Fundamentals of Spectroscopy

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Lecture 42
Raman Activity of Vibrations

Hello all welcome to the lecture. In the last lecture, we got introduced to the concept of Polarizability ellipsoids.

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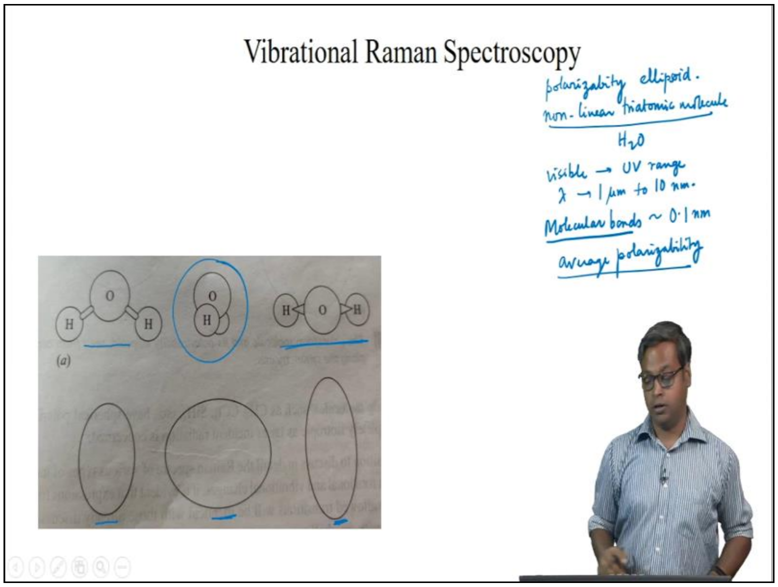

Vibrational Raman Spectroscopy

polarizability ellipoid.
non-linear triatomic molecule
H_2O
visible → UV range
$\lambda \to 1\,\mu m$ to 10 nm.
Molecular bonds ~ 0.1 nm
average polarizability

Let us first consider the shapes of Polarizability ellipsoids of more complex molecules. So, in the last lecture, we talked about the polarizability ellipsoid of a diatomic molecule that is hydrogen. So now, let us consider the non linear triatomic molecule which is water. By analogy with the discussion on hydrogen, which we discussed in the last lecture, we might expect the polarizability surface to be composed of two similar, ellipsoids one for each bond.

But we must remember that the oscillating electric field which is applied for Raman spectroscopy is usually of the radiation visible in the ultraviolet range. So, the wavelength that is Lambda is of the order of 1 Micron, or 1 micrometre to 10 nanometre. On the other hand, the molecular bonds have the dimensions of around 0.1 nanometer so the radiation cannot probe the final details of bond polarizability. Instead the radiation can sense the average polarizability.

So the radiation can sense polarizability in various directions to the molecule. In case of water, the polarizability is found to be different along all three of the major axis of the molecule. So, all the three ellipsoids are also different. So, the ellipsoids in various orientations are shown in this figure. So for this orientation we have this ellipsoid, for this different orientation ellipsoids looks like this. And if you look from this direction the ellipsoid looks like this.

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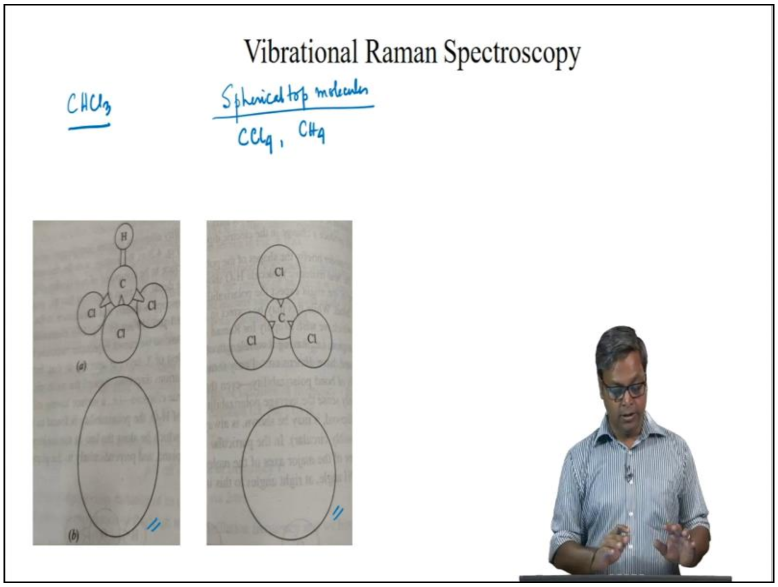

Vibrational Raman Spectroscopy

$CHCl_3$

Spherical top molecules

CCl_4, CH_4

For symmetric top molecules, for example, CHCl3, or chloroform, they have polarizability ellipsoid rather similar to those of linear molecules as we can see in this figure. And finally for spherical top molecules like CCl4 or methane, the polarizability surfaces are spherical. Since they are completely isotopic as far as the Incident radiation is concerned. And this is shown in this figure. So now, let us move on to Vibrational Raman spectroscopy and focus on the Raman activity of vibration.

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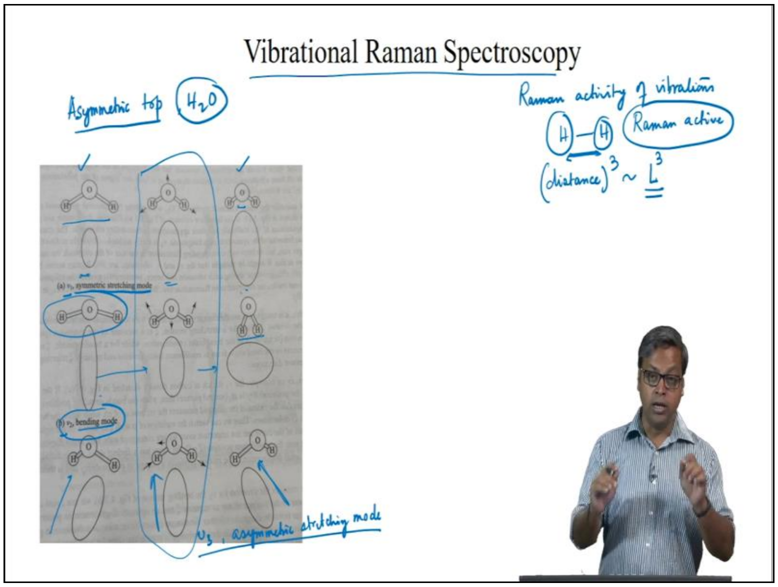

Vibrational Raman Spectroscopy

Asymmetric top H_2O

Raman activity of vibrations

H—H Raman active

$(\text{distance})^3 \sim L^3$

ν_3, asymmetric stretching mode

If a molecule has no symmetry it is straight forward to decide whether the vibrational modes will be Raman active or inactive. In fact in this case, we can assume these modes are Raman active. However, when the molecule has considerable symmetry it is not always easy to make the decision since much consideration is needed to understand whether or not the polarizability changes during the vibration. For a diatomic let us say like Hydrogen, one has only one vibrational mode and that is along the bond axis.

Roughly, the polarizability is related to volume. We have seen this in the last lecture. As the polarizability has the dimension of distance cube or we can write length cube. So, length by distance cube is volume does the change in volume indicates a change in the polarization. Thus, during the vibrational motion of a diatomic molecule, the volume changes and does the polarizability will change and so this vibration is Raman active.

For polyatomic molecules the problem is a bit more complicated. So let us consider the asymmetric top molecule, water. So we will consider the asymmetric top that is water, the polarizability ellipsoid of water are shown in the figure. So there are three fundamental modes. Mu1, which is the symmetric stretching mode we have Mu2, which is the bending mode and also we have Mu3, which is the asymmetric stretching mode.

So, the equillibirum configuration for all this modes is at the centre and the extreme positions are shown either on the left or the right? And the shapes of the polarizability ellipsoid for each confirmation of each mode are shown in this figure. During the symmetric stretch, the molecule as a whole increases or decreases in size, when a bond is pressed the electrons mourning it was formally held by the nuclear. And so the bond becomes more polarizable.

Thus, the polarizability ellipsoid increases when the bond stretches and decreases in size or volume, when the bond compress, but an approximately constant ship is maintained. On the other hand, during the burning motion, that is for Mu2, due to the shape of the ellipsoid that changes the mode. For large amplitude vibrations the molecules change from almost linear configuration to that of a diatomic molecule.

So, in asymmetric stretch, which we have here the third one the bond shape and size remains approximately constant. But the direction of the major axis change remarkably. Thus all three modes, Mu1, Mu2, Mu3 involve changes in polarizability ellipsoid in one form or the other. And thus all these modes are Raman active.

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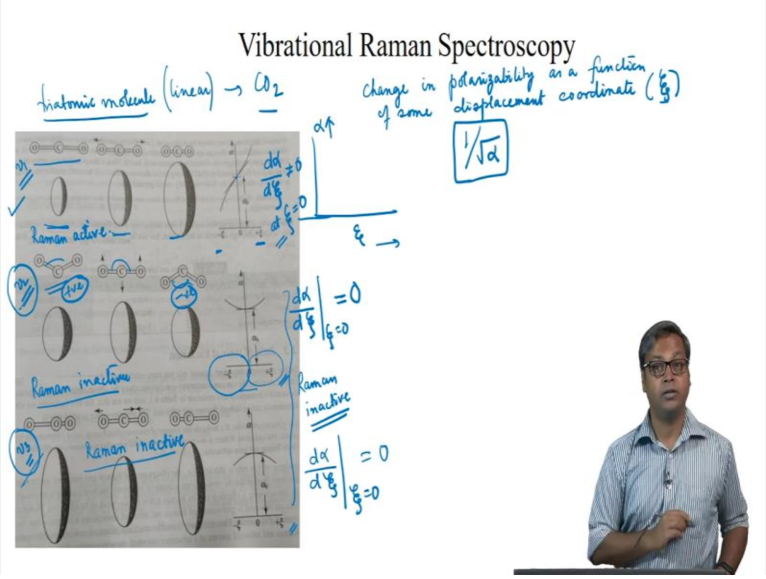

Vibrational Raman Spectroscopy

So now let us consider the triatomic molecule. However we will consider a linear molecule which is carbon dioxide. The extreme and equilibrium configuration of the 3 fundamental modes and their polarizability live soil are shown here. So this is my Mu1, which is asymmetric stitch.

This is Mu2, which is bending and this is Mu3, is asymmetric stretch. So, for the symmetric stretching mode, the molecule changes during the motion.

So there is a corresponding fluctuation in the sides of the ellipsoid making this mode Raman active. But on the other hand the other two modes that is Mu2 and Mu3 are Raman inactive. It might appear that in case of Mu3, or the asymmetric stretch or Mu2, that is bending the molecule changes shape and so does the ellipsoid. But we need to consider this more carefully and to do this let us look into the change in polarizability as a function of some displacement coordinate.

Displacement coordinates, we will represent is displacement co-ordinate by Zi, so for the stretching motion this Zi is a measure of the extension. So, whenever the bond is extended, we have a positive charge and when the bond is compressed then, we will have a negative charge. So, are you are looking into the change in polarizability as a function of Zi, we are plotting here Zi on the x-axis and polarizability that is alpha in the y axis.

For the bending mode the Zi measures the displacement of the bond angle that is the O C O bond angle from the equilibrium value. So the Zi is positive and negative referring to opposite displacement reaction. So, going back to the symmetric stretch of carbon dioxide if the equilibrium value of the polarizability is alpha zero, that means at Zi equal to 0, the value of polarizability is alpha zero then Alpha increases and decreases when the bond stretch and contract respectively.

This is because, as we have discussed in the previous list, the ellipsoid is proportional to 1 by root over Alpha. So, when alpha increases, the ellipsoid become smaller and when Alpha decreases, ellipsoid becomes flatter. So this figure shows the change in the shape of the size of the ellipsoid. And so these plots show the change in Alpha with respect to the displacement of water. So we can see that near the equilibrium for the symmetric stretch, the cart has a distinct slow.

In other words, we can write, d Alpha by d Zi is not equal to 0 at Zi equal to 0.Thus for small displacement, the motion produces a change in polarizability and therefore this Mu1 is Raman

Active. Now we considered the bending motion or Mu2, we can count at downward displacement of the oxygen atoms as negative Zi or this is my negative Zi, or the upward displacement of the oxygen atom as positive chi, this is the case where I have the upward displacement. This is the case of my positive Zi.

So this figure shows the change in polarizability and we can see the change in polarizability is exactly the same for both positive and negative. So, now we can say d alpha d chi is 0 and hence for small displacements, there is effectively no change in the polarizability and the motion is Raman inactive. Same argument applies for this Mu3 or the asymmetric stretch. Here the polarizability decreases for positive and negative displacement co-ordinate. So again, we can write the d Alpha d Zi is 0.

So, for small displacements, there is no change in polarizability and again Mu are symmetric stretching mode of Co2 is Raman inactive.

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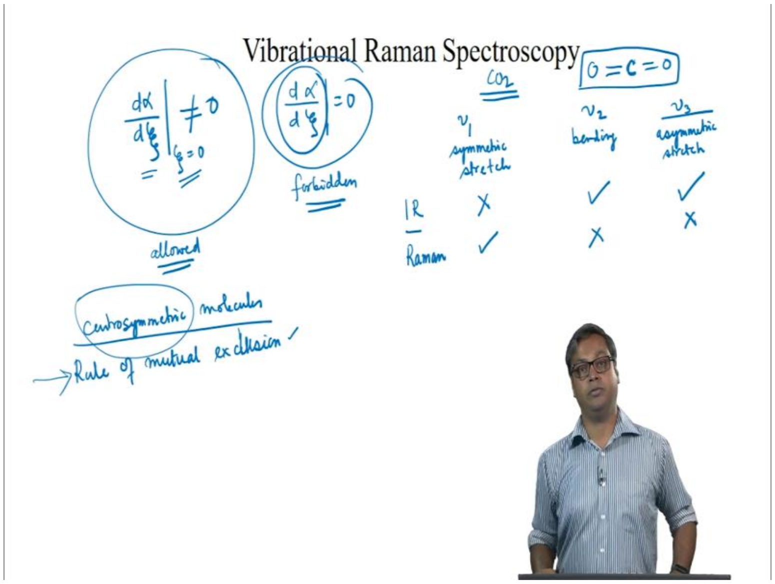

Vibrational Raman Spectroscopy

$$\left.\frac{d\alpha}{d\xi}\right|_{\xi=0} \neq 0$$

allowed

$$\frac{d\alpha}{d\xi} = 0$$

forbidden

$O=C=O$

CO_2

	ν_1 symmetric stretch	ν_2 bending	ν_3 asymmetric stretch
IR	✗	✓	✓
Raman	✓	✗	✗

centrosymmetric molecules

→ Rule of mutual exclusion ✓

So, for a mode to be Raman active in general we need to have d Alpha by d Zi these two be non zero at Zi equal to 0. However, in general, the slope that is the d Alpha d Zi, would have different values at equilibrium position since we have seen that Raman spectrum is forbidden when the d Alpha d Zi is 0 and allowed for d Alpha d Zi not equal 0. So this is my allowed case and this is my forbidden case.

So, we can imagine that the degree of allowedness varies with the value of this slope that is d Alpha d Zi. Thus, if the polarizability of chi has a large slope, the position of Raman slope will be strong and if the slope is small then the Raman line will be at peak. For example, for the symmetric vibrations, these vibrations give rise to Intense Raman lines. On the other hand, the non symmetric ones are usually weak and sometimes and non absorbent in particular of bending motion is generally a very weak Raman line.

So, let us look into the Raman and IR activities of the different modes of CO2. So, for CO2 we have these different modes. We have Mu1, which is symmetry. We have Mu2, the bending mode and Mu3, which is the asymmetric stretch, Mu is symmetric stretch. So now, I have already seen that the IR, Mu1 is IR inactive and Mu2, Mu3 are IR active. And today we have seen in case of Raman spectroscopy, Mu1 is Raman active and Mu2 and Mu 3 are Raman inactive. It can be seen that the modes which are higher active are Raman inactive and vice versa.

That the higher active modes are Raman Active and vice-versa is a general rule valid for all Central symmetric molecules. And we can see this Carbon di oxide, which is O double bond C double bond 0 is a central atom is a central symmetric molecules. This rule is valid that if it is higher active it will be Raman inactive and vice versa. And this rule is the rule of mutual exclusion. So if there is no centre of symmetry, then, most vibrations are both IR and Raman active. So there is, in that case there will be no rule of mutual exclusion.

The Converse of this rule that is the rule of mutual exclusion is also true that is observance of Raman and IR spectrum showing no common line implies that the molecule has a centre of symmetry. However, as just a note of caution, we have already discussed, a vibration maybe Raman active, but too weak to be observed. However, if some vibrations are observed to be coincident with Raman and IR then, it is certain that the molecule has no centre of symmetry.

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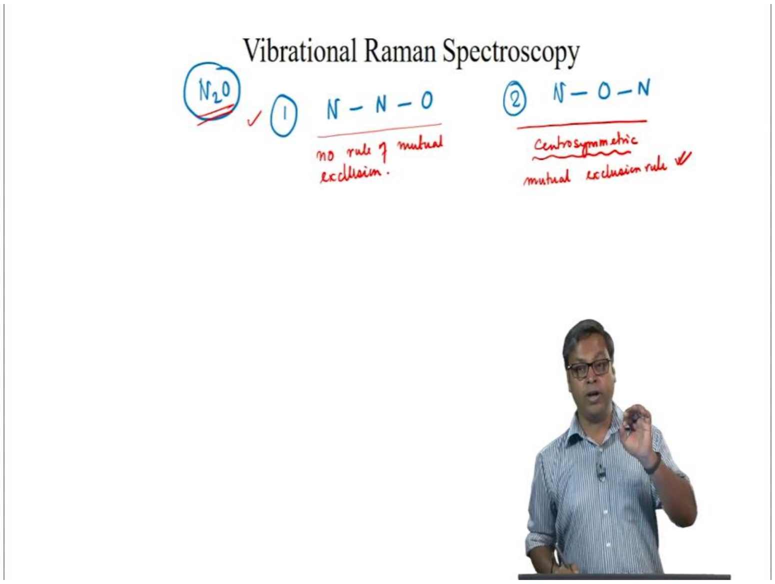

Vibrational Raman Spectroscopy

N_2O

✓ ① N – N – O

no rule of mutual exclusion.

② N – O – N

Centrosymmetric

mutual exclusion rule ✓

So now, let us take one more example little thing about the molecule which is a triatomic molecule that is N2O. And if you do not know the structure we can think that there can be 2 possible structures. In one case I can write the sequence as N-N-O and in the second case, I can write as N-O-N. So, if the structure is one that is N N O and then there is no inversion centre for this linear molecule. Thus, the mutual exclusion principle will not be valid. If the structure is 1 there will be no rule of mutual exclusion so all the modes will be Raman as well as IR.

One the other hand, if the actual structure is N-O-N then, in a linear molecule but it is also a Centro symmetric molecule. We can think that this molecule as something similar to CO2 or carbon dioxide. Thus, it will confirm to mutual exclusion rule. If it is N-O-N, then this mutual exclusion will be N. For all the modes will not be IR and Raman IR. In other words the IR active vibrations will be Raman inactive and the Raman active vibrations will be IR inactive.

So for experiment, it has been found that all the vibrational modes of this molecule into mode are both IR and Raman active and so this result along with the rule of mutual exclusion tells that the structure of N2O is one that is N-N-O and not to that is N-O-N in other words, N-O-N is not central symmetric.