

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

**CDEEP
IIT BOMBAY**

**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

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**LECTURE NO. – 06
Rigid Rotor Model for
Diatomic Molecules**

So now what we do is, now that we have done a little bit of sketchy discussion of how spectra are recorded. Now we go on to discuss actual spectroscopy of certain kinds.

And remember the questions that we're asking to start with is how do you determine molecular parameters, in quantum mechanics you have studied things like bond length, bond strength, right, bond angle. Now, okay those have been in my class for them again this is, I appreciate but Max Planck had said that everything, your experimental results are the only truth, everything else is poetry and imagination, not to undermine poetry and imagination but we should be able to see things experimentally.

How do I determine experimentally? How strong a bond is? How do I determine experimentally, how long a bond is by spectroscopy? And the first kind of spectroscopy we are going to discuss tells us how long a bond is, bond length, and that spectroscopy is rotational or microwave spectroscopy.

Right, of course at least once in the class I should show you the entire electromagnetic spectrum so that I have a clear conscious, I can never remember all this, so you also don't need to remember, but the kind of know what it is. We're focusing in this part of the electromagnetic spectrum, the most important relation as we have said 3, 4 times already in this class is your bold resonance condition $h\nu = E_2 - E_1$, different parts of electromagnetic radiation come in resonance with different kinds of energy gaps, this is the first one that we see, we write in terms of energy frequency of time scale, UV ways these are the values, right, just look at the frequency 10 to the power 15, 10 to the power 12, this is what we discussed in our, when we talked about

your Fourier transformation, and microwave is 10^9 hertz, okay, these are the kind of frequencies, UV visible essentially is, when you do UV visible spectroscopy, you explore those electronic levels about which you've studied in detail in your contempt chemistry class, let's say 4 to 5.

IR and microwave discussed nuclear motion. IR talks about vibration, microwave talks about rotation, okay, and the reason why we can neglect one kind of spectroscopy while dealing with another kind is provided to us by this Born Oppenheimer approximation, I believe Born Oppenheimer approximation is known to you, what does it say? What is Born Oppenheimer approximation? Yeah, can we raise above Born Oppenheimer? Okay Vandhan tell us, so Vandhan is saying is that when we consider movement of electron we can neglect the movement of nucleus because it takes place in different time case, right, so in other words what we, Born Oppenheimer approximation says is that this problem is completely separable, you can separate different parts of the component, so Hamiltonian is sum of different Hamiltonians, wave function is product of different wave functions, so when that happens you can, as you know separate the problem into different components and you can worry about one problem at a time.

Of course Born Oppenheimer approximation doesn't always hold, break down of Born Oppenheimer approximation is not all that uncommon, and when that happens things get a little more complicated, but to start with at least we are going to work within the ambit of Born Oppenheimer approximation.

So what we do is we pretend when we talk about rotational spectroscopy, we pretend that the molecule is rotating and not doing anything else, we don't worry about anything else. Let us go right away to the rigid rotor model. We are talking about a rotating molecule, to keep things simple a rotating diatomic molecule, okay, and to do this we first of all need to build the model that fits the situation, and the simplest model when you have a diatomic rotor is a rigid rotor model, right, once again we have studied this in physics course 11 and 12, rigid rotor, 2 bodies connected by a rod rotating with respect to each other, okay. 2 body problems are always well, it sounds very funny if I say 2 body problems are problematic, but so let us say 2 body problems are not easy to solve, right, complex.

What do we always do whenever we have a 2 body problem, we try to reduce it into one body problem. And in case of rotation, it is not very difficult to reduce it also. How do you reduce a 2 body problem to 1 body problem? By the use of center of mass, right, and what is called reduced mass, right? Yeah, so let us say this is our molecule HCL, we want to study it, 2 body problem, it is not very difficult to reduce it into the problem of a single body with reduced mass μ rotating about a mass less center with radius of the circle being radius of gyration, any question? Okay, okay, radius of gyration, say R_0 .

Now of course spectroscopy as we said is quantum mechanics in action, so first thing that you have to do is set up Schrodinger equation, and what you need for Schrodinger equation is you need a wave function and you need a Hamiltonian.

Now you people have studied hydrogen atom problem, right? Hydrogen atom problem is a central field problem, so it was expressed in terms of your spherical polar coordinates R θ

phi, and in this R was a coordinate of one kind, it was a length, and theta phi together since both are angles essentially they make up another kind of coordinates that is angular coordinate, right.

So now see when we talk about something that is a rigid rotor, it is rotating with unchanged R_0 , would we agree if I say that the Hamiltonian is going to be identical to that of the angular part of the hydrogen atom problem, same Hamiltonian that we have in hydrogen atom except for the fact that if you remember the hydrogen atom Hamiltonian, what is the R part of the Hamiltonian? It has a ∇_R , that ∇ to ∇^2 things like that, right, now if R does not change, what will be the first derivative or second derivative with respect to R, right, so R is not changing at all, so you don't talk about it, so what we are left with is that ∇_θ , ∇_ϕ kind of terms, so the Hamiltonian that we have essentially boils down to the angular part of the Hamiltonian that we had for your hydrogen atom problem, okay.

What will the wave function be? What is hydrogen atom wave function? In the simplest possible term that you can think of, now when I say simplest possible term don't tell me sai, is the product of an R dependent part, theta dependent part, phi dependent part, is that right? Remember, for hydrogen atom what did we say? $\psi = R$ dependent part multiplied by capital theta which is dependent on small theta, and capital phi which depends only on small phi.

Now when I try to talk about a rigid rotor, I don't need this one right, right, because R is fixed, the only parameters that I have R theta and phi here, so the wave function that I essentially have is capital theta multiplied by capital phi, okay. And as you know this is called the spherical harmonics, right, so you already know what the Hamiltonian is, you already know what the wave function is.

Now let us see what the equation would be. Does anybody remember, what's the angular part of hydrogen atom wave functions stands for? Hydrogen atom Hamiltonian stands for? Is it related to some physical quantity? Angular part of the Hamiltonian, which physical quantity would it be related to? Angular momentum, exactly it's related to angular momentum.

So if I ask a little further, how can it be related? So it's an operator, right? How can it be related to the angular momentum operator? And how can we get energy from there? Okay, let us see if you remember this. Do you remember that this L^2 operator operating on Y, which is function of theta phi, what does that give you? What is the value of square of total angular momentum? $L \times L + 1$ multiplied by \hbar^2 , we all remember this, here what we'll do is just to remind ourselves that we are not talking about hydrogen atom, but we are talking about rigid rotor, we are going to write not L, but J, capital J, so this would give you $J \times J + 1$ multiplied by \hbar^2 , do you all agree with this? If there is a question please ask? No question? What is J? J is the rotational quantum number, which quantum number of hydrogen atom is it analogous to? L, what are the possible values of J? J, 0, 1, 2, so on and so forth, okay.

Now let us see if you can write the expression for energy. Now if you remember your rotational dynamics, what is the relationship between rotational energy and angular momentum? $L^2/2I$ isn't it? $L^2/2I$, what is I? Moment of inertia and what is that? μR_0^2 , very good. Do you understand what I'm writing? Rotational energy is given by square of angular

momentum divided by $2I$, where I is your angular momentum which is, no what am I saying? Momentum inertia, momentum inertia which is equal to μR_0^2 square, okay.

So on the left hand side, so this is my equation anyway, on the left hand side if I divide it by $2I$, I should divide the right hand side by $2I$ as well, so I'll divide right away by say $2 \mu R_0^2$ square, okay, let us expand a little bit, $J \times J+1$ multiplied by H^2 divided by, what is H cross? H cross is $H/2 \pi$ right, so H cross square is H^2 divided by $4 \pi^2$ square, 4 multiplied by 2 that is 8 , $8 \pi^2$ square μR_0^2 square.

There is something that I did not write, and nobody corrected me, yes, so this is my equation, from here what I can write is energy for rotational level J is given by H^2 divided by $8 \pi^2$ square μR_0^2 square multiplied by $J \times J+1$, and this is energy and say joule, okay, I mean so far so good, right, whoever have studied rotational spectroscopy I think know this by heart anyway, okay.

Now generally in rotational spectroscopy we prefer to work not with energy in joule, but wave number, centimeter inverse. How do I go from energy to wave number? $E = h \nu$, yeah, equal to $h c \bar{\nu}$, so $\bar{\nu}$ should be E/hc , so you don't have to remember anything really, you can just work things out if you forget, so if I want epsilon J in centimeter inverse then I just have to divide by hc and what you get is H divided by $8 \pi^2 \mu R_0^2 J \times J+1$, well I did not write C , I said it, okay.

Now if you look at this H is the constant, 8 of course is the number, π is the constant, C is the constant, μ is the constant for a particular atom, it's not a universal constant, same is true for R_0^2 square, right. So for a particular molecule I can call this a constant B , but we have to remember that this constant B is characteristic of the molecule we are studying, it is not a universal constant please remember that, okay, so this is your expression epsilon $J =$ don't forget epsilon J is in centimeter inverse, $B(J+1)$ okay, since the rest of the discussion is easy, I'll just quickly go through them in the slides.

Okay this we have discussed already, this is your $8 \pi^2 \mu R_0^2$. Now selection rule as you know is $\Delta J = \pm 1$, next day we'll start with the discussion of why it is $\Delta J = \pm 1$, even that will come from the wave function, okay. Now for that you should do some homework in case you have forgotten, you should go back and read your hydrogen atom notes once again, hydrogen atom is very important, it keeps coming back to haunt you again and again. You need to remind yourself what is actually the form of the theta dependent part of the wave function, can you tell me? This theta dependent part into R dependent part of wave function right, that's what am I saying, theta dependent part into phi dependent part, so phi dependent part I remember, it is E to the power $l m \phi$.

What is the theta dependent part of the wave function? Which polynomial? Laguerre, Hermite, Legendre, none of the above. Legendre polynomial, right, these polynomials were named after a mathematician who was a legend, so his name was Legendre, no not really, his name was Legendre he became a legend, nothing to do with each to other, right, let him be alone, don't, so Legendre right, this is a Legendre polynomials.

Do you know Legendre polynomial in what? For this wave function, is it Legendre polynomial in X or Y or Z? Or none of the above? None of the above, so what is it in Legendre polynomial in? Not theta, cos theta, don't forget it is Legendre polynomial in cos theta, okay, and do you know of the recursion formula, how this Legendre polynomials are related to each other? Okay, that is what we'll need, we'll discuss in next step, fine.

For now let us just live with the fact for 3, 4 days that selection rule $\Delta J = + - 1$ is there, if that is the case ΔE would be $2B(J+1)$ I'm not done, I still need 5 minutes more. $\Delta E = 2B(J+1)$ right, so you're familiar with this energy ladder I hope, this is very simple, you just plug in the values of J into this expression you will see, these are the values that you get and we take home message from here is that energy gap keeps increasing as you go higher up the ladder for a rigid rotor. And the spectrum actually goes through a maximum.

Even before we talk about it goes through a maximum, first thing we should understand is the energy gap, so the gap between lines is equal in all cases, because you see this is one transition, right, this transition is what? $2B$, what is the next transition? Because 0 to $6B$ is 1, but then you can also have $2B$ to $6B$, so $2B$ to $6B$ that is a next line, that is $4B$. Next line would be $6B$ to $12B$ actually, so these lines are going to occur at 0, $2B$, $4B$, $6B$ so on and so forth, the gap between two successive lines will always be your $2B$.

And that brings us to the application of microwave spectroscopy in understanding bond length right away, because you know that B is $H/8 \pi^2 C \mu R_0^2$, right, so everything else is known, if you can experimentally determine B , well I'm assuming that you know that it is HCL, so you know what is atomic weight of hydrogen atomic weight of chlorine, then the only unknown in that case is R_0 , so right away from this spectrum you can determine the bond length of a diatomic molecule using a rigid rotor approximation, okay. So next day we'll start from the question why does the spectrum go through a maximum, okay, now you can leave.

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