Quantum Mechanics and Molecular Spectroscopy
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Lecture-37
Interpretation of Rotational Spectra

Hello, welcome to lecture number 37 of the course quantum mechanics and molecular spectroscopy. As I told you in the previous lecture that you know we are going to look at some solved problems. So, today I am going to talk about the problems related to rotational spectroscopy ok. So, when you record a rotational spectrum you get you know numbers be you know things like that, how do you interpret the spectrum?

And what you have to do to get the spectroscopic correct? One of the things that you do in the rotational spectroscopy records the rotational spectra of isotopomers, what do I mean? Okay. Now if I have molecule HCl ok.

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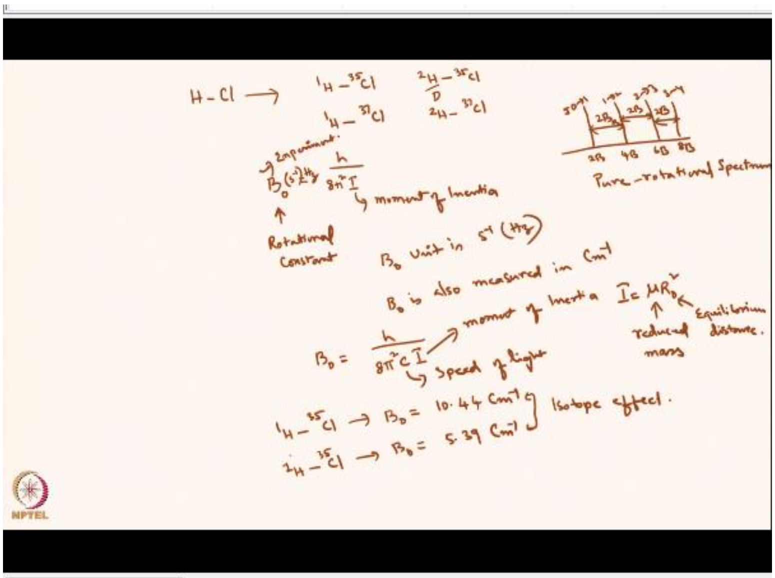

Now there are various isotopes that I can think of. So, if I have HCl molecule then there are I can have 1 hydrogen 35 Cl or I could have 1 hydrogen 37 Cl. So, 27 and 35 two are isotopes of the chlorinate or one could have 2 hydrogen and 35 Cl. So, by the way this is also called D ok, deuterium is nothing but the isotope of hydrogen with 2 molecular atomic mass or you could have 2 hydrogen 37 Cl ok.

One could look at various isotopes and you see when you look at the rotational constant B or let us call it as B 0 because at the equilibrium distance, this is given by h by 8 pi square I, where I is the rotational constant, I is the moment of inertia sorry moment of and B 0 is the rotational constants. Now how do you get met, P 0 can be measured by experiment. So, when you record the rotational spectrum we know that the separation between the lines.

So, this is 2 B 4 B 6 B, this is 0 to 1 1 to 2 j values j = 0 j =1 j = 1 = 2 to 3 3 to 4 etc. 8 and the separation between them is 2 B ok. This is pure rotational spectrum ok. Now when you have rotational constant B 0, so that you can 2 B or 2 B 0 can be directly measured from the experiment ok. So, this is experiment ok, but generally so this is B 0 if you look at this thing it will come out to be in hertz or second inverse or hertz.

In this case the unit of B 0 is second inverse or hertz ok, but generally B 0 is also measured in centimeter inverse. So, B 0 is also measured in centimeter inverse. So, you can do a quick conversion. So, if I measure B 0 in centimeter inverse then my B 0 will now be equal to h by 8 pi square CI, where C is speed of light. And what is I? Moment of inertia and I is given by mu R 0 square.

So, where mu is the reduced mass, R 0 is the equilibrium distance ok. So, this is the necessary. So, in experiment it turns out after doing the experiment in one experiment what they found? That 1 H 35 Cl, the value of B 0 = 10.44 centimeter inverse and similarly value of 1 sorry 2 H Cl 35, the value of B 0 = 5.39 centimeter inverse. So, you see when I substitute the hydrogen with interim there is a drastic change in the value of the B 0 ok. This is what I call as isotope effect. Now let us use this and try to evaluate what is the length or the equilibrium length of the HCl molecule or DCL molecule.

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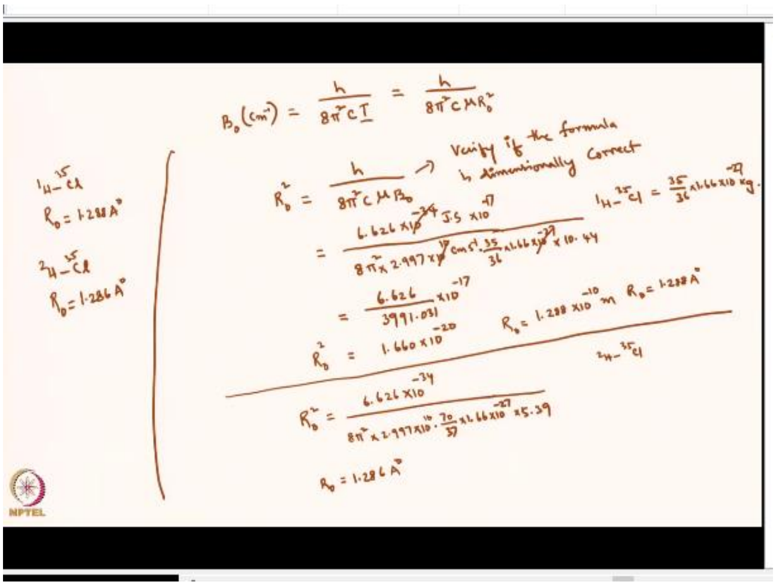

Now we know that B 0 in centimeter inverse is given by h by 8 pi square CI which is also given by h by 8 pi square C mu R 0 square. So, I can slightly rewrite this equation in R 0 square is equal to h by 8 pi square C mu B 0. So, I am going to use this formula and plug it in and see what I will get. Now h is nothing but 6.626 into 10 power - 34 joules second, you can see this, you can verify if the formula is dimensionally correct ok.

Now 6.626 in 10 power -34 is the value of h, that will be in joule second is not it? So, it is an action constant joule second 8 pi square C is 2.997, since I am looking at this centimeter inverse I am looking at speed of light in centimetres per second. So, that will be 2 point into 10 power 10 centimetres per second into mu okay, mu I need the reduced mass. So, if I look at 1 H 35 Cl, then my reduced mass will be nothing but 35 by 36 into 1.66 into 10 power - 27 kilograms.

So, that will be nothing but 35 divided by 36 into 1.66 into 10 power -27 into value of B 0 which is 10.44 ok. So, I can do little bit of equations and change I mean do algebra. So, this 34 and this 27 will cancel and then you will get 10 power -7 and this 10 power 10 and this I can cancel and write 10 power 17 ok. So, what I will get is that 6.626 divided by 3991.031 into 10 power -17.

So, that is going to be the value, just you can now do the math I have already done it. So, this will be now be equal to 1.660 into 10 power - 20. So, R 0 square. So, I take a square root R 0 will be now equal to 1.288 into 10 power - 10 meters you know 1.288 10 power -10 meters is nothing but your angstrom. So, this R 0 will be nothing but 1.288 angstrom. Similarly for if I take the same value R 0 square = 6.626 into 10 power – 34 divided by 8 pi square into 2.997 into 10 power 10.

now instead of I have to take 2 H 35 Cl, so deuterium isotope, DCL. So, that will be nothing but into 70 divided by 37 because 2 into 35 70 2 + 35 37 into 1.66 in 10 power -27 into, now the value of the rotational constant is 5.39 centimeter inverse. If I do the math what I will get is? R 0 = 1.286 angstroms ok. So, what I get is the following? for 1 HCl 35 that is HCL with 35 etc. where R 0 = 1.288 angstrom and 2 HCL 35 that is DCL R 0 = 1.286 angstrom okay.

So, minute changes in the isotopes do affect the lengths ok, here the changes in third decimal okay. So, you should have that kind of calibration that will allow you to differentiate the bond lengths at third decimal okay and mind you that the rotational spectroscopy is the only spectroscopic technique by which one can measure bond lengths ok. Now this is just as I said. So, let me just tell you quickly ok. How we can use this problem to look at something else ok?

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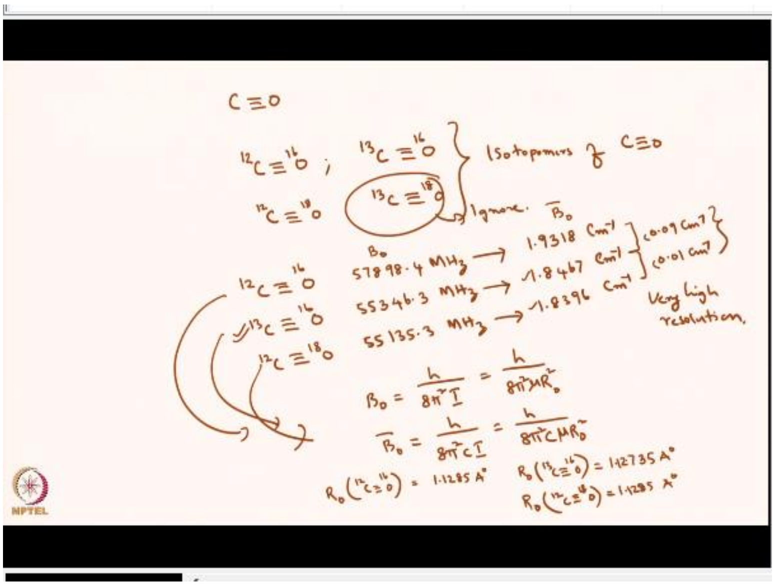

Now the other problem that one can look at in the rotational spectroscopy is let us suppose a carbon monoxide molecule CO. Now CO can have various isotopes, one of the isotopes the standard one is 12 C O 16 okay, the other one will be 13 C O 16, the third one will be 12 C O 18 of course the fourth one will be 13 C O 18, there is also oxygen 17 but will not get into that.

But these are the 4 possible isotopes that one can isotopomers. So, these are isotopomers of C O. Now I do not have data for this. So, I will go to ignore ok. So, for 12 C O 16 and 13 C O 16 and for 12 C O 18 the B 0 in hertz is given by 57898.4 megahertz and this is 55346.3 megahertz and this is 55135.3 megahertz. Now I can always convert megahertz or hertz into centimeter inverse.

So, if I convert this, this will come out to be 1.9318 centimeter inverse and this will be nothing but 1.8467 centimeter - 1 and this will be nothing but 1.8396 centimeter inverse. If you look at the difference this is less than 0.09 centimeter inverse and this is less than 0.01 centimeter. Now if I have to distinguish between this and this then my resolution of my spectrometer should be better than 0.01 centimeter inverse or at least half of them or this should be 0.09 centimeter inverse.

So, if I have to distinguish the isotopomers of my carbon monoxide the microwave spectrum the spectrometer that records these rotational spectra ok, should have very high resolution. So, that I can separate out this isotopomers, by the way oxygen it is in not available, but carbon 13 is 1% natural abundance ok. In fact there are spectrometers in which you can record the spectrum of this using natural abundance ok.

Now when I use this data and convert ok. So, I can use this data to convert I know the values of B 0. So, these are B 0 in centimetres. So, by the way when you got in centimeter and its also called B 0 bar okay. So, I have this in mega hertz and also in centimeter inverse, I can use the value B 0 = h by 8 pi square I, this is nothing but h pi 8 pi square mu R 0 square or B 0 bar, that is in centimeter inverse is h by 8 pi square CI or h pi 8 pi square C mu R 0 square, I can use one of them.

And plug in the values of mu, of course when you have these the values of mu will keep changing, then it turns out when you calculate all this will get R 0 for 12 C 16 O = 1.12 85 angstroms and you get R 0 for 13 C O 16 = 1.2735 angstroms and for R 0 for 12 C 18 O will be 1.127 1.1285 angstroms. I might have done some mistake here you can recheck. So, this is how one can use the rotational spectroscopy data to calculate the bond lengths okay? And one also has to calculate bond lengths of several isotopomers to get the statistically correct answer okay, we will stop it here, thank you very.