Fundamentals of Spectroscopy

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Lecture-19
Polyatomic Molecules I

Hello everyone welcome to the lecture today we will discuss polyatomic molecules. In the first lecture on rotation of spectroscopy we discussed that for an extended rotating object the angular velocity Omega and the angular momentum L need not point in the same direction.

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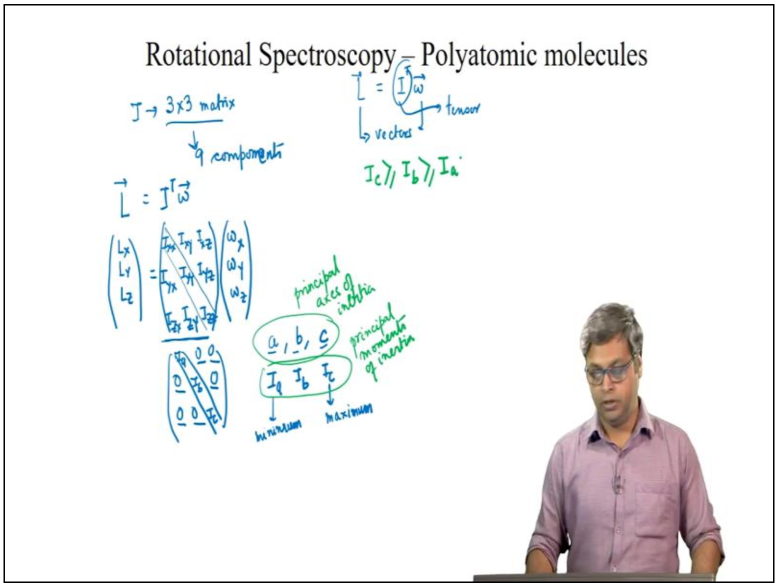

Rotational Spectroscopy – Polyatomic molecules

$I \to \underline{3\times3 \text{ matrix}} \to 9$ components

$\vec{L} = \overset{\leftrightarrow}{I}\vec{\omega}$

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

$$\begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

$\vec{L} = \boxed{I}\vec{\omega}$

a, b, c

$I_a \quad I_b \quad I_c$

$I_c \geqslant I_b \geqslant I_a$

In such cases the angular momentum is related in general to the angular velocity by l equals I Omega where L and Omega are vectors and the I is a tensor. So, tensor is represented generally by a matrix in a 3 dimensional space I is a 3 by 3 matrix which means it has 9 components thus L equals I Omega vector L equals I which is a tensor Omega can be explicitly defined as in the XYZ Cartesian coordinates I can write L as LX LY LZ equals I will write first Omega which is a vector which is Omega X Omega Y Omega Z and then I have the tensor which is a 3 by 3 matrix I have I XX I YY I ZZ .

So these are the diagonal elements and I have 6 of diagonal elements that is I XY I XZ I YX I YZ I ZX I ZY the values of the elements depend on the choice of the axis so the center of mass of the molecule. For a particular choice of axis this matrix can become a diagonal matrix that is the half diagonal terms that is the 6 of diagonals that we have will all become 0 but the diagonal terms will be non0. So, these axes are called a b and c axis.

So the moment of inertia will be I a, I b and I c. so, this I a, I b and I c represent the moment of inertia along the a, b and c axis. Conventionally the axis about which the moment of inertia has its maximum value, so let us say the moment of inertia I can write I a I b I c, so if the moment of inertia has the maximum value it is known as the c axis. So, we can write I c is maximum the axis about which the moment of inertia has its lowest value is known as the a axis, so we can write I a is minimum.

So these axis a and c along with the other axis that is b are known as the principal axis of inertia, so we can write a, b and c as the principal axis of inertia and the corresponding moments of inertia that is I a, I b and I c are the principal moments of inertia thus any rotating body or any rotating molecule has 3 values of I I a I b and I c and we can write I c greater than equal to I b greater than equal to I a.

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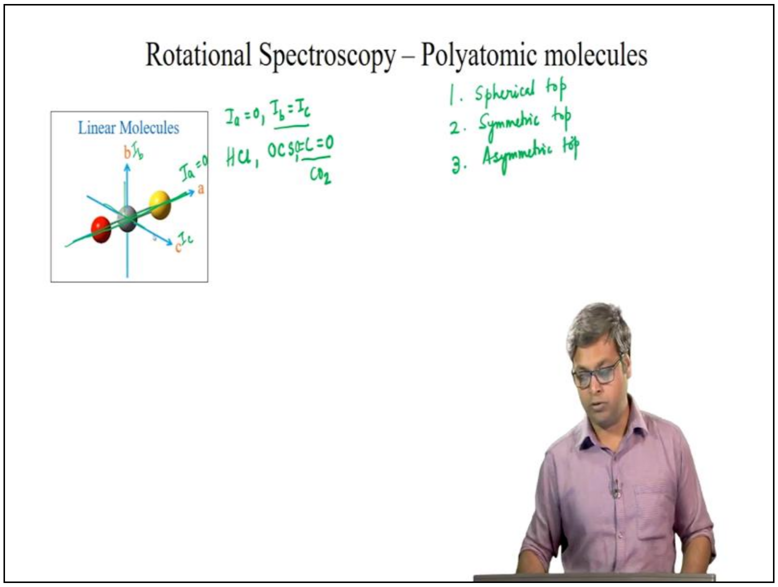

Rotational Spectroscopy – Polyatomic molecules

$I_a = 0$, $\underline{I_b = I_c}$

HCl, OCS, $\underline{O=C=O}$

CO_2

1. Spherical top
2. Symmetric top
3. Asymmetric top

So, now we will start looking into these polyatomic molecules. So, we will start with the linear molecule, so linear molecule are either diatomic or linear polyatomic molecules, so there are special cases where one of the axis is the axis of the molecule. And it passes through the center of mass of the molecule and the other 2 axes are perpendicular to the molecular axis. So, the axis along the molecular axis the moment of inertia along that axis that is I a here equals 0 and the I's along the other 2 directions that is I b and I c are equal.

So, these molecules can be represented as I a equals 0 I b equals I c in other words there is only one value of I because I b equals I c, so there is only one value of I for linear molecules and examples of polyatomic linear molecules are HCl OCS CO2 but we should remember that CO2 has no dipole moment so it will not show any rotational spectrum. So, in general any molecule can be classified as 3 top or rotor categories.

So, one is spherical top or spherical rotor then we have symmetric top or symmetric rotor and finally we have asymmetric top or asymmetric rotary.

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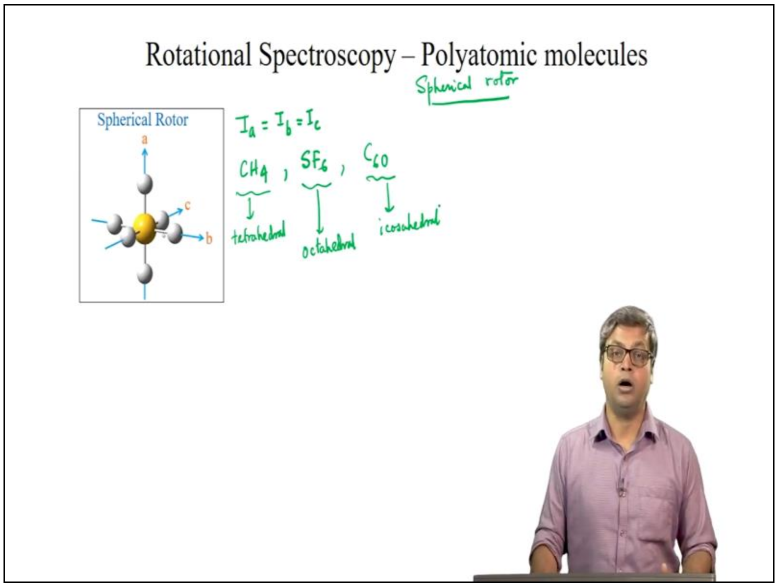

Rotational Spectroscopy – Polyatomic molecules

Spherical rotor

$I_a = I_b = I_c$

$\underbrace{CH_4}_{\downarrow \text{ tetrahedral}}$, $\underbrace{SF_6}_{\downarrow \text{ octahedral}}$, $\underbrace{C_{60}}_{\downarrow \text{ icosahedral}}$

So, we will look into these categories one by one, so first let us focus on spherical rotor. So, spherical rotors can be octahedral or tetrahedral molecules they are called spherical rotors as all 3 principal moments of inertia along the 3 principal axis are equal. So, we can write I a equals I b equals I c as all the I’s are equal the choice of axis is immaterial. So, the examples of spherical rotors are methane that is CH4 SF6 and C 60 that is fullerene.

So CH4 is a tetrahedral molecule SF6 is an octahedral molecule and C60 his icosahedrons. So, these molecules as you can see have no dipole moment and again they are not going to show a rotational spectrum.

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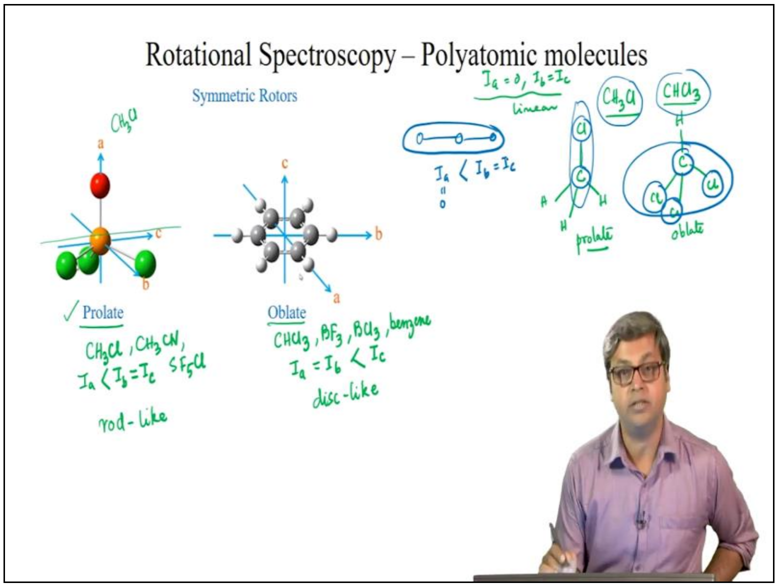

Rotational Spectroscopy – Polyatomic molecules

Symmetric Rotors

$I_a = 0,\ I_b = I_c$
linear

$I_a < I_b = I_c$

✓ Prolate

CH_3Cl, CH_3CN, SF_5Cl
$I_a < I_b = I_c$
rod-like

Oblate

$CHCl_3$, BF_3, BCl_3, benzene
$I_a = I_b < I_c$
disc-like

So, let us move into symmetric rotors for symmetric rotors 2 of the principal moments of inertia are equal. But the third one is unequal that way we can think that linear molecules where we had I a equals 0 I b equals I c so this is for linear molecules we can think that this linear molecules are a special case of symmetric tops. So, for symmetric tops or symmetric rotors we have 2 types we have prolate symmetric top and oblate symmetric term.

So, we will first discuss prolate symmetric term. So, examples of prolate include CH3Cl, so for prolates I a is less than I b and I b is equal to I c, so the larger moment of inertia they are equal and I a is smaller than both I b and I c which are equal. So, just to reiterate the rotational axis goes through the center of mass but not to the central carbon atom for this molecule that is CH3Cl this is because these 3 hydrogen atoms actually are not in the same plane as that of the carbon atom so, the other example so prolate top includes CH3 CN and also SF5CL.

So, the other kind of symmetric top is the oblate symmetric term examples of oblate we can write CHCL3 that is chloroform. We can have BF3 BCL3 or benzene. So, for oblates we have i a equals I b and I a and I b and less than I c. So, you can see in prolate we had I a which is less than I b equals I c what it is oblate the largest moment of inertia is I c is unequal to the other 2 that is I a and I c. so, unless one calculates the moment of inertia along the principal axis it will not be obvious whether a molecule is a prolate or oblate.

However prolate or oblate normally represents the molecular shape. So, we can say the prolate is rod like and oblate is disk like. So, let us take the examples of CH3Cl and CHCL3. So, let us draw the molecules so we have carbon chlorine and 3, hydrogen's. So, in the first case and in the other case we have carbon hydrogen and 3 chlorine atoms. So, as we know CHCL3 that is oblate and CH3CL this here that is prolate.

So, if we look carefully into CH3CL the major mass is coming from the carbon atom and the chlorine atom or we can say the major mass is distributed along the CCL bond. The masses of hydrogen's are negligible as compared to that of the carbon and the chlorine atom. So, it has more of a rod-like shape but the major masses are distributed along the CCL bond. On the other hand if we consider chloroform the major masses are distributed between the 3 chlorine atoms and the carbon atom.

So CHCL3 or chloroform has a disk like shape so we can also see that the linear molecule can also be considered as prolate as a linear molecule has a rod like shape, so it also matches the shape and we can say I a which is equal 0 is less than I b equals I c.

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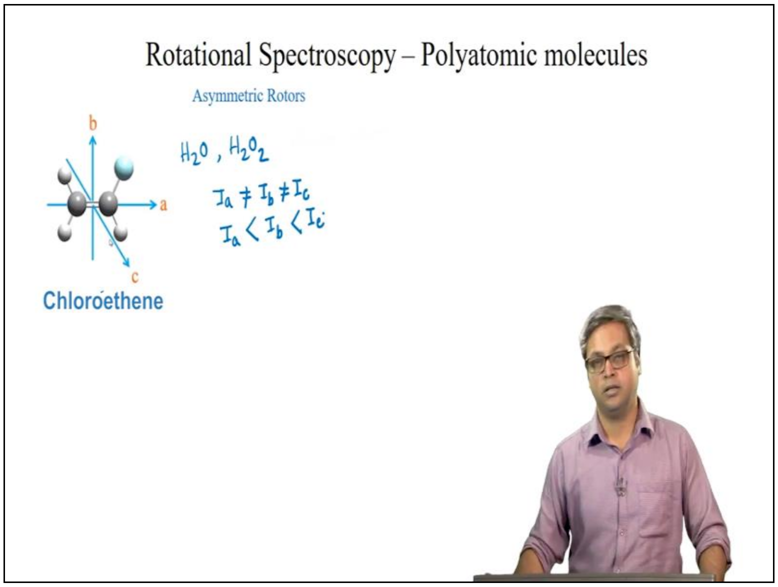

Rotational Spectroscopy – Polyatomic molecules

Asymmetric Rotors

H_2O , H_2O_2

$I_a \neq I_b \neq I_c$

$I_a < I_b < I_c$

So, the final category we have is asymmetric top or asymmetric rotor. In fact a vast majority of molecules are asymmetric. So, examples of asymmetric top are water there is H2O hydrogen peroxide or the one that is shown here in this figure. So, for a symmetric rotor we can write I a not equal to I b not equal to I c and also I a is the lowest value of the moment of inertia so I a is less than I b which is less than I c.

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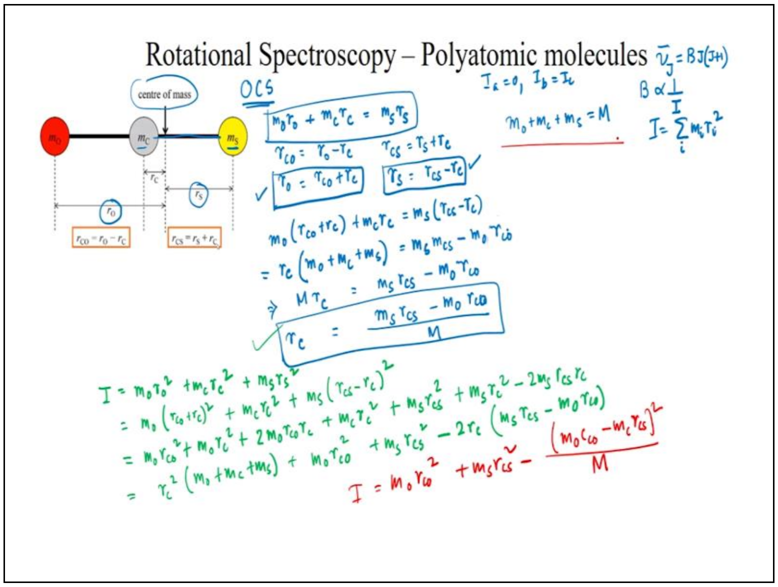

Rotational Spectroscopy – Polyatomic molecules $\bar{\nu}_J = BJ(J+1)$

OCS

$I_a = 0,\ I_b = I_c$

$B \propto \frac{1}{I}$

$I = \sum_i m_i r_i^2$

$m_O + m_C + m_S = M$

$\boxed{m_O r_O + m_C r_C = m_S r_S}$

$r_{CO} = r_O - r_C$ $\quad r_{CS} = r_S + r_C$

✓ $\boxed{r_O = r_{CO} + r_C}$ $\quad \boxed{r_S = r_{CS} - r_C}$ ✓

$m_O(r_{CO} + r_C) + m_C r_C = m_S(r_{CS} - r_C)$

$= r_C(m_O + m_C + m_S) = m_S m_{CS} - m_O r_{CO}$

$\Rightarrow M r_C = m_S r_{CS} - m_O r_{CO}$

✓ $\boxed{r_C = \frac{m_S r_{CS} - m_O r_{CO}}{M}}$

$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2$

$= m_O(r_{CO} + r_C)^2 + m_C r_C^2 + m_S(r_{CS} - r_C)^2$

$= m_O r_{CO}^2 + m_O r_C^2 + 2m_O r_{CO} r_C + m_C r_C^2 + m_S r_{CS}^2 + m_S r_C^2 - 2m_S r_{CS} r_C$

$= r_C^2(m_O + m_C + m_S) + m_O r_{CO}^2 + m_S r_{CS}^2 - 2r_C(m_S r_{CS} - m_O r_{CO})$

$I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O c_{CO} - m_C r_{CS})^2}{M}$

So, let us go back to the linear polyatomic molecules. In fact we have already solved the rotational problem for the linear system in case of diatomic molecules. The solution is the same as the diatomics it does not matter how many atoms are there on the line. The rotational spectrum will look the same. The characteristics of these molecules in terms of moment of inertia are identical. So, we can write I a equals 0 I b equals I c this means the rotational energy levels for a linear polyatomic system is going to be identical as the diatomic molecule.

So, for diatomic molecules we got nu bar J equals B times J times J + 1 if we ignore the centrifugal distortion. The rotational constant B as we know is inversely proportional to the moment of inertia, so we can write B is inversely proportional to the moment of inertia this moment of inertia here is associated to the b and c axis because I a equals 0 so which are the same so I b equals I c and because I b equals I c they cannot be distinguished.

The difference between a diatomic linear molecule and a tri atomic linear molecule is the triatomic molecule is larger. So, the moment of inertia will be greater as we know I is given by summation small i m i T i squared, so the more atoms are there on a line the greater will be the moment of inertia. But does this larger moment of inertia reflect on the rotational spectrum. So, because I is greater it means the rotational constant B is going to be smaller.

As the spectral lines are separated by 2 B or the spectral lines are to be apart the spectral lines in polyatomic systems will be much closer together that means they are much closer compared to what they were in case of the diatomic system. This is similar to a particle in a box system the larger the box the closer are the energy levels in polyatomic molecules the rotational wave function can spread over much larger region.

So, the energies will be smaller and the energy levels will be closer together. So, let us look into a molecule a tri atomic linear molecule that is OCS, so we have a trinomial in your molecule OCS, so OCS has one oxygen atom one carbon atom and a sulphur atom all in a line. The sulphur atom is much heavier than both the carbon and the oxygen atoms. So, the center of mass will lie somewhere along the C is bond.

So, we can define the distances r 0 r c and r s, such that r 0 is the distance by how much the oxygen atom is separated from the center of mass and we can say the carbon atom is r c distance away from the center of mass and the heaviest return that is a sulfur is r s distance away from the center of mass. So, the condition that enables us to identify the center of mass is in oxygen r oxygen so it is not 0 that is O, m carbon r carbon equals m sulphur r sulfur.

So we are interested in the structure of the molecule remember rotational spectroscopy gives us the structure in terms of bond length. So, we are not really interested in what the distances are from the center of mass but we are interested in what the bond lengths are. So, we can define the bond length in terms of the distances. So, we can write r co equals r o – r c in other words I can write r o equals r co + rc. So, we can also write r cs equals r s + r c.

So from this we can write r s equals r cs – rc, so now if we compute the moment of inertia let us see what we get. So, using this expression and these 2 expressions we can write mo r co + rc + mc rc equals m s rcs - rc so from here we can write if we take rc common so we can write m o + mc + m s equals m s m cs - m r co. Now if I write the total mass that is m o + mc + m s equals capital M I can write m rc equals m s rc s - m r co in other words I can write rc equals m s r cs - mo r co divided by capital M.

So now we know that the moment of inertia for this linear traffic molecule is given by I equals m o r o squared + m c r c squared + m s r s squared. So, now we can write m o and r 0 we can write as r co + r c squared then I have mc rc squared + ms and rs I can write as r cs - rc squared. So, now we can simplify and write m o r co squared + m o rc squared + 2 m o r co rc + m c r c squared + m s r c s squared + m s rc squared - 2 m s r cs r c.

So, if I take the rc square common I can write m o + mc + m s + m o r co squared + m s r cs squared - 2 r c m s r cs – m o I co so now we have already found out an expression for rc, so if we replace rc with this expression what we will arrive at is I equals mo rc squared + m s r cs squared - will have mo rco – mc rcs all squared divided by capital M where capital M is m o + mc + ms. Now the question is can we determine the 2 bond lengths the co and cs and the cs bond length from the calculation of the rotational constant V from the spectrum.

Because if we get b we know we can get I and I is a function of the bond length. So, the question is can we obtain both the bond lengths.

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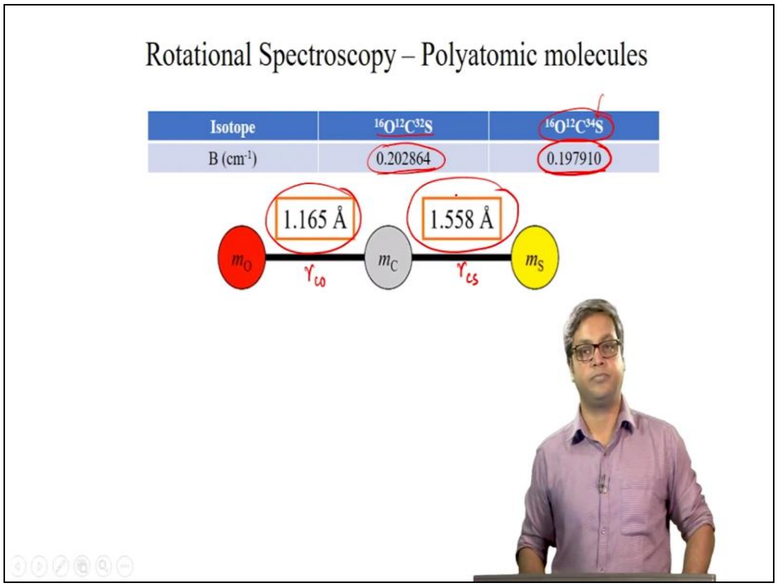

Rotational Spectroscopy – Polyatomic molecules

Isotope	$^{16}O^{12}C^{32}S$	$^{16}O^{12}C^{34}S$
B (cm^{-1})	0.202864	0.197910

If we only have the value of B for OCS that is for 60 O 12 C 32 S we cannot get both the bond lengths. For example the B for this molecule is 0.202864 wave numbers but the moment of inertia has 2 unknowns in it the 2 bond lengths. So, we cannot from one value of rotational constant B we cannot get the bond lengths, so we need 2 values of B so we can get a second value of B if we isotopically substitute the sulphur atom by 34 sulphur.

And the value of this isotopically substituted molecule is 0.197910 because it has different mass that means it has different moments of inertia. So, it will have a different rotational constant as we see instead of 0.202864 it is now 0.197910 but as we have discussed on the lecture on isotopic substitution that the bond length will not be different that is the structure of the molecule will not differ for the isotopes.

Thus with the 2 rotational constants we can set up 2 different equations in which we have 2 unknowns and then we can solve them simultaneously to get the co and the cs bond length. So, if we solve we will get is r co as 1.165 angstrom and r cs as 1.558 angstrom.