Fundamentals of Spectroscopy

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Lecture-15
Rotational Spectroscopy: Isotope Effect

Hello everyone, today we will start by solving a problem where we will look into a real rotational spectrum of carbon monoxide and estimate the bond length of carbon monoxide.

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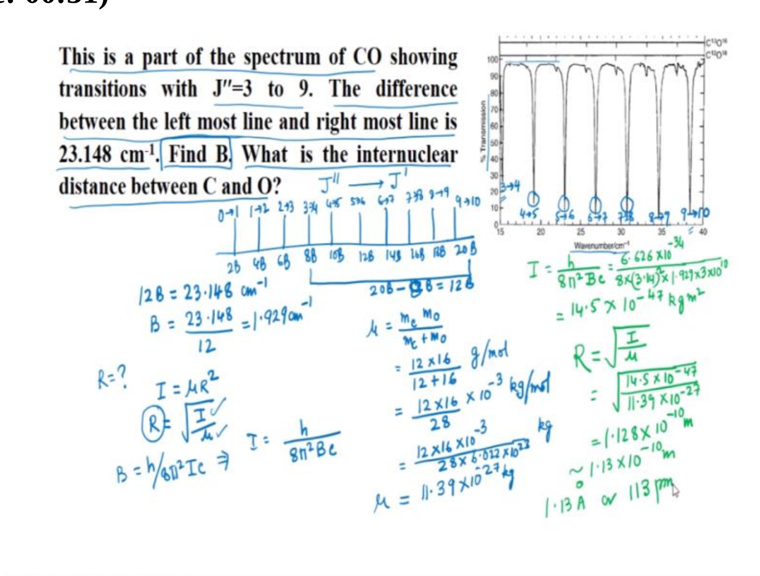

So, let us look into the problem here is a real rotational spectrum of carbon monoxide. On the x axis, we are plotting wave number or centimeter inverse. On the y axis, we are plotting percentage transmission. So, at whichever wave number there is some absorption of light the percentage transmission is not 100 or in other words, in these wave numbers, the percentage transmission are less or much less than 100.

So all these different lines that we get are the wave numbers where light has been absorbed. So this is the rotational spectrum. Now, this is just a part of the spectrum of carbon monoxide, showing transitions with J double prime = 3 to J double prime = 9. So, we have talked about in the last lecture, that for any transition, the transition happens from J double prime to J prime. So, the peaks that we see here are the lines that we see here. The first line is from for the transition from J = 3 to 4.

The second line is from 4 to 5 the third line is from 5 to 6, then 6 to 7, 7 to 8, 8 to 9. And the rightmost line is for the transition for J = 9 to J = 10, so the difference between the left most line and the right most line is 23.148 wave numbers. So let us try to see a rotational spectrum. The first line, which is 0 to 1 line comes out 2B then we have 1 to 2 transition at 4B 2 to 3 transition at 6B and 3 to 4 transition 8B so the left most line In this spectrum.

Which is a part of the spectrum is actually the fourth line in the rotational spectrum. So then we have lines 4 to 5, at 10B 5 to 6, 6 to 7, 7 to 8, 8 to 9, and 9 to 10. So, these lines come at 12B 14B 16B 18B and 20B in other words, the separation in wave numbers between the left most line in the real spectrum that is being shown and the rightmost line is 20B - 12B or 8B that is 12B. Now according to the problem.

The difference between the left most line and the rightmost line is 23.148 centimeter inverse does we can write 12B = 23.148 centimeter inverse or B = 23.148 divided by 12 that is 1.929 centimeter inverse. So, we have found the fast part of the problem, we needed to find B, B is 1.929 centimeter inverse. The next question is what is the inter nuclear distance between C and O. So, we have to find R.

So we know that I, there is a moment of inertia is given by mu R square or R is given by root over R / mu again we know B = h / 8 pi square I see from here we can write I = h / 8 pi square B C. So, we have to find I, we have to find mu, then we can find the inter nuclear distance between C and O. So let is try to find mu first. So, mu is given by m carbon times m oxygen divided by m carbon + m oxygen. So that is 12 times 16 divided by 12 = 16 grams per mole.

So that is 12 times 16 times 10 to the power - 3 divided by 28 kilograms per mole that is 12 times 16 times 10 to the power - 3 divided by 28 times the Avogadro number that is 6.022 times 10 to the power 23 kilogram and this is 11.39 times 10 to the power - 27 kilogram. So, that is the value of mu so now, let us try to find the value of I so I = H / 8 pi square B C. So that is 6.626 times 10 to the power - 34 divided by 8 times 3.14 squared times B, that is 1.929 times 3 times 10 to the power 10.

So if you solve this, the value of I that we get is 14.5 times 10 to the power - 47 kilogram meter squared. So we have to find the value of R, R = root over I / mu that is root over 14.5 times 10 to the power - 47 divided by 11.39 times 10 to the power - 27 and if we do this what we get is 1.128 times 10 to the power - 10 meter. So, we can write this as approximately 1.13 times 10 to the power - 10 meter or in other words 1.13 angstroms or 113 that is 113 Pico meters.

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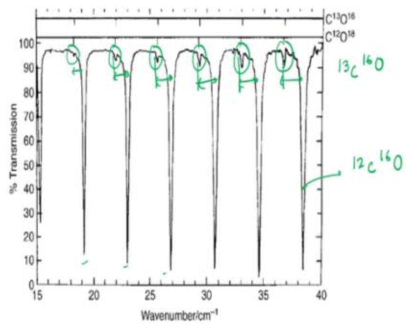

So now, let us look into the rotational spectrum of carbon monoxide again a part from this distinct peaks, there are a few small peaks though these small peaks we can identify in the spectrum so these small peaks shown in the spectrum are due to the natural abundance of the 13 C isotope that is it is from 13 C 16 O the larger peaks are coming from 12 C 16 O. So, if we closely look, we see that the isotopic peak moves away from this main peak as the value of J increases. So, now we will look into the effect of isotope substitution on a rotational spectrum.

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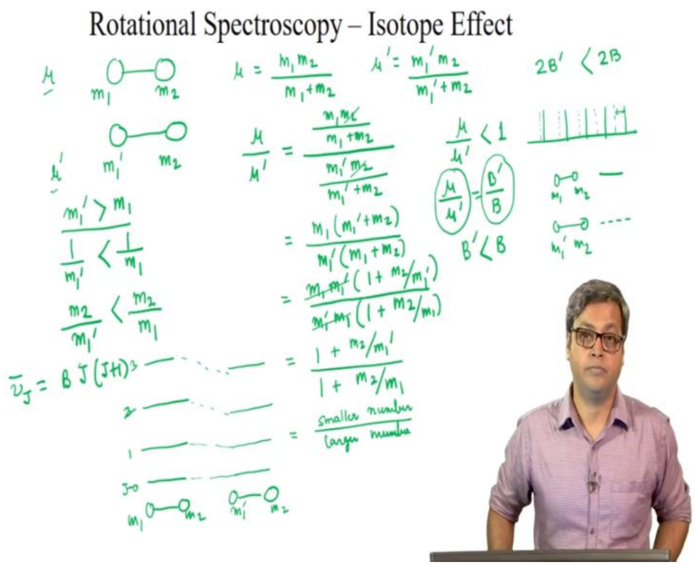

So, when a particular atom in a molecule is replaced by isotope, the molecule will be chemically identical with the original one and the nature of the chemical bond will remain unchanged. In other words, there is no appreciable change in the inter nuclear distance on isotropic substitution. However, since the reduced masses are different, there is a change in the moment of inertia, because the moment of inertia is directly proportional to the reduced mass and hence, there is a change in the B value of the molecule. So, let us say we have a dynamic molecule.

So, the masses are represented by m 1 and m 2 and the reduced mass is mu let us say we make an isotopic substitution of m 1. So, we have a new dynamic molecule that is m 1 prime m 2. And let us say for this case, the reduce mass is mu prime. So, the mass of the other atom as we see is m 2. And let us assume that m 1 prime is the heavier isotope and m 1 is the lighter isotope. In other words, m 1 prime is greater than m 1.

So, because we are representing the reduced masses by mu and mu prime, we can write mu = m 1 m 2 divided by m 1 + m 2. Similarly, we can write mu prime = mu 1 prime m 2 divided by m 1 prime + m 2. So, if we take the ratio that is mu / mu prime, but we get this is m 1 m 2 / m 1 + m 2 divided by m 1 prime m 2 divided by m 1 prime + m 2. So, we can write this, we can cancel out into, we can write this as m 1 times m 1 prime + m 2.

In the numerator and m 1 prime times m 1 + m 2 in the denominator. So now we can take m 1 prime common in the numerator we can write m 1 m 1 prime, 1 + m 2 / m 1 prime in the numerator and in the denominator we can take m 1 common so we can write m 1 prime m 1. Then in the bracket we have 1 + m 2 divided by m 1. So if we cancel out m 1 prime m 1 from the numerator and the denominator.

We can write this as 1 + m 2 / m 1 prime divided by 1 + m 2 / m1 so as you m 1 prime is greater than m 1, we can write that 1 / m 1 prime is less than 1 / m 1 now if we multiply m 2 both on the left hand side and the right hand side, what we get is m 2 / m 1 prime is less than m 2 / m 1. So what we see in the numerator, we have m 2 / m 1 prime, which is less than what we have 1 + m 2 / m 1 in the denominator.

So we can say, the numerator we have a smaller number. And in the denominator, we have a larger number. In other words, this we can write this mu / mu prime is less than 1 and as B is inversely proportional to mu, we can write that mu / mu prime = B prime / B. So, as the LHS are the left hand side is less than 1, the right hand side RHS is also less than 1 thus B prime is less than B.

So now the question is, how will this be reflected in the rotational spectrum so first of all, we know the energy level that is nu par J is given by B times J times J + 1. So when we have the heavier isotope, or in other words, we have B prime, which is less than B. So let us try to draw the energy levels. Let us say J = 0 1 2 3. So this is for m 1 m 2. Now, if you try to draw it for the isotopically substituted molecule.

m 1 prime m 2 then J = 0 remains the same, but the B factor kicks in from J = 1. So we have J = 1 level for this isotopically substituted molecule with a heavier isotope is slightly less compared to m 1 m 2 is again, less for J = 2 and even this for J = 3. In other words, this effect is more pronounced as the value of J increase so we also know that 2B is the spacing between any 2 consecutive line of the rotational spectrum.

The spectrum of the heavier isotope will show a smaller separation between the lines. In other words, for the heavier isotope, the separation is 2B prime. So this 2B prime will be less than the molecule which has the lighter isotope or where the separation is 2B. In other words, if I want to draw the spectrum, let us say I draw m 1 m 2 with a solid line. So I have these transitions rotational lines.

Now, if I have m 1 prime m 2 which I am trying, let us say with the dashed line. So, this dashed lines will be somewhat come earlier compared to the solid lines and the gap between the solid line and the corresponding dashed line will increase as the value of J increases.

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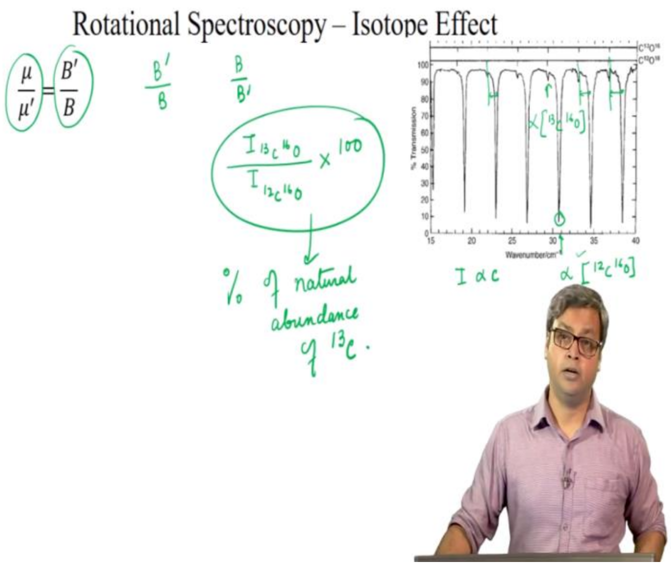

So, now, let us look again at the experimental spectrum, we see as the value of J increases the gap between the isotopically substituted line and the other line that is between C 13 and C 12 increases from what we had at lower J values. So, we can now explain the isotope effect from the experimental spectrum of carbon monoxide. So, we can find that B and B prime from the experimental spectrum. So, which will also provide us with this ratio B prime / B or we can also find B / B prime.

In other words, because B prime / B = mu / mu prime, we can get or we can obtain the atomic mass of the isotope directly from the rotational spectrum. We will have a better idea when we see a problem related to this. Moreover we can also find the natural abundance of a certain isotope by comparing the intensities of the peaks at a particular J level, because we know that intensity is proportional to concentration.

So let us consider it one of these peaks let us we consider this B. So, the intensity of this peak is proportional to the concentration of the 12 C 16 O. On the other hand, the intensity of this peak that is proportional to the concentration of 13 C 16 O, because both the peaks are proportional to the respective concentrations, if we take the intensity coming from the 12 C peak and the ratio of this intensity of coming from the 13 C peak to the 12 C peak and multiply it with 100 what we get we get is the percentage of natural abundance of 13 C so, let us now look into a few problems related to isotopic effect.

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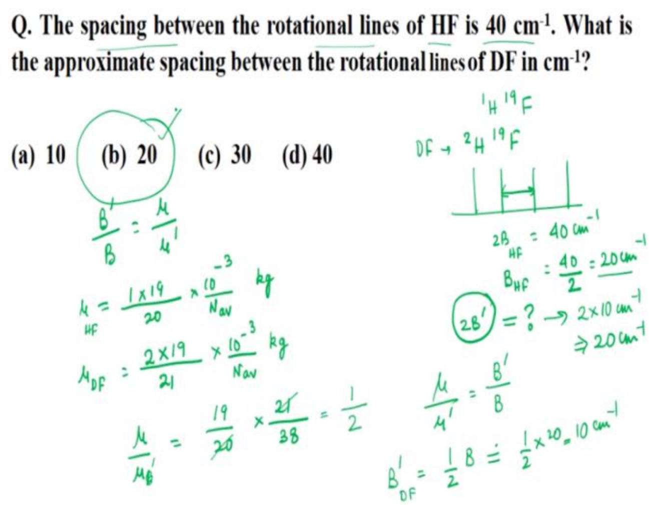

So the first question we have is the spacing between the rotational lines of HF is 40 wave numbers and the question is what is the approximate spacing between the rotational lines of DF in centimeter inverse. So, HF we can write H that atomic weight 1 fluorine atomic weight 19 and DF. So, D is an isotope of H, because I can write DF as H with atomic weight to 19 F. So, the question is for HF, I have a rotational spectrum and the spacing between the lines that is 2B for HF = 40 wave numbers.

So, B for HF is 40 / 2, that is 20 wave numbers. So, what we need to find? We need to find the 2B prime because the auditorium is the heavier isotope. We are defining B prime for the auditorium and we have to find the approximate spacing between the lines. So, we have to find that 2B prime. So we have to find this one. Let us see how we can do this. So we know that B prime by B = mu / mu prime.

So we can write mu. That is for HF that is 1 times 19 divided by 20. And we can write 10 to the power - 3 divided by Avogadro number that is in kg. So mu for DF is 2 times 19 divided by 21. That is 2 + 19 times 10 to the power - 3 divided by Avogadro number in kg. So we can write that mu / mu prime = 19 divided by 20 times 21 / 38. So approximately if we cancel out 20 and 21 what we get is mu / mu prime = 1 / 2.

In other words, mu / mu prime = B prime / B or B prime = 1 / 2 times B. So we found out B = 20 wave numbers. So, that is half times 20. That is 10 wave numbers. So B prime which is DF is 10 wave numbers in other words 2B prime is 2 times 10 wave numbers that is 20 wave numbers. So, our answer in this multiple choice question is B or the approximate spacing between the rotational lines of DF in centimeter inverse is 20.

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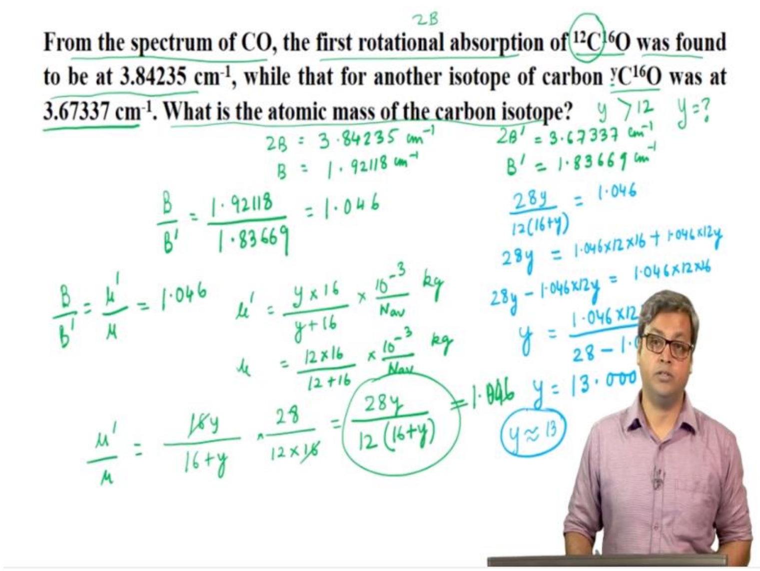

So, now, let us look into the next problem. So, from the spectrum of carbon monoxide, the first rotational absorption of 12 C 16 O no was found at 3.84235 wave numbers. So, the first rotational absorption comes at 2B so we can write 2B = 3.84235 wave numbers. In other words, what we can write is that B = 1.92118 wave numbers. The next part of the question is while that for another isotope of carbon, the isotope atomic weight is not given. So, this this is why so, why carbons 16 oxygen was at 3.67337 wave numbers.

So, first of all we should remember we are talking about 2 isotopes of carbon and because the value of B for 12 C is greater, obviously, from our understanding now, we know that why should be greater than 12 that means. We can say that why is a heavier isotope compared to 12? So let us write that as B prime. So we can write that 2B prime = 3.67337 wave numbers, in the world is B prime = 1.83669 wave numbers.

So in the question, we have to find the atomic mass of the carbon isotope, or we have to find what is the value of y. So we can immediately write B / B prime = 1.92118 divided by 1.83669. That is 1.046. So we know that B / B prime = mu prime / mu. So mu prime / mu = 1.046. So we can write mu prime equals. So this is the y C 16. So y times 16 / y + 16 times 10 to the power - 3 divided by Avogadro number kilogram.

We can rate mu = 12 times 16 divided by 12 +16 times 10 to the power - 3 divided by Avogadro numbers. Kilogram in other words, mu prime / mu = 16y divided by 16 + y times 28 divided by 12 times 16. We can cancel out 16. We can write this equals 28y divided by 12 times 16 + y. So this expression equals 1.046. So we can write 28y / 12 times 16 + y = 1.046. So if you simplify that will write 20y = 1.046 times 12 times 16 + 1.046 times 12y.

So we can write 28y - 1.046 times 12y = 1.046 times 12 times 16. In other words, we have to find y. So y = 1.046 times 12 times 16 divided by 28 - 1.046 times 12. So if you do this calculation, you will find y = 13.0005. So we can read approximately y is 13 so we are talking about the 13C isotope. So, from this we can find that the atomic weight of 13C is 13.0005 from an experimental data. So this is within 0.02% of the best value obtained in other ways. In other words, the decrease separation observed for isotopes allows us to evaluate precisely the atomic weights of the isotopes.