Chemistry II: Introduction to Molecular Spectroscopy
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Lecture -16
Diatomic Molecules Microwave Energies and Transitions

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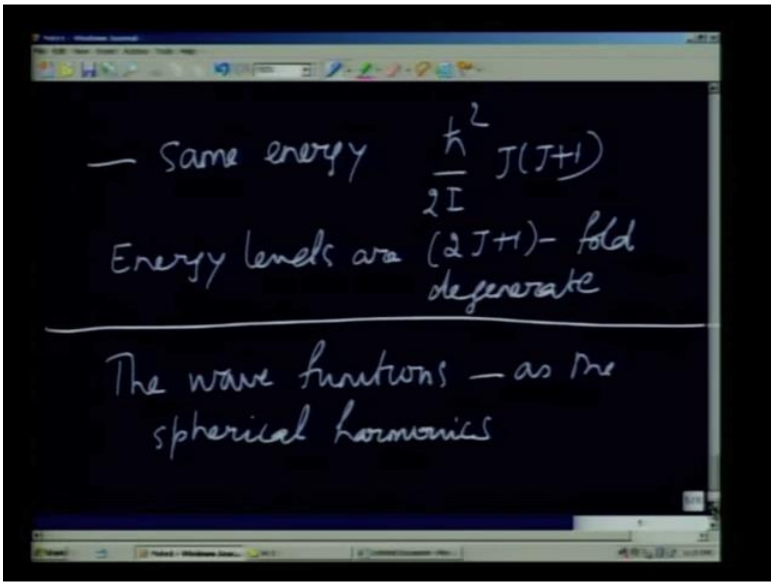

— Same energy $\frac{\hbar^2}{2I} J(J+1)$

Energy levels are $(2J+1)$- fold degenerate

The wave functions — as the spherical harmonics

Welcome back to the lectures in Chemistry. In this lecture, we shall continue from the previous screen if you recall on microwave spectroscopy of the diatomic molecules. We talked about the degeneracy of the wave functions. The wave functions associated with each of these energy levels have the same form as the spherical harmonics.

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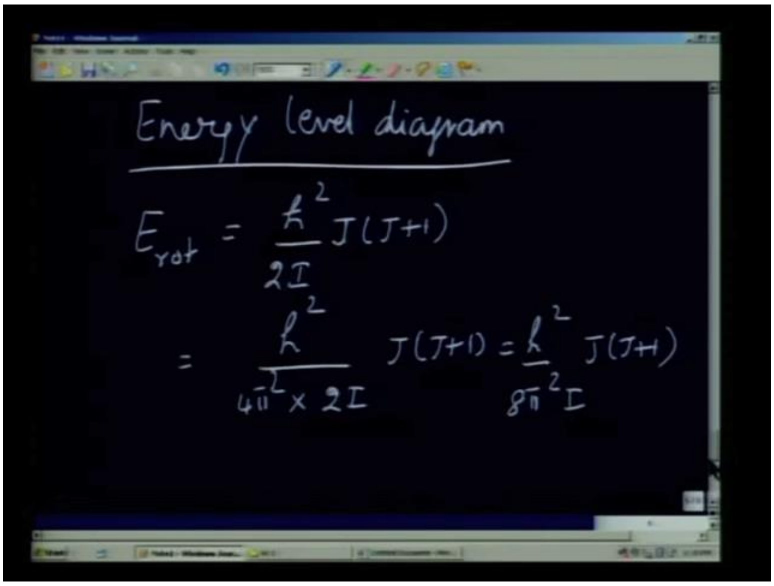

Energy level diagram

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$

$$= \frac{h^2}{4\pi^2 \times 2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1)$$

Now let us look at the energy level diagram or the microwave spectrum before, I do this let me introduce the convention that spectroscopy is use when we write the rotational energy on mechanical rotational energy associated with the system as H bar squared by 2 I into j plus 1 that is right, this out explicitly it is H square by four phi squared into 2I J into J plus 1 which is H square by 8 phi square I into J plus 1.

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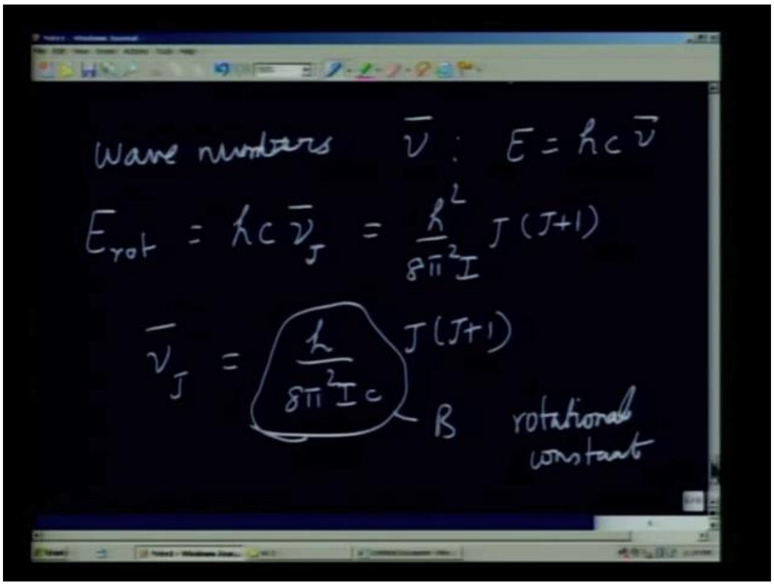

Wave numbers $\bar{\nu}$: $E = hc\bar{\nu}$

$$E_{rot} = hc\bar{\nu}_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\bar{\nu}_J = \boxed{\frac{h}{8\pi^2 I c}} J(J+1)$$

B rotational constant

Now, remember that there is another way of writing the energy in terms of wave numbers wave numbers new bar such that E is given by this formula HC newborn therefore, if we write the E rotational energy as HC new bar corresponding to the quantum number J H is a constant C is a constant H is planks constant C is the speed of light. Therefore, there is no association the new bar is associated with the quantum number J and that is given by hate square by 8 phi square I J into J plus 1 and therefore, if we write the wave numbers new J new bar J as H by 8 phi squared I see J into J plus 1 spectroscopy have a notation for this constant and you see this is a molecular constant H is a planks constant the C is the speed of light and I is of course, the moment of inertia associated with the molecule.

So, this is a constant associated with each molecule and this is given the symbol B and it is called the rotational constant for diatomic molecule. Therefore, the value new bar J is B J into J plus 1 is what everybody uses.

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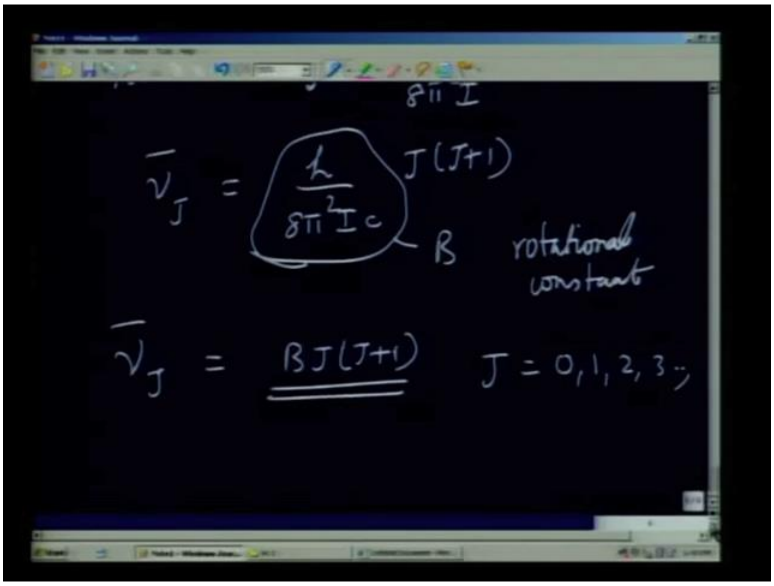

$$\bar{\nu}_J = \frac{h}{8\pi^2 I c} J(J+1)$$

B rotational constant

$$\bar{\nu}_J = \underline{\underline{BJ(J+1)}} \qquad J = 0, 1, 2, 3, \ldots$$

Now, what is the dimension of B it is very clear from the way it is written H by 8 phi square IC and the fact that J takes only J is equal to 0 1 2 3 ask quantum numbers. It is very clear that J does not have any dimension and therefore, the dimension of B has to be the same as the dimension of the new bar J which is a wave number unit and wave number unit is 1 by length that is the number of waves in a given unit length.

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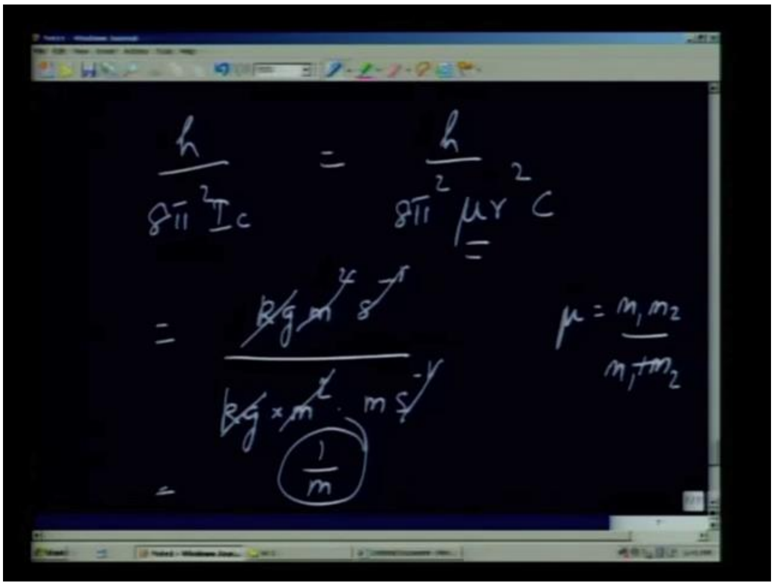

$$\frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \underline{\mu r^2} c}$$

$$= \frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-1}}}{\cancel{kg} \times \cancel{m^2} \cdot m\,\cancel{s^{-1}}}$$

$$= \boxed{\frac{1}{m}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

If you remember the definition of wave numbers therefore, this is per unit length or per centimeter in our centimeter inverse let us see if B has the same dimension H by 8 phi squared IC is nothing other than H by 8 phi square mu R square C recalling the definition of phi and h has the units joule second which is kilogram meter squared per second divided by mu in kilograms. It is a reduced mass remember mu is M1 M2 by M1 M2 and therefore, it has the dimension of the mass kilogram R square is meter squared and C speed of light is nothing, but meter per second therefore, canceling out to the appropriate quantity what you end up with is 1 by meter plus B has the dimension of the wave number given that J is a quantum number. Therefore, dimensionally we are saying right things that is correct and the quantity b is a characteristic of every diatomic molecule how it is.

It is dependent on 2 parameters corresponding to the molecule one is the reduced mass of the molecule and the other is the internal comic distance between the 2 atoms in the molecule. Now for on both counts it depends on the given molecule given by atomic molecules and therefore, B is very specific to the given molecule it is a property of the molecule under the rigid wrote our assumption.

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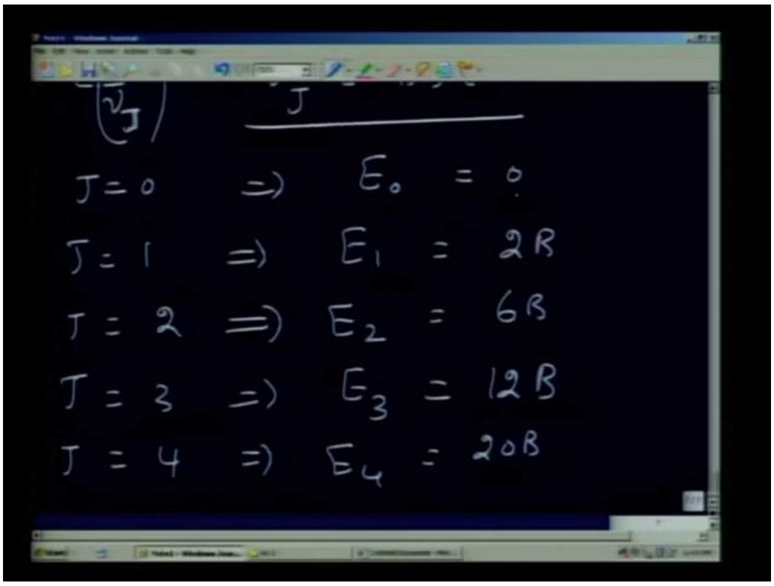

$(\bar{\nu}_J)$ $\quad$ J

$J = 0 \Rightarrow E_0 = 0$

$J = 1 \Rightarrow E_1 = 2B$

$J = 2 \Rightarrow E_2 = 6B$

$J = 3 \Rightarrow E_3 = 12B$

$J = 4 \Rightarrow E_4 = 20B$

Now, let us look at the energy levels E as a function of new J bar that is what we want right since the formula for nu J bar is B J into J plus 1 that is right a few values J equal to 0 corresponds to E 0 which is 0 J equal to 1 corresponds to E 1 which is 2B J into J plus 1 J is equal to 2 corresponds to E 2 the second energy level which is 3 into 3 it is 6 B and J equal to 3 for example, E 3 is 12 B and so on. Let us me write just the last next one more quantity J equal to 4 and write E 4 also as 20 B.

Therefore what you see is the energy levels increasing as a function J square J into J plus 1 for very large values of J functions like J square before, we see that the energy levels increase and the differences between the energy levels which is what you see as a spectroscopic transition now will be determined by the differences that you have between these levels.

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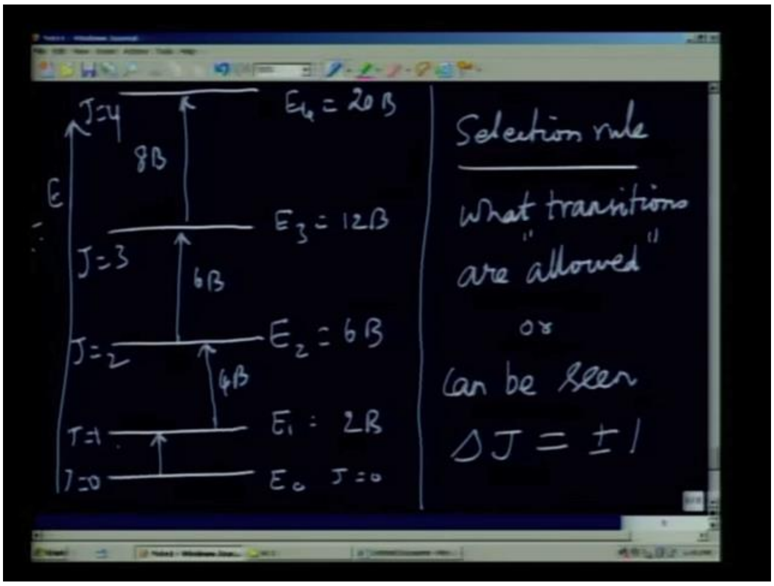

Selection rule

What transitions "are allowed"

or

can be seen

$\Delta J = \pm 1$

So, let us draw the energy level diagram now E 0 is 0 that is J equal to 0 E 1 if we draw this it is 2B E 2 is 6 B therefore, on a scale of the appropriate energy this is the increasing energy scale in the system value E 2 is 6 B the difference between E not and E 1 is 2B the difference between E 1 and E 2 is 4 B. And write the next one it is 8 8 3 is 12 B and the difference between this 2 is 6 B and of course, E 4 goes out of the screen here is 20 B somewhere let me write of the top and the difference here is now 8 B.

So, successive energy levels corresponding to the value J equal to 0 J equal to 1 J equal to 2 J is equal to 3 and J is equal to 4 as you see it the successive energy levels defer by 2B 4 B 6 B and 8 B there is a selection rule in quantum mechanics for spectroscopic transitions that can take place in a rigid diatomic molecule the selection role is that what transitions are allowed or can be seen for rigid diatomic molecule.

The transitions that are allowed correspond only to this value delta J is equal to plus or minus 1 which means that if the molecule is in the state J equal to 1 it can undergo a transition if the microwave radiation is shown on the molecule it can undergo a transition to the next level J equal to 2 by the process of absorption or it can undergo a transition from J equal to 1 to J equal to 0 by the process of emission which is either spontaneous emission are stimulated emission either one of these processes.

But it cannot jump from J equal to 1 to J equal to 3 under this assumption or within this model of setting up the rigid hamiltonian as a classical hamiltonian converting it into the quantum and following through this rigid approximation this model does not permit a transition from AJ plus 2 or AJ minus 2 or AJ2 J plus 3 or J minus 3 delta J has to be plus minus 1.

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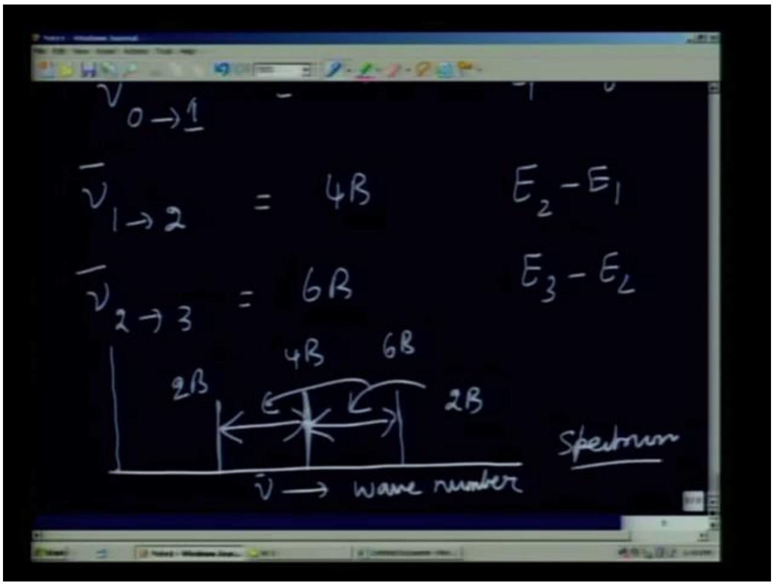

$\bar{\nu}_{0\to 1}$

$\bar{\nu}_{1\to 2} = 4B \qquad E_2 - E_1$

$\bar{\nu}_{2\to 3} = 6B \qquad E_3 - E_2$

Now, with that you see that the first new 0 to 1 new bar corresponds to 2B because that is nothing, but the energy difference between E 1 and E 0 the new bar between 1 and 2 transition from energy level 1 to 2 is for B. Which is the energy difference between E 2 and E 1 and the new bar 2 to 3 is 6 B the energy differences between E 3 and E 2 and what you see is nothing, but if you were to obtain the spectrum of this molecule you will see if we plot this as the wave number unit and we plot the absorption or the absorbance along the way axis what you will see is a transition corresponding to the frequency 2B which is a transition from the ground state rotational state to the J equal to 1 state you will see one other transition if there are enough molecules in the J equal to 1 state you will see a transition from 1 to T 2 if you plot the absorbance we will see a transition corresponding to 4 band if the molecule is in the J equal to 2 state the absorption spectrum from J equal 2 J equal to 3 will give you align corresponding to 6 B.

So, what you see is a series of equidistant lines spectral lines remember that the energy levels are not equidistant the energy levels separate are separated from each other by different orders different values 0 2B to 2 4 6 B 6 to 12 the energy levels of not equidistant, but the spectrum that you obtained which are due to the transition between these energy levels the spectrum is equidistant.

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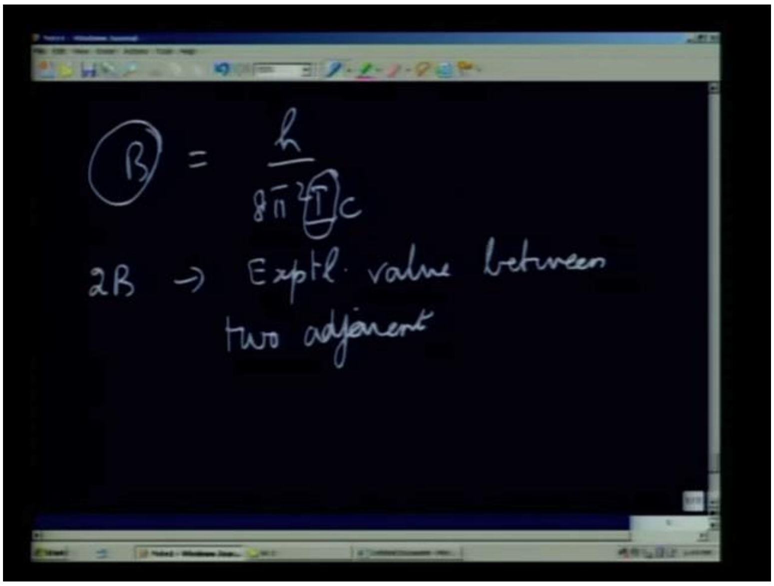

$$\textcircled{B} = \frac{h}{8\pi^2 \boxed{I} c}$$

$2B \rightarrow$ Exptl. value between two adjacent

Therefore any 2 lines adjacent line the gap between them gives you a value of 2B if you recall that B is nothing other than H by a phi square IC and if you know from the experimental spectrum the gap between 2 successive lines as 2B as the experimental value between 2 adjacent lines then a measurement of this from the experimental spectrum immediately tells you how to get the value for I by simple multiplication.

And given that you know what molecule you are taking the spectrum whether it is hydrogen chloride our carbon monoxide for example, molecules which are permanent dipole moment which are the only ones that you can see using microwave spectra you see that the reduced was is something that you know immediately and therefore, knowing I from the experimental spectrum allows you to calculate the inter atomic distance with that molecule.

The more accurately you know that value of B the more accurately you can calculate the value of the inter atomic distance and so on. Today after 50 60 years of research and microwave spectroscopy one can get the bond distances in experimental diatomic spectra up to about the third or the fourth decimal in angstroms which is a very, very high level of accuracy.

Therefore, experimental microwave spectroscopy is the most important means for determining the intercom existences in a diatomic molecule experimentally and informing the value through various theories you can predict the value of the moment of D intercom distance and verify with the experiments let us see a typical a few the atomic molecular spectra before we move on to the next topic in this subject.

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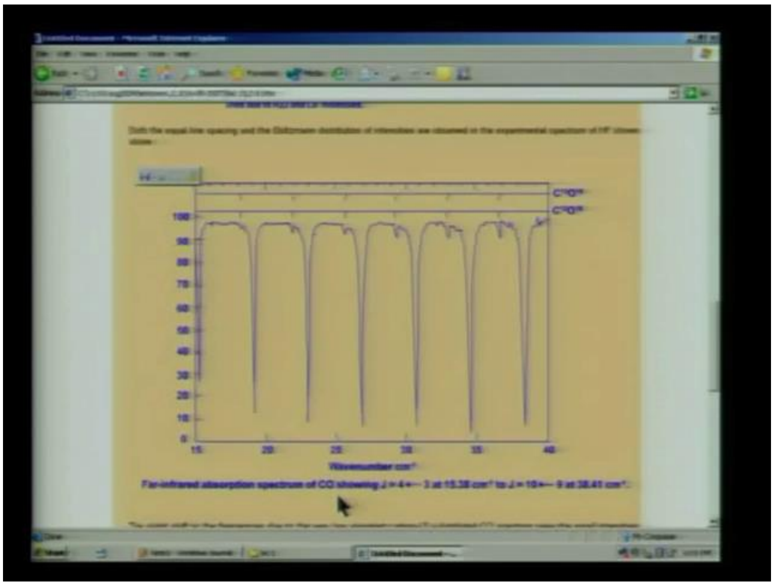

Far-infrared absorption spectrum of CO showing $J = 4 \leftarrow 3$ at 15.38 cm^{-1} to $J = 10 \leftarrow 9$ at 38.41 cm^{-1}.

I will show you 2 spectra here the spectrum that you see in this picture is the spectrum of carbon monoxide and let me read the lines of the text here it is the X axis is wave number axis which corresponds to centimeter inverse 10 centimeters 20 centimeters etcetera in verses and then, the Y axis corresponds here to the absorption the extent of absorption and you see a beautiful equidistant spectrum as you see between the nearby picks and the scale here tells you that this is an overlapping spectrum of 2 molecules molecule carbon monoxide with the carbon isotope the naturally amended isotope C12 and O16 that is a lower line.

Corresponding to these tips that you see here the small the larger ones C12 O16 and then you have the C13 O16 it is natural abundance of C13 is very low and you should know immediately. Why the isotopic muscles will give rise to different spectrum. But for both cases what you see is between the different lines that you have here 1 2 3 4 5 or between the lines here 1 2 3 4 5 they are equidistant that the 2 different isotopes of carbon give 2 different spectra should be obvious from this formula.

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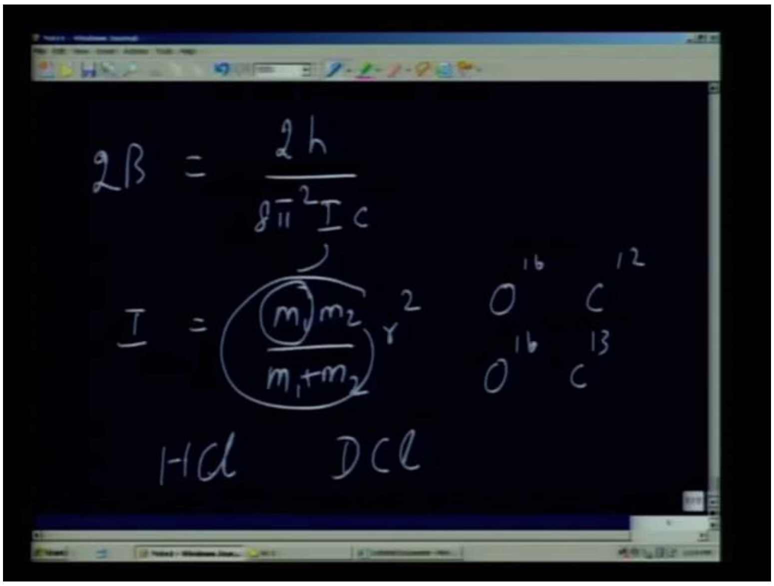

$$2B = \frac{2h}{8\pi^2 I c}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

O^{16} C^{12}

O^{16} C^{13}

HCl DCl

Which is given by that the to be is nothing, but 2H by 8 pi squared IC and I is M1 M2 by M 1 plus M 2.

Therefore if the mass of one of the atoms is oxygen 46 and the other atom is carbon 12 you get one value for the this times R squared you get one value for the reduced mass and if the molecule is oxygen 16 and the carbon 13 then, you get another value for reduced bars and therefore, you see that you get 2 different spacing’s rotational spacing’s for the same molecule dependent on the isotopic masses of the compound. Now where do you think that this difference will be maximum the difference will be maximum you recall the reduced mass will differ by a maximum value if for example, one of the masses doubled you take the hydrogen spectrum take HCL and if you compare the hydrogen chloride spectrum with deuterium chloride DCL you see the reduced mass will differ by a large amount and therefore, any replacement of hydrogen by a deuterium or tritium will give you a very larger ship in the microwave spectrum of the compound. Therefore, isotopic masses do play a role in a significant role in the microwave spectra of many of these compounds. In fact, we will use this to determine all the different moments of inertia of a polyatomic molecule and that is how experimentally this is done.

So, the energy level is one part of the story as you recall from the first lecture in a spectrum we are interested in at least 2 or 3 different things and as far as this course is concerned we are interested in 2 of the 3 things namely the line positions and the line intensity the line which are very complicated. So, we will try avoid the description online bits is usually a subject for the advanced course in molecular spectroscopy. Let us look up to the we have looked at the line positions for a diatomic molecule as basically happening in a spectrum with respect to plot with respect to the frequency or a wave number that it will happen at 2b 4b 6b 8b etcetera.

So, there is the discretization of the energy of the molecule due to the fact that we solve the Schrodinger equation and which gives raise to quantum numbers here both the degrees of rotation degrees of freedom have the same moments of inertia and therefore, we have only 1 free running parameters namely the moment of inertia and we get a quantum number dependence J into J plus 1 as the energy level. So, in a sense the line positions are now very clearly understood as far as the rigid microwave spectrum of molecules concerned.