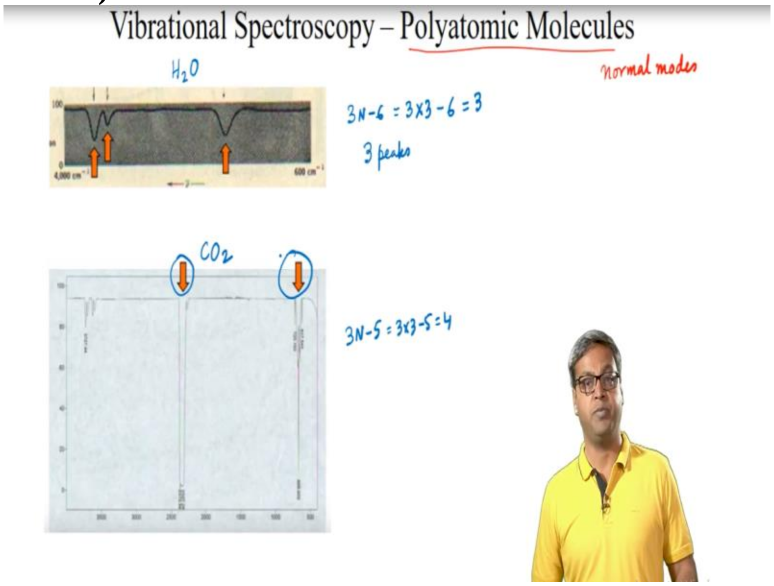
Fundamentals of Spectroscopy

Prof. Dr. Sayan Bagchi,
Physical and Materials Chemistry Division,
National Chemical Laboratory - Pune

Prof. Dr. Anirban Hazra,
Department of Chemistry,
Indian Institute of Science Education and Research – Pune

Lecture- 34
Vibration of Polyatomic Molecules 2

(Refer Slide Time: 00:24)



Vibrational Spectroscopy – Polyatomic Molecules

normal modes

H_2O

$3N-6 = 3\times3-6 = 3$

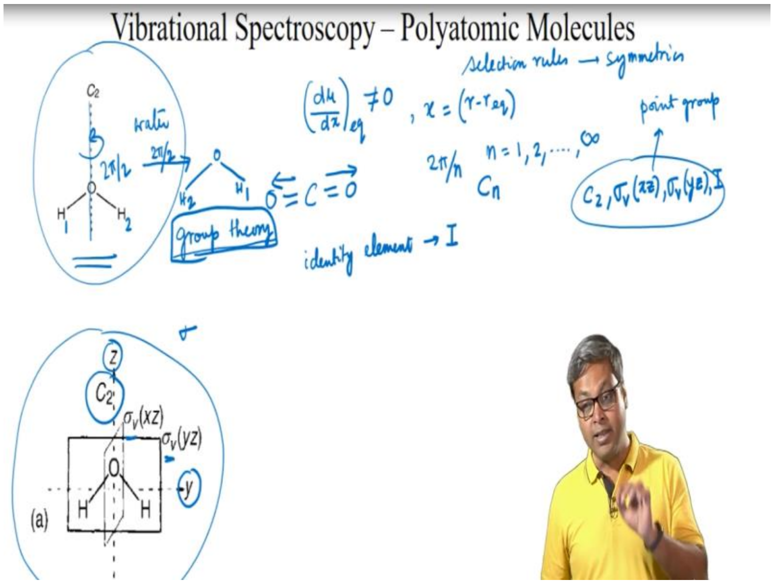
3 peaks

CO_2

$3N-5 = 3\times3-5 = 4$

Hello everyone, welcome to the lecture. In the last lecture, we started discussing about polyatomic molecules. We discussed about normal modes and looked into the spectrum of water and carbon dioxide. So, this is the spectrum or IR spectrum of water and this is the IR spectrum of carbon dioxide. So water has 3N - 6 that is 3 times 3 - 6 that is 3 vibrations, because water is nonlinear and also 3 peaks are observed in the IR spectrum for carbon dioxide because carbon dioxide is linear there are 3N - 5 that means 3 times 3 - 5 that is 4 vibrations. However, only 2 peaks are observed in the IR spectrum.

(Refer Slide Time: 01:48)



Vibrational Spectroscopy – Polyatomic Molecules

So, in this lecture, we will discuss the selection rules for vibrational spectroscopy and how these can be determined from the symmetries of the vibrational normal modes. The gross selection rule remains the same as that of the diatomic molecule. That is, the dipole moment must change as the vibration passes through the equilibrium position. Mathematically this can be expressed as dmu dx at equilibrium position not equal to 0 where x is the displacement from the equilibrium position given by r - r equilibrium.

This selection rule is identical to that of a diatomic molecule except that the displacement is now a combination of the atomic coordinates that is the normal coordinate. So the symmetric stretch of carbon dioxide, so let us draw the symmetric stretch. So, here both the CO vibrations are in phase. So, this symmetric stretch of carbon dioxide is higher inactive, as it does not generate a dipole moment at any point during the vibration.

This explains why there are only 2 vibrational bands in the infrared spectrum of carbon dioxide rather than 4 one is missing, as the 2 bending modes are degenerate. And the second is missing as the symmetric stretch is higher inactive. So, now we will discuss the symmetries of vibrational wave functions. We want to look at the symmetries of the vibrational states in order to determine the selection rules for IR spectroscopy, we will be considering the vibrations of water.

So, we see the water molecule in this fear and we will determine which water vibrations are higher active. Before we go into the details, we should understand that the application of symmetry arguments to molecules has the origin to something known as group theory. We would look into the basics of group theory from our more qualitative level, we will start with the elements of symmetry.

So let us look into the water molecule in water, the rotation of the molecule by 2pi / 2 radians. So if you rotate this molecule along this axis by 2pi / 2 radians, it produces an identical configuration to the observer. So, if I write this as H 1 and H 2, and if I do our 2pi / 2 rotation around the axis, what I get is H 1 on the right side and H 2 on the left side, but because these hydrogen atoms are indistinguishable, we cannot distinguish between the conformer before the rotation and the conformer after the rotation.

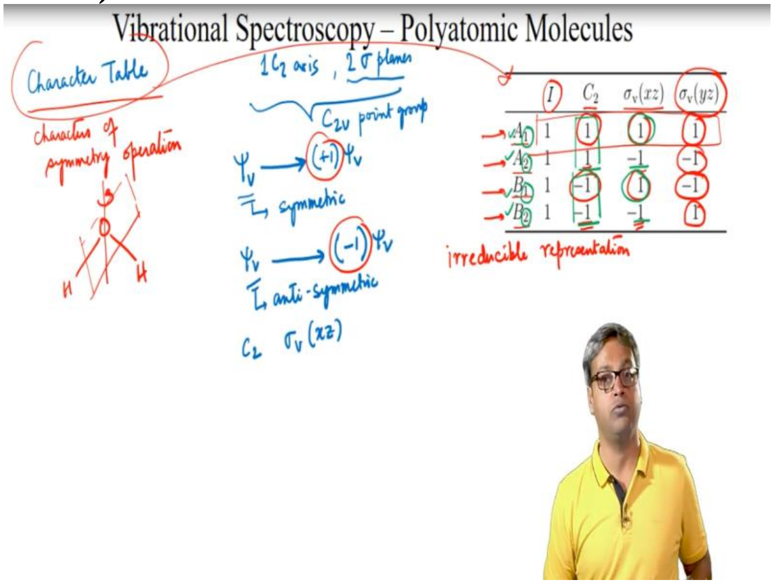
In other words, rotation of any molecule by 2pi / n radians, where n can be 1 2 dot dot dot up to infinity about an axis is produces an equivalent configuration, which to a stationary observer is indistinguishable from the initial 1, the molecule has an enfold axis of symmetry and the symbol for such a symmetry is given by C n. So, like C n, there are other elements of symmetry if a molecule has a plane of symmetry.

Such that reflection of all the nuclei through the plane to an equal distance on the opposite side produces a configuration indistinguishable from the initial 1, it is known as the plane of symmetry and the symbol for such symmetry is given by sigma. So, let us look again into water. So, in this figure, the axis are labeled. So, we have this as the z axis and this as the y axis. So, the water which is a planar molecule.

the vertical axis in this plane is the z axis and the horizontal axis is the y axis and the axis that is going below and up the plane of the water molecule is the x axis, the subscript v in this sigma stand for vertical, which implies that the plane is vertical with respect with the highest full axis that is the C 2 axis or the z axis in this case, and this defines the vertical direction. Moreover, all the molecules possess the identity element of symmetry.

So, this identity element is given by I. So, there are several other symmetry elements for more complex molecules more complex than water. However, as we limit our discussion to water, the elements of symmetry, that water has our C 2 sigma v along the x z plane sigma v along the y z plane and I. The symmetry elements of a molecule constitute something known as the point group. The point groups are so called because when all the operations of the group are carried out, at least one point is unaffected. In this particular case of water, any point on the C 2 axis is unaffected.

(Refer Slide Time: 09:49)



Vibrational Spectroscopy – Polyatomic Molecules

Character Table

characters of symmetry operation

$1 C_2$ axis, 2σ planes

C_{2v} point group

$\psi_v \rightarrow (+1)\psi_v$

↳ symmetric

$\psi_v \rightarrow (-1)\psi_v$

↳ anti-symmetric

C_2 $\sigma_v(xz)$

	I	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

irreducible representation

So, as water contains 1C 2 axis, so, water contains 1C 2 axis and 2 sigma Plames of symmetry all of which contain the C 2 axis water belongs to the C 2v point group. If the element of symmetry of the wave function is preserved during a symmetry operation, the symmetry operation has no effect on the wave function. And because the symmetry operation has no effect on the wave function, we can write psi v which is a wave function after the symmetry operation remains the same, that is + 1 times psi v.

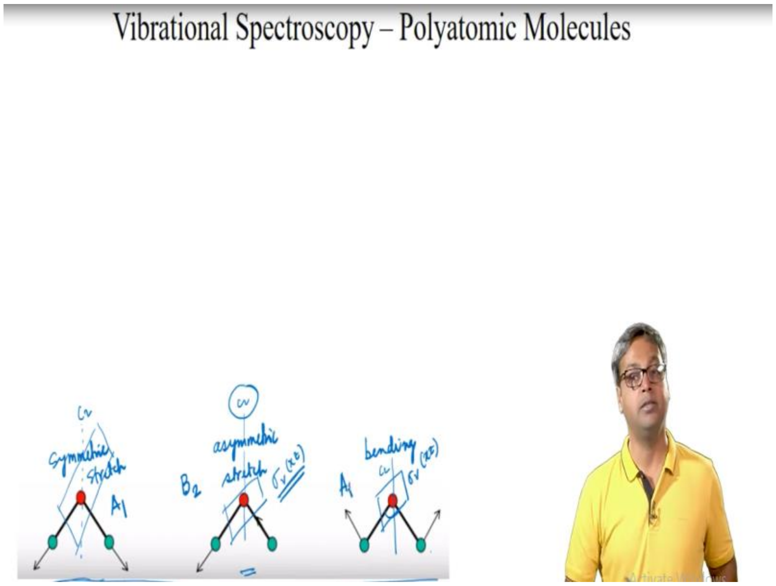
Thus we can say that psi v is symmetric to the symmetry operation, on the other hand, if the wave function changes sign by carrying out the operation, so, psi v changes sign during the operation. So, it becomes - 1 times psi v we can say that psi v is anti-symmetric to the symmetry operation. So, for the water molecule the C 2 and the sigma v x z operations have no effect on the wave function.

So, we can create something known as the character table where the elements that is this + 1 or - 1 of this character table are known as the characters of symmetry operation with respect to the symmetry operation. So, here we show the character table of water or the C 2v point group, the character with respect to I must always be + 1 because this is an identity operation. We can see that sigma v y z is generated from C 2 and sigma v x z that means, if we have the water molecule and we perform the C 2 operation and also perform the sigma v x z operation.

Then what we end up with is sigma v y z operation. So, thus the characters with respect to sigma v y z is the product of characters with respect to C 2 and sigma v x z. So, we can see here that when C 2 and sigma v x z both are + 1 the sigma v y z is + 1 when they are both - 1 the product again is + 1. However, when this C 2 is + 1 and sigma v is - 1 the product is - 1 and here also when C 2 is - 1 and sigma v is + 1 then sigma v y z here the product is - 1. So, each of these 4 rows of characters is called the irreducible representation.

This is the irreducible representation of the group. And for convenience, each is represented by a symmetry species that is A 1 A 2 B 1 and B 2. The A 1 species is said to be totally symmetric, since all the characters are last 1. The other 3 species are not totally symmetry, the symmetry species levels are conventional A or B indicates symmetry or anti symmetry respectively to C 2. So, we can see, whenever C 2 is + 1, we have A and whenever C 2 is - 1 we have B. Similarly, the subscripts 1 and 2 indicates symmetry or anti symmetry with respect to the sigma v x z Plame. So, we can see whenever the sigma v z is + 1 we have 1 and when it is - 1 we have 2.

(Refer Slide Time: 15:56)



Vibrational Spectroscopy – Polyatomic Molecules

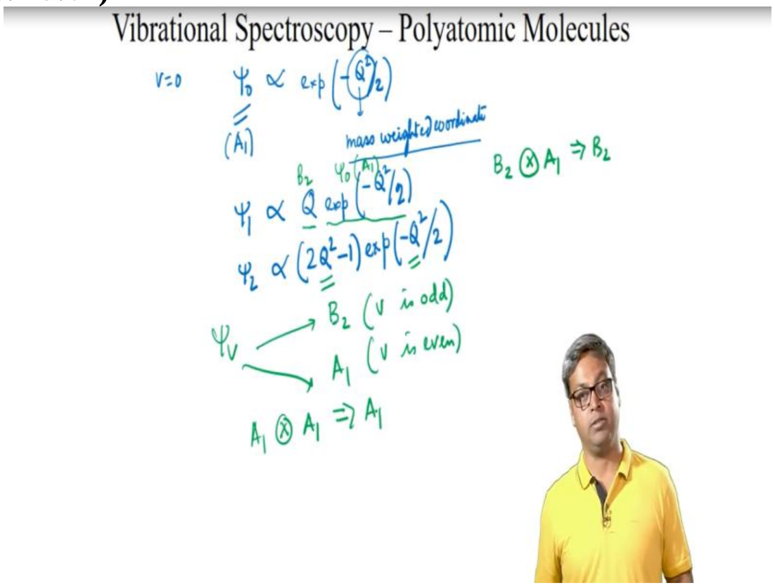
The water molecule has 3 normal modes of vibration as shown in this figure. So, we can label these modes. So, the first one is the symmetric stretch. The second one is the asymmetric stretch, and the third one is the bending mode. So, using the C 2v character table, the wave functions psi v for each can be easily assigned to symmetry species. The symmetric stretch can be identified as the displacement in both this OH bonds.

Where both these OH bonds are in phase the displacements are phase with each other the normal mode has A 1 symmetry, because now, if we plot the C 2 axis as well as if we plot the sigma v x z plane it produces or the symmetry operations produce identical configurations. So, this has A 1 symmetry. So, we can see this is because the mode is symmetric to both C 2 and sigma v x z symmetry operations.

The asymmetric stretch shown here can be identified as the vibration in which the displacements of the OH bonds are out of phase with each other. The normal board is anti-symmetric with respect to C 2 or the sigma v x z Plame and because it is anti-symmetric to both C 2 and sigma v x z. So, because of the anti-symmetry to C 2 we have B and anti-symmetry to sigma v we have B 2. So, it has the B 2 symmetry, the bending vibration is the vibration in which the HOH angle is increasing and decreasing.

As we can see, this normal mode is also symmetric with respect to C 2 and the sigma v x z plane and because it is symmetric to all the symmetry operations, it has A 1 symmetry. So, now, let us look at the ground vibrational state.

(Refer Slide Time: 19:07)



Vibrational Spectroscopy – Polyatomic Molecules

v=0 $\psi_0 \propto \exp\left(-\frac{Q^2}{2}\right)$

(A_1)

mass weighted coordinate

$\psi_1 \propto \overset{B_2}{\underline{Q}}\, \underbrace{\exp\left(-\frac{Q^2}{2}\right)}_{}$ $\psi_0\,(A_1)$

$B_2 \otimes A_1 \Rightarrow B_2$

$\psi_2 \propto (2Q^2-1)\exp\left(-\frac{Q^2}{2}\right)$

$\psi_v \rightarrow B_2$ (v is odd)

$\psi_v \rightarrow A_1$ (v is even)

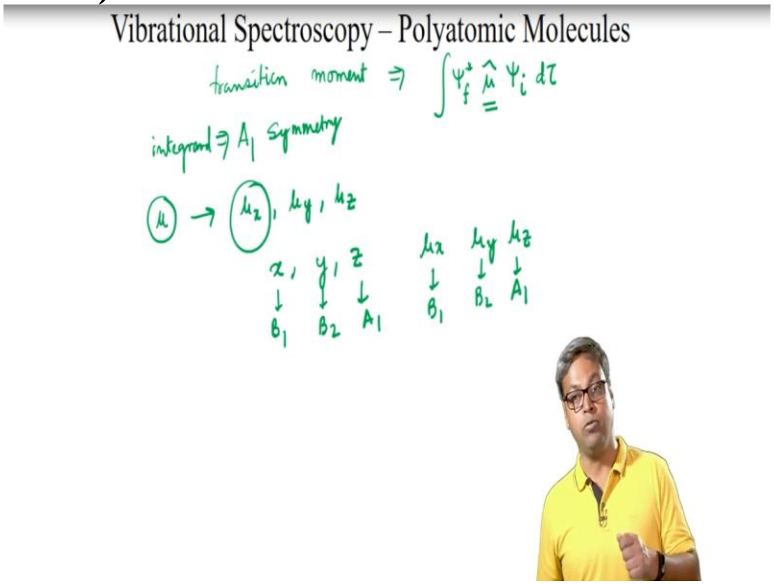
$A_1 \otimes A_1 \Rightarrow A_1$

That means at v = 0 and the wave function of this v = 0 can be represented by psi 0, which is proportional to exponential of - Q square / 2. So here Q is the mass weighted coordinate. If we apply any symmetry operator to this function, then Q matching sign. For example, the anti symmetric stretch with B 2 symmetry is anti symmetric with respect to the C 2 operation. However, the Q square is always symmetric and thus this psi 0 is totally symmetric or we can say psi 0 is A 1 for water.

Now, let us look into the excited vibrational states. So the first 2 vibrational excited states can be represented by psi 1 and psi 2 so psi 1 can be represented as proportional to Q times exponential - Q square / 2 and psi 2 is proportional to Q square - 1 times exponential – Q square / 2. Thus psi 1 is the product of Q, which has b 2 symmetry. And this part is psi 0 and psi 0 has A 1 symmetry thus psi 1 for the asymmetry stretch has B 2 times A 1 that is B 2 symmetry overall, the V equals 2 state has the A 1 symmetry like the ground state.

Because here we are dealing with only Q square. So it can be seen that in fact psi v has B 2 symmetry when v is odd, and A wants symmetry when v is even the bend and the symmetric stretch, both has A 1 symmetry. And since A 1 times A 1 is also equal to A 1, all their states have A 1 symmetry. So, how does identifying the symmetry of the vibrational states help us identify the selection rules? We know that the intensity of a transition is proportional to the square of the transition dipole moment.

(Refer Slide Time: 23:01)



Vibrational Spectroscopy – Polyatomic Molecules

transition moment $\Rightarrow \int \psi_f^* \underline{\underline{\hat{\mu}}}\, \psi_i \, d\tau$

integrand $\Rightarrow A_1$ symmetry

$\mu \rightarrow \mu_x, \mu_y, \mu_z$

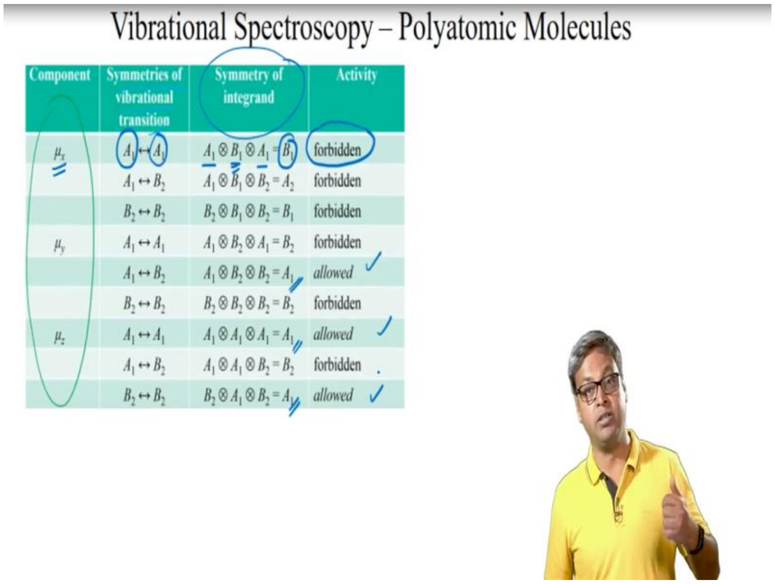
$$\begin{array}{ccc} x, & y, & z \\ \downarrow & \downarrow & \downarrow \\ B_1 & B_2 & A_1 \end{array} \qquad \begin{array}{ccc} \mu_x & \mu_y & \mu_z \\ \downarrow & \downarrow & \downarrow \\ B_1 & B_2 & A_1 \end{array}$$

And this transition moment is given by integration of the final state. That is psi star final, the dipole moment operator, the initial state of the psi i d tau by definition, an integral is just a number just symmetry operations have no effect on it. But the integrand maybe operated by the symmetry operators, and if there is any symmetry operator, that changes the sign, it will change the sign of the whole integral. So there is a contradiction unless the integral is 0.

So the integrand must have and overall A 1 symmetry in other words, it must be totally symmetric. If it has to be nonzero the dipole moment mu because we have this dipole moment operator so, this mu can be broken down to mu x mu y and mu z. So, this mu x can be written as a sum of the charges times the x coordinate of the charges. So, based on the choice of our axis, so this x, y and z coordinates of the C 2 v has B 1 B 2 and A 1 symmetry.

So, the mu x, mu y mu z, they also have B 1 B 2 and A 1 symmetries as we have already discussed, the vibrational states of water has either A 1 that is when v equals even or B 2 that is when v equals odd symmetries. So, we can construct the possible symmetries of the integrand of the transition dipole moment.

(Refer Slide Time: 25:50)



Vibrational Spectroscopy – Polyatomic Molecules

Component	Symmetries of vibrational transition	Symmetry of integrand	Activity
μ_x	$A_1 \leftrightarrow A_1$	$A_1 \otimes B_1 \otimes A_1 = B_1$	forbidden
	$A_1 \leftrightarrow B_2$	$A_1 \otimes B_1 \otimes B_2 = A_2$	forbidden
	$B_2 \leftrightarrow B_2$	$B_2 \otimes B_1 \otimes B_2 = B_1$	forbidden
μ_y	$A_1 \leftrightarrow A_1$	$A_1 \otimes B_2 \otimes A_1 = B_2$	forbidden
	$A_1 \leftrightarrow B_2$	$A_1 \otimes B_2 \otimes B_2 = A_1$	*allowed* ✓
	$B_2 \leftrightarrow B_2$	$B_2 \otimes B_2 \otimes B_2 = B_2$	forbidden
μ_z	$A_1 \leftrightarrow A_1$	$A_1 \otimes A_1 \otimes A_1 = A_1$	*allowed* ✓
	$A_1 \leftrightarrow B_2$	$A_1 \otimes A_1 \otimes B_2 = B_2$	forbidden
	$B_2 \leftrightarrow B_2$	$B_2 \otimes A_1 \otimes B_2 = A_1$	*allowed* ✓

So, here we are constructing the possible integrand. So, here we have the components of the dipole moment. And in the second column we are having the symmetries of vibrational transitions. And in the third column, we are constructing the entire symmetry of the integrand. So, we can see that mu x is B 1. So, if we have a transition from A 1 to A 1 then our triple product becomes A 1 times B 1 times A 1 and this is B 1 and as we know the total integrand has to be A 1.

That means, this case is forbidden. So, we have to find out where this integrand is totally symmetry. So, we can see that there are only 3 cases where the transitions are allowed as the number of vibrations in water is equal to the number of allowed transitions, all the vibrations in water are higher active. Thus, in today's lecture, we have used the symmetries of the vibrational states to gain insight about the selection rules.