

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

NPTEL

NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-10

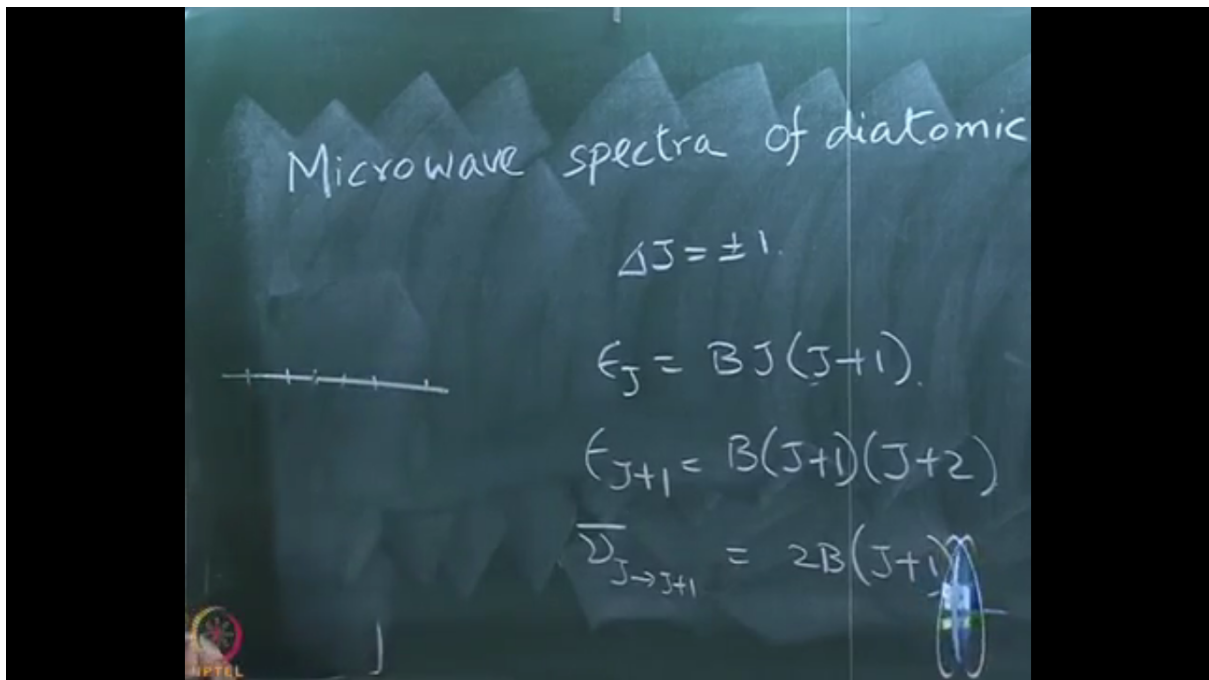
Microwave Spectra: Diatomic Molecules

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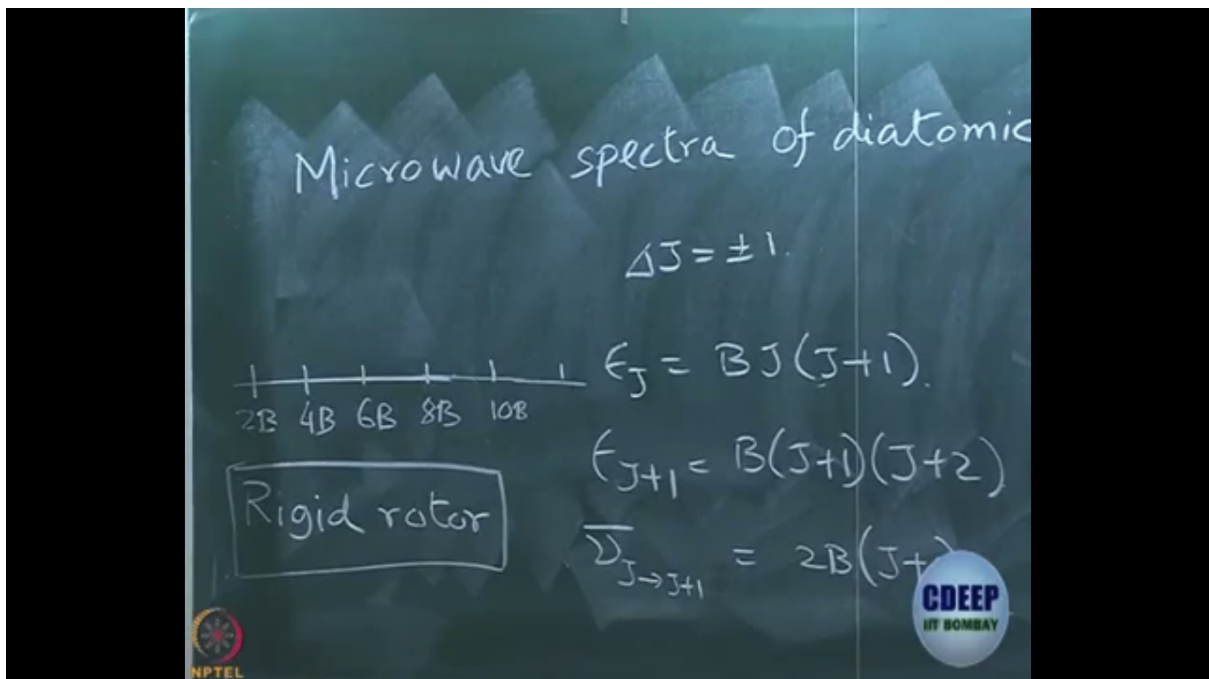
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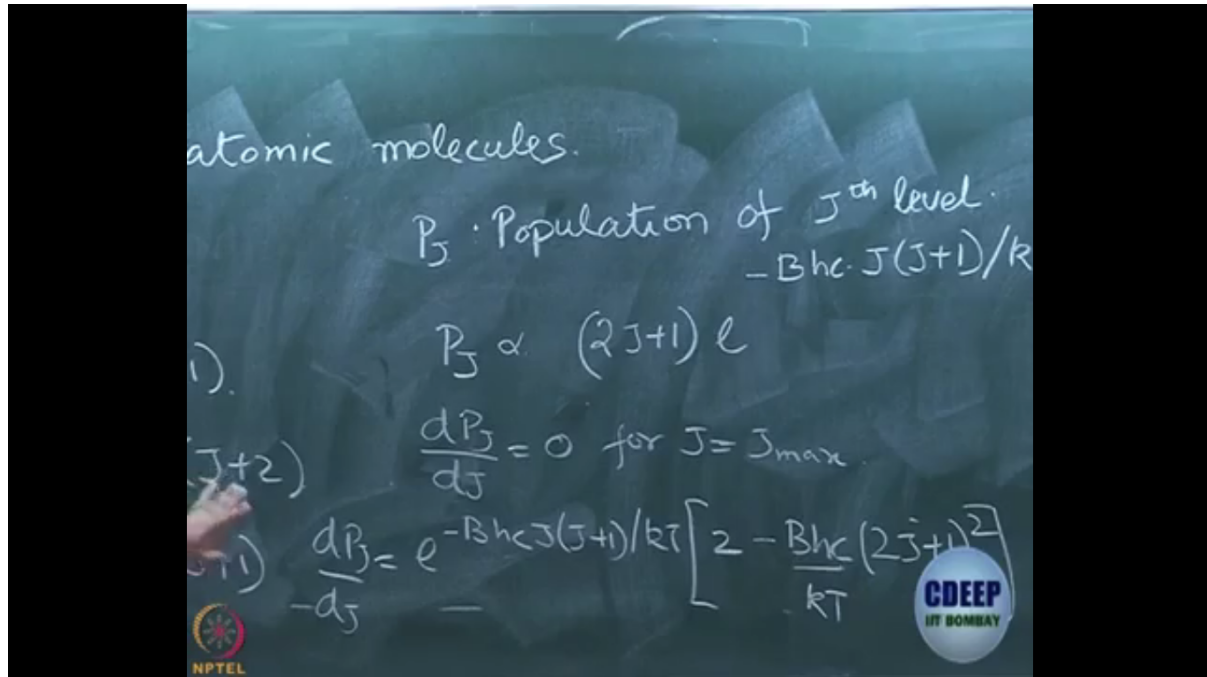
So far we have discussed the background that is required to now enable us to understand what microwave spectra look like and why. One thing we have said already is that the separation has to be equal. Why does it have to be equal? Because the selection rule is  $\Delta J = \pm 1$ .  $E_J$  is  $BJ(J+1)$ . So of course,  $E_{J+1}$  would be  $B(J+1)(J+2)$ . So if I write  $\bar{\nu}$ ,  $\bar{\nu}$  is the wave number, it one way of writing the frequency of transition. For  $J$  to  $J+1$ , that turns out to be how much,  $2B(J+1)$ . So where will the first line, where do you expect the first line? Do you expect the first line a 0? See, it cannot be 0, isn't it, because if there is a transition, transition has to take place  $\Delta M$  is 0,  $\Delta J$  is what matters.



It cannot be 0 because if a line occurs at 0 that means there is no transition. So first line occurs at  $J=0$ ,  $J=0$  is the smallest value anyway. first line occurs at  $2B$ . what about the next one? Then? Somehow I managed to invent a new numeral letter, new alphanumeric

character? Next one? 6B. So there is no point in working out each and every one of those. We understand that they are going to be equispaced and so on and so forth.

Equispaced for what kind of a rotor? Don't forget, for a rigid rotor. Before we finish today, we hope to introduce expression for energy for a non-rigid rotor and then I'll leave it to you to figure out what the spectrum of a non-rigid rotor is supposed to look like.



So x-axis is defined, now we have to worry about the y-axis. What do you have on the y-axis? Intensity. What does intensity depend upon? It depends upon the intrinsic probability of transition. If you want to put it in terms of something that is experimentally observable that would be your epsilon, molar absorption coefficient.

So let us for the moment assume that molar absorption coefficient of each transition is the same. All  $\Delta J = \pm$  transitions are equally probable. Let us just assume this. Later on we'll come back to it and see whether it is absolutely correct or whether it is correct to an extent that we can live with it or whether it is an absolutely wrong assumption. For now, let us go with it.

So then the only thing that is left is population. If you have a line arising out of a level with a greater population, then by brute force, it would be a more intense line. So now we have to worry about population of the Jth level. Population of Jth rotational level.

Now, I believe you are familiar with Boltzmann distribution. What is Boltzmann distribution? Well, ratio of population of two levels is equal to degeneracy multiplied by  $e^{-\Delta E/kT}$ . So I can write like this  $P_J$  is proportional to, what is degeneracy of each J level?  $2(J+1)$ , we are all confident about that.  $2(J+1) e^{-\Delta E/kT}$ , isn't it. So let me write the expression for  $E_J$ . What is the expression for  $E_J$ ?

$B(J+1)/kT$ , is that right? Well, generally, you don't write  $kT$  in centimetre inverse. So it is better to convert  $e_J$  to  $E_J$ . So you have to write  $hc$  here also. That is why I left the gap. So  $-Bhc \cdot J(J+1)/kT$ .

Before we go ahead and discuss this, let me digress a little bit and ask you a different question which will not tell us anything about the spectrum but it's a fundamental question about rotational levels. What is the energy of the lowest energy level of rotation? For  $J=0$ , what is the energy? 0 which means the molecule is not rotating. If it's not rotating then its energy is  $0 \pm 0$  and no potential energy, only kinetic energy.

So momentum is  $0 \pm 0$ . So no uncertainty in momentum. But then if it is fixed then uncertainly in position, what is uncertainty in position? Why? Well, you are right. What we are saying is uncertainty in position is infinity that is why uncertainty in momentum equal to 0 is okay but can you explain to me why uncertainty in position is infinity?

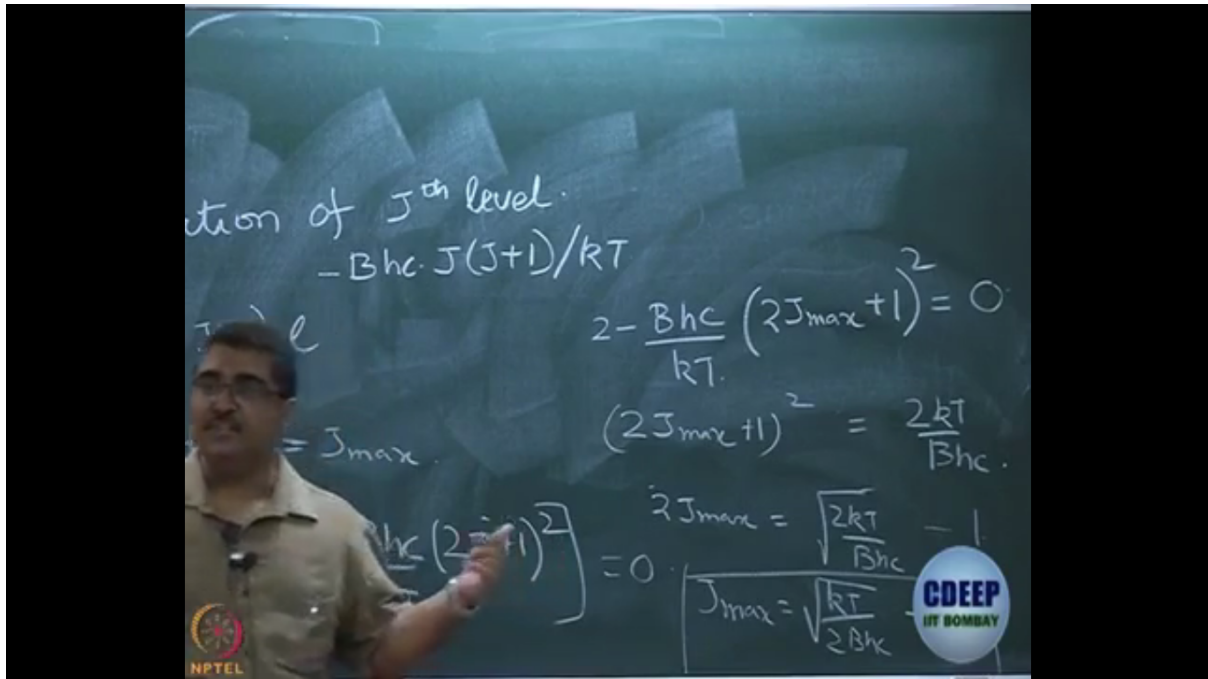
Position is absolutely uncertain, why? Well, you don't know what is  $\theta$  and you don't know what is  $\phi$ , isn't it?  $\theta$  can be anything from 0 to 180 degrees.  $\theta$  can range from 0 to 180 degrees and in this case,  $\theta$  can be anything from 0 to 180 degrees. So it is uncertain completely over the range of  $\theta$ . Similarly  $\phi$  can be anything. That is why it still does not violate uncertainty principle. Well, this is the wrong CH107 batch to ask the question because I think we asked you this problem in quiz or something like that and I think also know this. Please remember. Because when we talk about vibration we are going to discuss zero point energy and we are going to say that for vibration energy can never be equal to 0 because then uncertainty principle is violated.

We'll discuss it at that time but for rotation, it's okay, it can still stop because you have complete uncertainty about  $\theta$  as well as  $\phi$ .

Okay, so now we come back to what we were actually discussing, population of the  $J$ th level is proportional to  $2(J+1)e^{-BhcJ(J+1)/kt}$ . If I want to find out what is the level with maximum population, how do I do it? Even before that, are the higher levels at all occupied? That is an important question. What is a typical energy gap between, say,  $J=0$  and  $J=1$ ? Well, that was on microwave spectroscopy. So what kind of energy are we talking about here? Say, five centimetre inverse, 10 centimetre inverse, no more than that.

So for this kind of energy gaps, higher levels actually get populated at room temperature. So it makes sense to talk about a population of the higher  $J$  levels as well. So this is what it is. So  $dP_J/dJ$  has to be equal to 0 for  $J=J_{\max}$ .  $J_{\max}$  means the  $J$  level with maximum population. What is  $dP_J/dJ$  from there? What is  $dP_J/dJ$ ? One thing I know is that this will definitely come out  $e^{-BhcJ(J+1)/kt}$ . This comes out if I differentiate the first time, then I get 2. If I differentiate the second term, then I get  $-Bhc/kT$  multiplied by  $J^2+J$ . So it is  $2J+1$ . Is this right? Is this  $dP_J/dJ$ ? Just check if I made any mistake. Sushnatu? Of course, you have to work it out yourself if you have to tell me whether I made a mistake or not. Let's do it quickly. Easy differentiation.

$e^{-BhcJ(J+1)/kt}$  that comes out anyway. Yes sir. Why? Yes. So what will it be? Will it be  $(2J+1)^2$ ? Yes. See, Sushnatu, you have to work it out otherwise I can make a mistake and I can teach you a wrong expression and you live with it for the rest of your life and that's not so good. So when I work out something you also work it out. Don't think that I'll always do it -- more often than not I make mistakes. So is this okay now? So when  $J=J_{\max}$  then what happens? This should be equal to 0.



If this is equal to 0 then what happens? This I don't have to worry about. What I write is  $2 - (Bhc/kT)(2J_{max}+1)^2=0$ . Is it right? So please do it yourself. Please do it yourself independent of what I am doing so that you can tell me whether I am right or wrong. So  $(2J_{max}+1)^2=2kt/Bhc$  and then we have  $2J_{max}=(2kt/Bhc)^{1/2}-1$ . So  $J_{max}=(kT/2Bhc)^{1/2}-1/2$ .

Is that right? Question? Okay, why the 0<sup>th</sup> level is not maximum population? Because first of all, if I don't do all this, if I just look at this population, what do you see  $(2J+1)e^{-Bhc}$  whatever, right? So this exponential term is a decay. What about this? It is a linear increase with respect to J. So you multiply a rising straight line with an exponential decay, what kind of thought do you expect? It goes from maximum. So that is the answer that I get from simple algebra or geometry or whatever it is. I am drawing pictures, so maybe it's geometry or it's algebra.

Otherwise if you think, if you think of the same thing, Boltzmann distribution, if I write  $P_J/P_0$ , what will it be? So you just subtract and then here instead of E, you have to write  $\Delta E$ , that is all. And what is  $\Delta E$ , what is the energy off  $J=0$ ? You just told me it is 0. So same expression. So what we see is that the ratio actually goes to a maximum.

So since the energy gap is small, if I think physically now, the room temperature is enough to cause a promotion. Suppose, do a thought experiment. Let us think that there is no rotation. We start with a situation like that somehow and then we expose it to the room temperature. The temperature will be enough to cause a redistribution of the population so that the upper levels also get populated. So as you go higher the levels, the factor that favours population of higher levels, of course, is degeneracy.

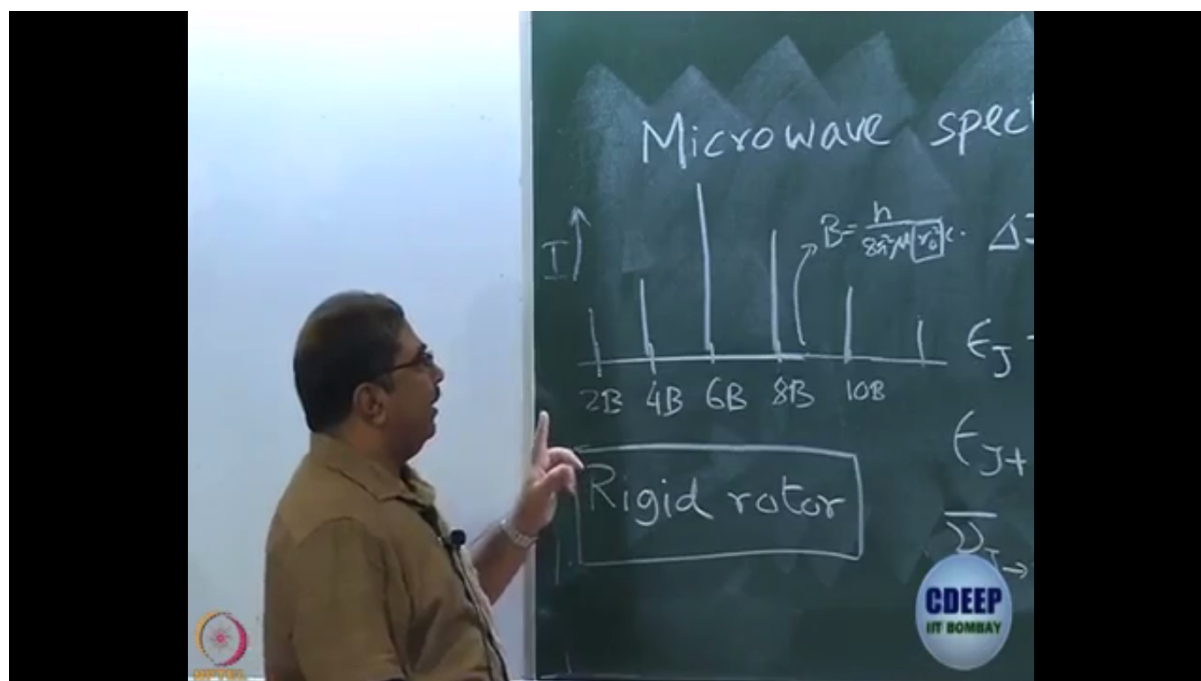
There are more level at a given energy. The factor that disfavours population of the higher levels is the energy gap. So the temperature will not be enough after a while. That is why it will eventually fall down.

Are you answered? So this is your expression for  $J_{max}$ . What is the problem with this approach? Okay, Shivam, tell us. Okay, I'll side, perhaps that is what you are trying to say anyway. see, when do we do differentiation? When you have continuous crows. Do we

actually have a continuous  $P_J$  versus  $J$  curve? We don't. we have  $P_J$  values for discrete  $J$  values. So we are kind of extending the scope a little bit.

So the answer we that we get, do you think this answer will always be integral? No. So you'll get something like 3.2 or 10.5 or something like that. But actually  $J_{\max}$  has to have an integral value. So from this approach you are only going to get an approximate value which will usually not be an integer. So what you need to do is you need to take the nearest integer. If you get 5.8 from here, then the correct answer is 6. If you get 10.2, then the correct answer is 10. If you get 9.5 then I don't know what the correct answer is.

Yes Sushnatu? Actually yes. So most likely it is 6, well it's somewhere either 5 or 6. At least we can zero down upon where the maximum will come. But what we've learnt from here is that the spectrum is going to look something like this. If it follows the population of the levels of origin of transition, it's going to go up and then come down. Of course, that discrete line spectra will go up and come down. Okay, so far so good?



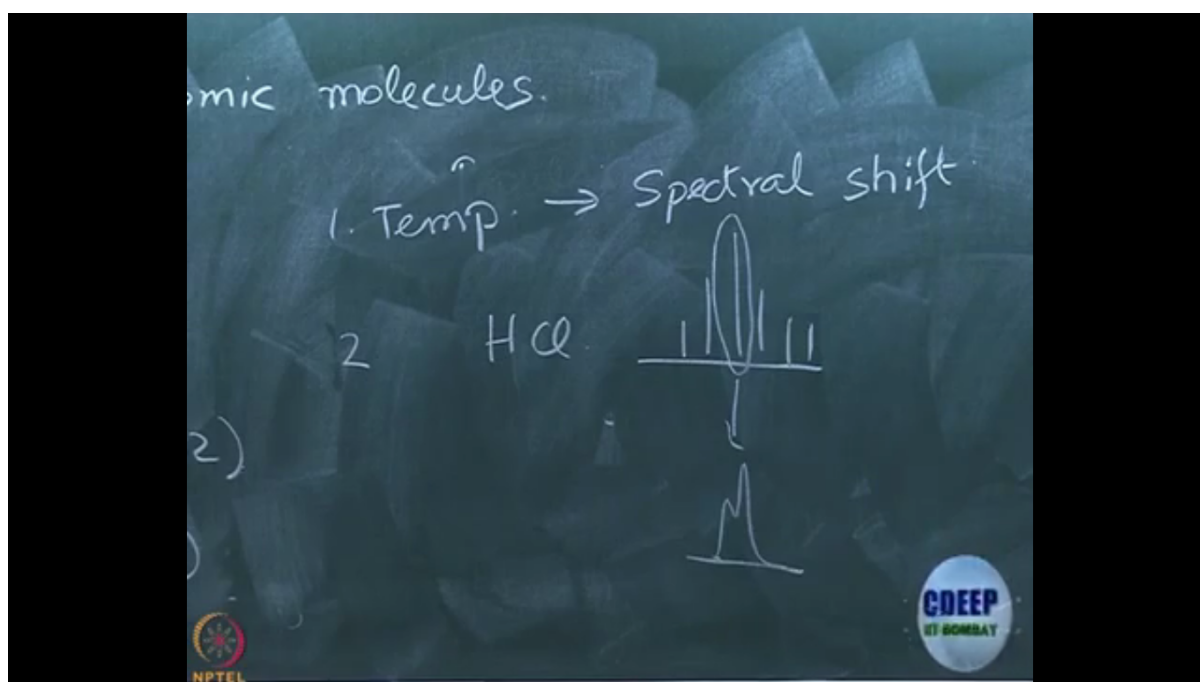
Now in the remaining nine minutes that we have today, let us try and understand a little more minute detail about the spectra. To repeat something we have done already, what is the molecular property about which we can get information from this spectrum? Bond strength, bond length, not bond strength. Bond strength comes from vibrational spectrum, bond length. Why, because each of these gaps is  $2B$  and  $B$  is, what is  $B$ ?  $h/8\pi^2\mu r_0^2 c$ . The only unknown is  $r_0$ ,  $r_0$  is basically the bond length.

So we can actually determine bond length. Now let us see how this spectrum would be effected by two different factors. First of all, continuing with the discussion that we had a little earlier, suppose I record a microwave spectrum at room temperature and then I record microwave spectrum of the same molecule at, say, 500 degree centigrade. Will they be same? Will they be different?

Okay, I am assuming that rigid rotor holds in bot the cases? I am assuming bond length does not change. If the bond length changes as a function of temperature, then of course, your spacing will also change. But if I can assume that bond length does not change then spacing

will remain same. What will change? Internal of spectral lines, how will it change? Yes. So this maximum,  $J_{\max}$  will move to higher value. If I increase the temperature then I can expect that  $J_{\max}$ , the  $J$  value for which we get the most intense line will move to higher values. So I can expect -- what kind of a shift is it? So I can expect the entire spectrum to undergo what is called a blue shift. Blue means higher energy, red means lower energy.

So other terms that I used are hypsochromic and bathochromic shift, but that has been my Achilles heel. Ever since my college days I've never been able to remember which one is bathochromic, which one is hypsochromic, and why will I unnecessarily use such big words when I have simple blue and red at my disposal. So if you want to use bathochromic and hypsochromic shift, be my guest; I'll always say blue and red.



So at higher temperature you expect microwave spectrum to undergo blue shift; at lower temperature you expect it to undergo a red shift. That is point number one. So we have discussed the effect of temperature. What do you expect with temperature? You expect some spectral shift.

Now we'll talk about something else. If you look at the same microwave spectrum let us say we are talk about HCl. We expect a spectrum that looks something like this. If the resolution of your spectrometer is good enough then what you see is each line looks something like this. Each line turns out to be a doublet. I am talking about HCl and I am addressing a class primarily of chemists. So can you tell me why?

Exactly. Chlorine, what is the atomic number of chlorine? 35.5. Why is it 35.5? because it's a mixture of two isotopes. Yes, 37 and 35, no 0.5 there. So now see what happens. It is not only  $r_0$ , you also have  $\mu$ . So if you have two isotopes present, then you actually have two kinds of molecules with two kinds of  $\mu$ s. For that you are going to get different values of  $V$ . So every line will actually consist of two lines. So if you can do a high resolution microwave spectroscopy then you can get an idea about isotopic abundance.

Before we discuss non-rigid rotor, that's where we'll end today's class with, let us just think for a while with this background, for what can the spectra be used? What can be possible

applications of microwave spectroscopy? One thing I've already said. You can determine bond length. What else? Well, one application is something that is now absolutely common place. I am sure everybody has used, if not at home, then definitely in the hostel. Everybody has used the microwave oven.

How does a microwave oven work? No, see, all along so far we have talked about rotation. There is no question of vibrating here. I don't know why but whenever I ask this question to any audience, including people who have completed M.Sc. and have come to us to do Ph.D. everybody talks about vibration, it's not vibration; it's rotation. Rotation of water molecules.

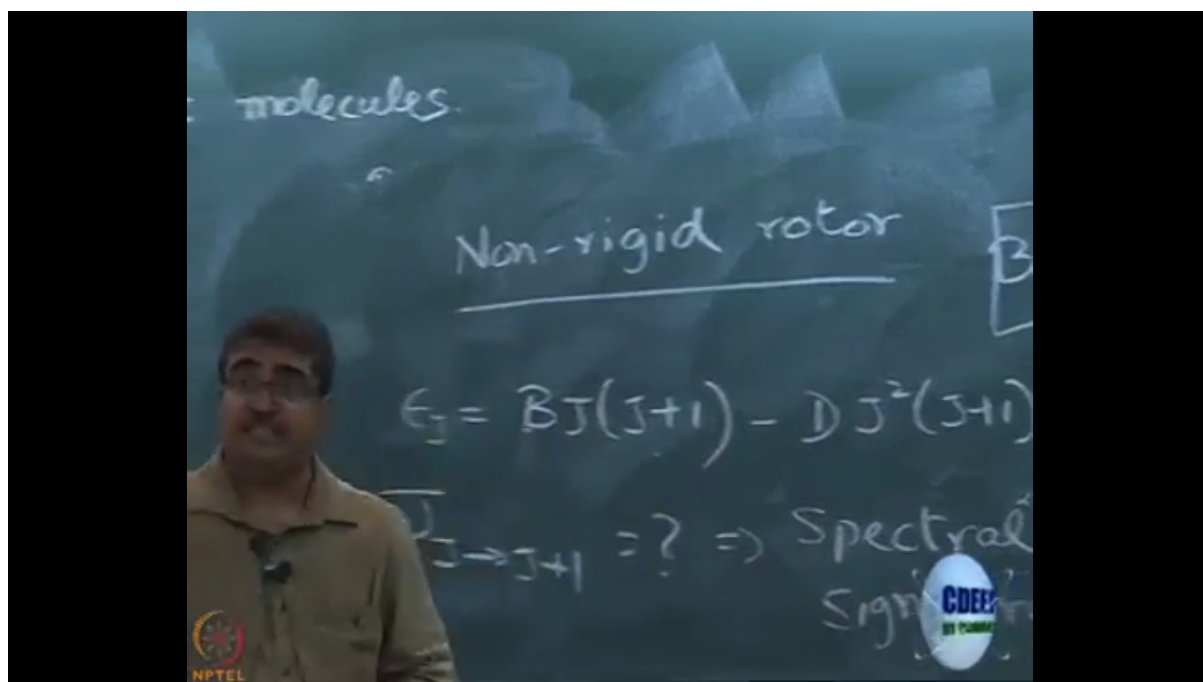
So see, the point is this, remember. One thing that we understood is that the molecule has to be dipolar and unless you are somebody who survives on eating steel, all the food that we eat has 70% water in it as Madhuri Dixit madam has been telling us for last few years over TV. Even we are 70% water. So what happens when you put the food inside microwave oven, oven typically has microwave radiation that is absorbed by water. So all the water that is there inside the food, water molecules, they start absorbing microwave radiation and start rotating, not vibrating, please remember. But then they cannot rotate forever. They come to a stop because of dielectric friction. Other molecules are there, other water molecules and non-water molecules around.

They cause these water molecules to come to a stop, but then all that energy has to be dissipated. Where does it go? All around. That is why the food gets heated up so quickly in a microwave oven because now you don't need a fire from outside. The fire if you want to call it is within and as you know, things are more efficient when the fire is within. So that's the reason why microwave oven can provide such efficient heating. But the point to note is that using a microwave oven, you can cook fish, but you can never fry fish. Why? Because if you want to fry fish, then you have to heat a while, you have to go to a higher temperature. But if you keep oil even for even 100 years inside a microwave oven keeping the oven on, oil will never get heated. Oil is completely non-polar. So you cannot fry things.

Now, before we end, hold on. We are not done yet. So far we have been pretending that molecules are rigid rotors. Such an approximation is always too good to be true. We are saying that when molecules rotate we don't have to worry and all, but actually we have to worry. Molecules are usually non-rigid rotors.

Why are they non-rigid rotors, because when they rotate one thing that can happen is that due to centrifugal force, the bond can happen a little bigger, centrifugal distortion. So what will it effect? It will affect the average value of  $r_0^2$ . So what happens to the effective value of B. If  $r_0^2$  becomes bigger, B becomes a little smaller, if you think that way.





If you think in terms of perturbation theory, now we are introducing non-rigid rotor. This is something that I'll ask you to study by yourself from Banwell's book. We'll not do the entire quantum mechanical treatment. So you'll only need the results. That's something you can understand if you just read Banwell's book, but the point is  $E_J$  is now written as  $B_J(J+1)$ . Well, this is the expression for the non-rigid rotor. Now that is the unperturbed system. You have studied perturbation theory and you know that whenever there is a perturbation -- what is the meaning of perturbation? A small change. If the change is huge, then the perturbation theory doesn't work. If it is small change, then what you can do is you can start with the original value and bring in correction terms. First order correction terms keeping in mind that the energies have to decrease a little bit is  $DJ^2(J+1)^2$ .

So you see this correction term becomes more and more important as you go higher and higher of the energy ladder which means the molecule is rotating with higher energy, that is why centrifugal distortion is more.

So I'll leave it to you to work out the expression for  $\bar{\nu}_{J \rightarrow J+1}$  and I leave it to you to figure out how will it effect. So what is this and how does it affect the microwave spectrum. What is the spectral signature of non-rigidity?