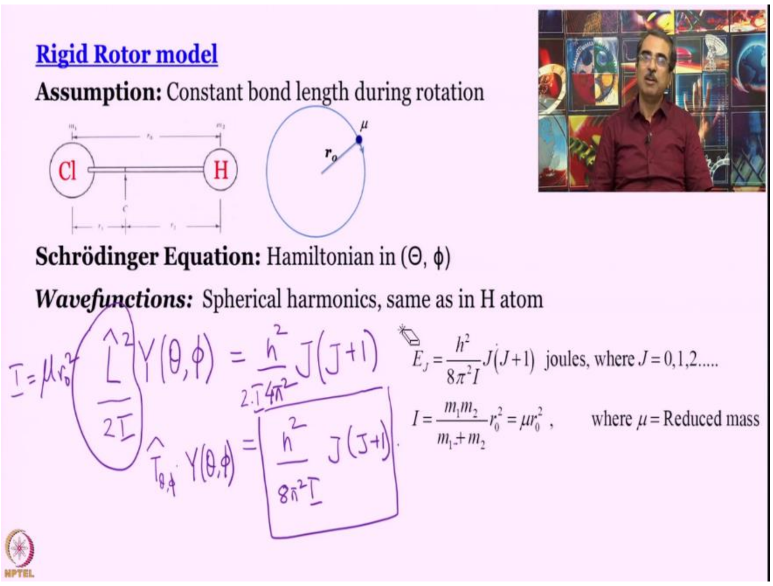
Schrödinger Equation: Hamiltonian in (Θ, ϕ)

Wavefunctions: Spherical harmonics, same as in H atom

$$I = \mu r_0^2$$

$$\frac{\hat{L}^2}{2I} Y(\theta,\phi) = \frac{h^2}{2 \cdot I \, 4\pi^2} J(J+1) Y(\theta,\phi)$$

$$\hat{T}_{\theta,\phi} \cdot Y(\theta,\phi) = \boxed{\frac{h^2}{8\pi^2 I} J(J+1)} \cdot Y(\theta,\phi)$$



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$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules, where } J = 0,1,2.....$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 , \quad \text{where } \mu = \text{Reduced mass}$$

$$I = \mu r_0^2$$

$$\frac{\hat{L}^2}{2I} Y(\theta,\phi) = \frac{h^2}{2 \cdot I \, 4\pi^2} J(J+1)$$

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The assumption here is that during rotation, the bond length does not change, once again it is an application of Born-Oppenheimer approximation. So, let us say this is the molecule we are talking about HCl, this is the bond length separation between the nuclei and we are considering the molecule to be stationary, I mean that we are considering the bond length to be same that means, the molecule is not vibrating or anything during rotation.

So, now see, this fine print that you see here are, the C here is the center of mass. And of course, Cl is much, much bulkier atom than hydrogen. So, the center of mass will be displaced toward Cl, r_0 is the bond length, this r_1, r_2 are there. And this is a little problematic model to use to start with, because there are two bodies, if you try to write the equation, you will have too many terms.

So, a common approach of something like this again coming from classical mechanics is that you reduce this two-body problem to a one-body problem. This is what the one-body problem looks like. So, the reduced mass, I hope you know what reduce mass is, we have discussed it earlier, $\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_{Cl}}$, m_H and m_{Cl} are the masses of hydrogen atom and chlorine atom respectively.

So, this problem is reduced with a little bit of manipulation which I believe we are studied in rotational dynamics in class 11 physics, this problem is reduced to a single mass, a single atom, a single particle with mass = reduce mass μ, rotating around massless chargeless center, separation between the center and this mass is r_0 the bond length.

Now, a couple of comments here. In HCl, what is μ going to be like? Is it going to be like the mass of hydrogen or is it going to be like the mass of chlorine? The answer is it is going to be like the mass of the hydrogen. So, it is almost like hydrogen is going around chlorine and chlorine is stationary, it is just that since we have used reduced mass, we do not need to consider the mass of chlorine anymore.

So, the center can be considered to be massless completely. Have we encountered the situation earlier? Actually, we have, is not it? When we set up Schrodinger equation for hydrogen, we had written the Hamiltonian theta phi. This was the inherent assumption. So, what we will do now is that we will try to see what the solutions are.

In fact, since the Schrodinger equation is similar to that of hydrogen atom angular part the wave functions are also the same as the nitrogen atom, spherical harmonics. Since we know that the wave functions are spherical harmonics same as hydrogen atom, we can try to work with them. What do we know about the spherical harmonics of hydrogen atom?

We know that the spherical harmonics we have written them as Y which are functions of theta (θ) and phi (ϕ). They are eigen functions of the L square operator with eigen value of $l(l+1)\frac{h^2}{4\pi^2}$. Here the difference with hydrogen atom is that this r is constant. So, we can try to find out what is the rotational energy here, how?

Remember the relationship between kinetic energy and angular momentum it is $\frac{L^2}{2I}$, is not it. So, if I take this L square operator and divide by 2I. What is I? I= μr_0^2, then what do I get, I get $\frac{h^2}{2I\,4\pi^2}\,l(l+1)$. We make only one change here, will not write *l*. When you talk about rigid rotor, it is conventional to write J as the quantum number instead of *l*.

What is J? J is the rotational quantum number, very, very similar or well for all practical purposes same as the azimuthal quantum number in hydrogen atom. So, let us write it a little better, this turns out to be $\frac{h^2}{8\pi^2 I}$ J(J + 1) Y(θ,ϕ). What does this mean? We said earlier that this here is the kinetic energy operator.

So, I can write it as maybe $\hat{T}_{\theta,\Phi}$. Y(θ, ϕ) . So, this is what we get an eigenvalue equation, this here is the eigenvalue. So, this is kinetic energy, it is as simple as that. Is there a potential energy for rigid rotor? No, because we have defined it as a one-body problem, as a mass going around a massless chargeless center.

So, in that case, if the center does not have any mass or charge then there is no question of potential energy that can arise, the energy of a rigid rotor is purely kinetic energy. So, let us erase now, so, this is what the expression is $E_j = \frac{h^2}{8\pi^2 I}$ J(J + 1)in joules. Now, generally it is conventional to not work in joules when we talk about microwave spectroscopy, we like to work in wave numbers.

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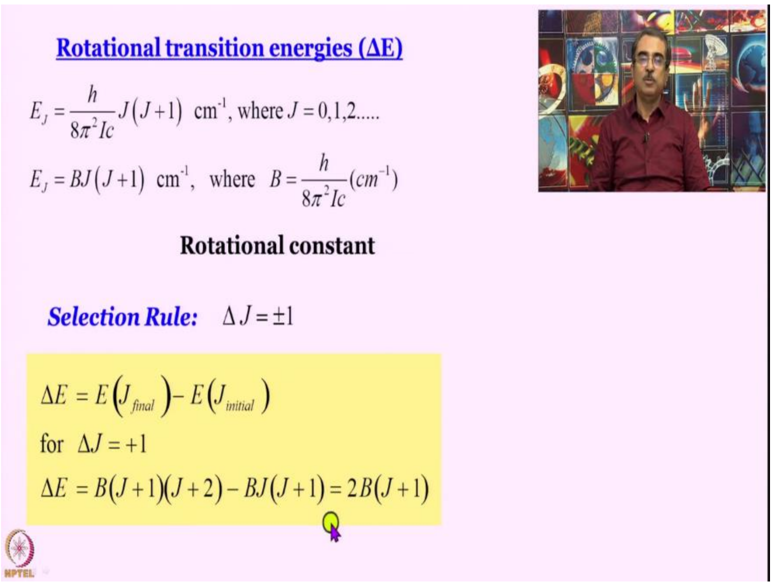


Rotational transition energies (ΔE)

$E_J = \frac{h}{8\pi^2 Ic} J(J+1)$ cm^{-1}, where $J = 0,1,2.....$

$E_J = BJ(J+1)$ cm^{-1}, where $B = \frac{h}{8\pi^2 Ic}(cm^{-1})$

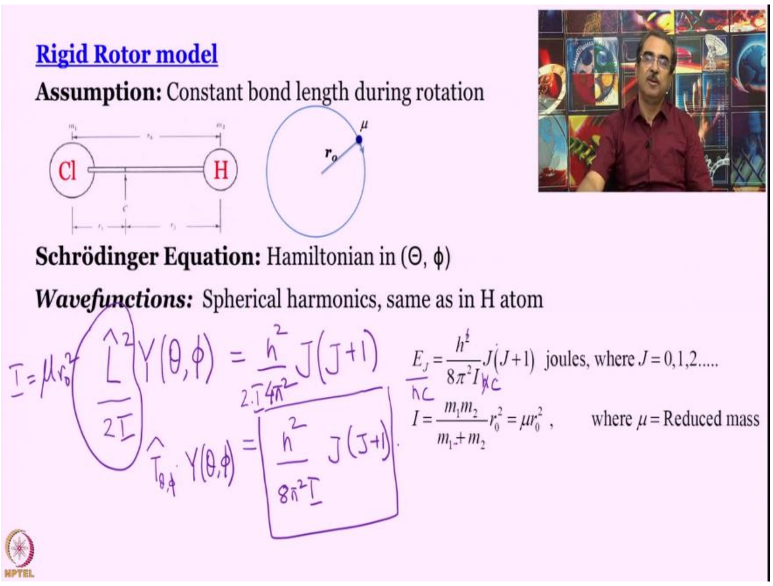
Rotational constant

Selection Rule: $\Delta J = \pm 1$

$\Delta E = E(J_{final}) - E(J_{initial})$

for $\Delta J = +1$

$\Delta E = B(J+1)(J+2) - BJ(J+1) = 2B(J+1)$



Rigid Rotor model

Assumption: Constant bond length during rotation

Schrödinger Equation: Hamiltonian in (Θ, ϕ)

Wavefunctions: Spherical harmonics, same as in H atom

$I = \mu r_0^2$

$\frac{\hat{L}^2}{2I} Y(\theta,\phi) = \frac{h^2}{2 \cdot I \, 4\pi^2} J(J+1)$

$\hat{T}_{\theta,\phi} Y(\theta,\phi) = \boxed{\frac{h^2}{8\pi^2 I} J(J+1)}$

$\frac{E_J}{hc} = \frac{h^{\cancel{2}}}{8\pi^2 I \cancel{h} c} J(J+1)$ joules, where $J = 0,1,2.....$

$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$, where μ = Reduced mass

So, how do I write the energy in wave numbers like this, this is the energy $\frac{h}{8\pi^2 Ic}$. How did we get it? How did we get this in the first place? How do we get energy in cm^{-1} ? Well, this thing has to be divided by h C, just bring in an h C here, what happens this h and this h goes and you have a C left in the denominator, that is what gives us the expression, actually this convention to write ε_j here.

Here, we have written E, $E_j = \frac{h}{8\pi^2 Ic}$ J(J + 1) cm^{-1}, where J is 0, 1, 2 exactly like your subsidiary quantum number of hydrogen atom. So, in short it is written $E_j = B$J(J + 1) cm^{-1}, where B is $\frac{h}{8\pi^2 Ic}$, this here is the rotational constant in centimeter inverse. This is a selection rule, I told you earlier that not all transitions take place.

So, selection rule without going into the derivation here is $\Delta J = \pm 1$. So, what would be ΔE for ΔJ = + 1, just substitute the values and work out B, what is the energy for the J'th level, B[J(J+1)], to know the energy of the (J+1)th level, I just have to write J+1 in place of J. So, it becomes B[(J+1) (J+2)], subtract this from here you get 2B(J+1).

So, what does it mean? It means that, it means two things, first of all the energy levels are separated by 2B(J+1) we are going to show you the diagram. Secondly, your rotational spectral lines will also occur at 2B(J+1), of course, we get line spectra. So, what do the spectra look like?

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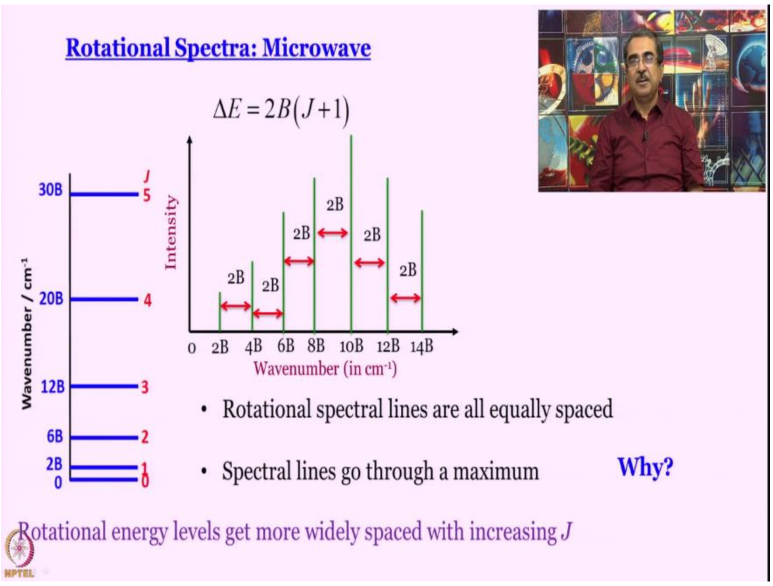

Rotational Spectra: Microwave

$$\Delta E = 2B(J+1)$$

- Rotational spectral lines are all equally spaced
- Spectral lines go through a maximum

Why?

Rotational energy levels get more widely spaced with increasing *J*

First let us draw this energy level ladder that we talked about, here it is B[J(J+1)]. So, if it is B[J(J+1)], when J = 0, it is 0. J =1, B[J(J+1)] is 2B, when B =2, then what happens? J is 2, J + 1 is 3, 2 into 3 is 6, 6B so on and so forth. So, as you see the energy gaps keep on increasing as you go higher up the ladder, does that ring a bell? Does it remind you of particle in a box?

Now, what about the spectrum? Where will the lines be? The first line will be for transition between 0 to 1, that will be at 2B. second line will be for transition between 1 and 2, that is 6B-2B= 4B. Third line might be for transition from 6B to 12B, J = 2 to J = 3 level, that is 6B and so on and so forth. So, this is what the spectra looks like, you get an equi-spaced spectra where spacing is 2B in each case, spacing between two successive lines is 2B. Of what use is that?

Well, since they are equally spaced, and from the spacing, you can find out what the B is, you can determine the bond length, can you? They do go through a maximum. Why they go through a maximum? We will come to that. But even before that, let me at least mention that, is not it clear that from the spacing of the spectral lines, we should be able to find out what the, if you know the reduce mass, which there are easier ways of finding, you can find out what the bond length is. We are going to come back to that.

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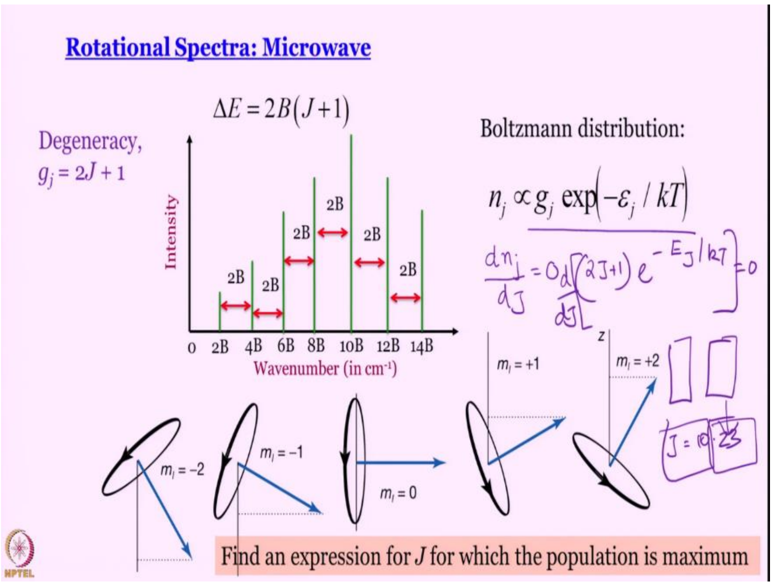


Rotational Spectra: Microwave

$\Delta E = 2B(J+1)$

Degeneracy, $g_j = 2J + 1$

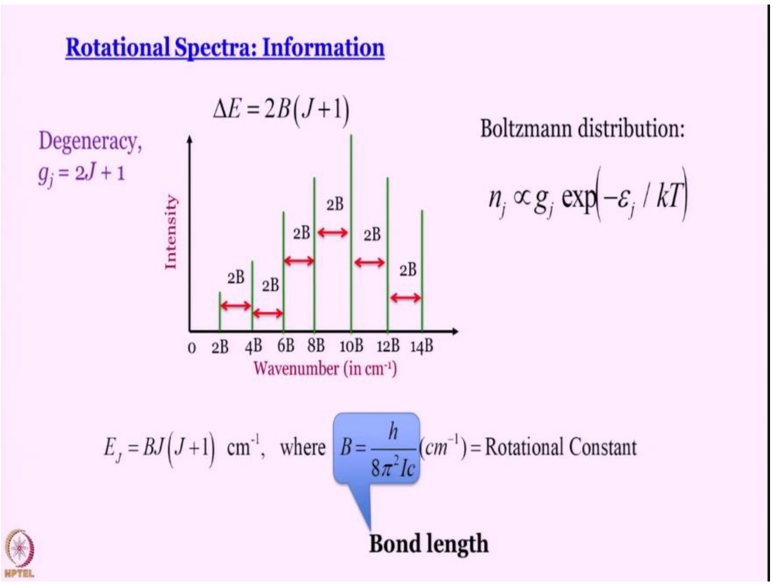
Boltzmann distribution:

$n_j \propto g_j \exp(-\varepsilon_j / kT)$

$\frac{dn_j}{dJ} = 0$ $\frac{d}{dJ}\left[(2J+1)e^{-E_J/kT}\right] = 0$

$J = 10.23$

Find an expression for J for which the population is maximum



Rotational Spectra: Information

$\Delta E = 2B(J+1)$

Degeneracy, $g_j = 2J + 1$

Boltzmann distribution:

$n_j \propto g_j \exp(-\varepsilon_j / kT)$

$E_J = BJ(J+1)$ cm^{-1}, where $B = \frac{h}{8\pi^2 Ic}(cm^{-1})$ = Rotational Constant

Bond length

Before that let us address this question. Why? Why is it that the spectrum goes through a maximum? This is why. See, each rotational level actually is (2J + 1) fold degenerate.

Remember those *l* levels, all of them were (2*l*+1) fold degenerate. And as we said, we just substitute small *l* by capital J here. So, you get these angular momenta pointing in specific different orientations.

And how many such directions are allowed depends very much on which J you are working with. So, g_j = 2J + 1. Here, we have given you an example of J = 2. So, degeneracy is there, what happens to degeneracy then? As you go higher up the level degeneracy increases. And what is Boltzmann distribution, it is $g_j\ e^{(-\varepsilon_j/\kappa T)}$.

So, epsilon goes up with J. So, e to the power minus epsilon j, epsilon here is just that e that we wrote earlier, $g_j\ e^{(-\varepsilon_j/\kappa T)}$will go down with increase in j. So, that is a decreasing function. Degeneracy is a straight line with J. So, multiply a straight line, with positive slope by a decreasing function, what do you get? You get something that goes to a maximum. This is why rotational spectra go through a maxima.

Homework for you is, find out an expression for j, in which population is maximum. I will just discuss how to do it. This is how you do it. Essentially, you take $\frac{dn_j}{dj}$=0. At maximum, the first derivative will be = 0. So, take a derivative of this, what is this? 2J + 1 $e^{(-\varepsilon_j/\kappa T)}$= 0.

So, what are the solutions? Is this right what I have written? Not really. So, $\frac{d}{dj}[(2J+1)e^{(-\varepsilon_j/\kappa T)}]$ =0 Now, you can do this differentiation, find out what you will get. And what you will get always is, you will get an expression with two terms, I am not telling you what the two terms are. You will substitute, you will get J = maybe 10.23. What does that mean? It means that, see, here we are using calculus, which inherently requires continuous variation, we do not have continuous variation here, we have discretization.

So, that is why this 0.23, or whatever it is it comes, you have to neglect this point, just work with the whole number that comes out, you can take the nearest integer that is going to be the value of J, where the population is going to be maximum. Please do it yourself. If you have any difficult, it is worked out the Atkins book as well as Banwell and McCash's book.

So, what is information that we find, I have played a spoilsport and we have already told you that when you look at this spectrum, from the spacing you know what to be is that is going to give you one length because I after all is μr_0^2. If you know μ, from here you find B, is a very elegant easy method of finding bond length. What kind of molecules? Only those molecules that are dipolar, H_2 cannot be done this way, you need Raman spectroscopy.

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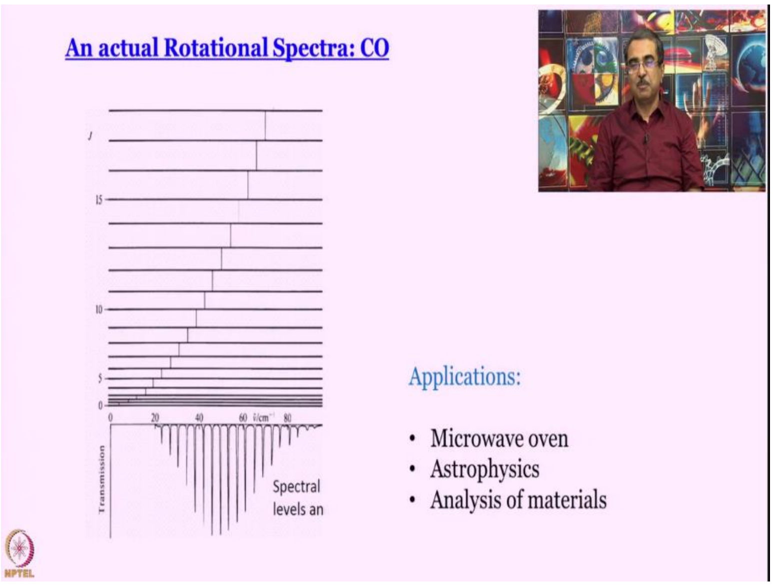

An actual Rotational Spectra: CO

Applications:

- Microwave oven
- Astrophysics
- Analysis of materials

Now, in the last lecture, we talked about what Plank had said about experiments. So, you cannot close it without showing you an actual spectrum, this here is a spectrum of carbon monoxide, rotational spectrum, you can see more or less equi-spaced. And here the potted transmission, that is why it is negative going.

But you can understand that if you would work out the spacing here between any two lines, you can, knowing the masses of carbon and oxygen should be able to work out the bond length. So, this is one of the applications but there are others. Second application is that common place thing that we are talking about microwave oven, why is it that food gets hot? If you place it in a microwave oven, why is it that food gets hot when you place it inside a microwave oven? Because unless you are somebody who eats nails and stones for dinner, most of the food that we eat is 70 percent water.

So, we place it in microwave oven, microwave of the frequency that is broadly absorbed by water is incident on your food and it actually goes through the glass and all container. So, all this water inside your food starts rotating and gets energized, they cannot keep rotating always they have to stop when they come to stop that is because of dielectric friction. And that is when this rotational energy there acquired is given to the surroundings that is the food in the form of heat.

And since there is 70 percent water, it is sort of like fire within, that is why microwave is a very efficient way of heating up food or cooking it. Mind this you cannot fry anything in a microwave because to fry you need to go beyond 100 degrees centigrade, you need to get your oil heated, oil is nonpolar, it is never going to heat up you can cook but you cannot fry in microwave.

Astrophysics is another area where micro-spectroscopy has a lot of application, look at microwave radiation and from there you can tell which molecule is there in that, but the environment of that particular star or even planet, I think. And it is used for things like fault analysis in analysis of materials. So, micro-spectroscopy is very useful not only for chemists or physicists, but also for engineers and people working in many other fields.