Fundamentals of Spectroscopy

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Lecture-33
Vibration of Polyatomic Molecules 1

Hello everyone welcome to the lecture. So far in all the lectures on vibrational spectroscopy, we have discussed diatomic molecules, we have talked about harmonic oscillator we have discussed and harmonicity and the effects of an harmonicity. In addition, we have looked into the row vibrational spectra of diatomic molecules. However, most of the molecules that we deal with in chemistry or polyatomic, that is, they consist of more than 2 atoms in a diatomic molecule.

We can realize of course, there is only one vibration as there is only one bond in a diatomic molecule, there cannot be more than one vibration. However, this is not the case for polyatomic molecules as we can certainly have more than one mode of vibration. So, we refer to these modes of vibration as normal modes.

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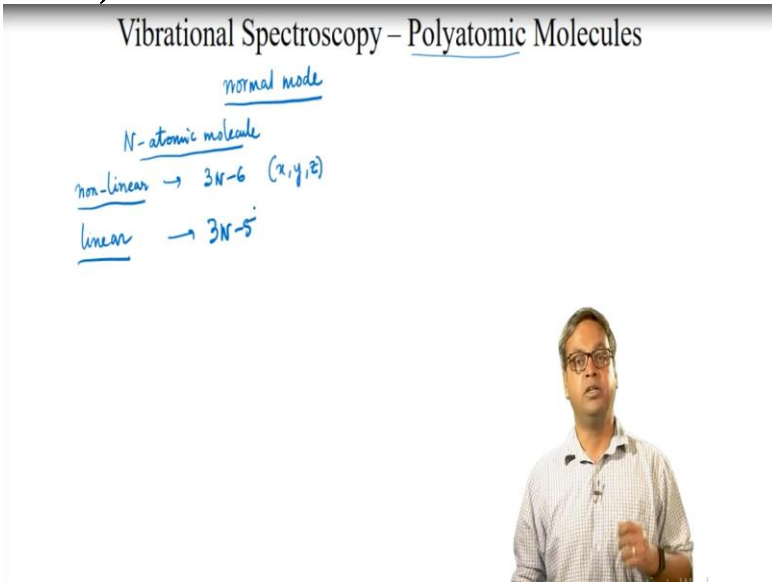

Vibrational Spectroscopy – Polyatomic Molecules

normal mode

N-atomic molecule

non-linear → $3N-6$ (x, y, z)

linear → $3N-5$

So we refer to these modes of vibration as normal modes, because a diatomic molecule has only one mode of vibration, there is a single fundamental band with polyatomic molecules, we can imagine that we can have a fundamental band associated with each mode of vibration, as you mean that all the normal modes are non degenerate and infrared active and in atomic molecule, so, let us start with an N atomic molecule that is a molecule consisting of N atoms has multiple normal modes of vibration.

In general, for an N atomic nonlinear molecule. So, we are now considering a nonlinear N atomic molecule. So, this nonlinear in atomic molecule will have 3 N - 6 normal modes of vibration. This follows from each atom having 3 degrees of freedom because of the need to specify their coordinates. For example, x, y, and z coordinates to define the position of each atom of the total 3 N degrees of freedom for the molecule 3.

The present the translation of the molecule as a whole along the x, y and the z axis, another 3 represent rotation of the molecule about each of these 3 axis. So, the remaining that is 3 N - 6 degrees of freedom, the present motions of the nuclei relative to one another, namely, the vibrations. Now, for linear N atomic molecule, there are 3 N - 5 normal modes of vibration, because there is no degree of freedom corresponding to rotation about the inter nuclear axis.

In other words, there is no moment of inertia about the axis we will talk about degrees of freedom and normal modes in more details later in this lecture. So, the simplest of the polyatomic molecules with more than one bond is a triatomic molecule.

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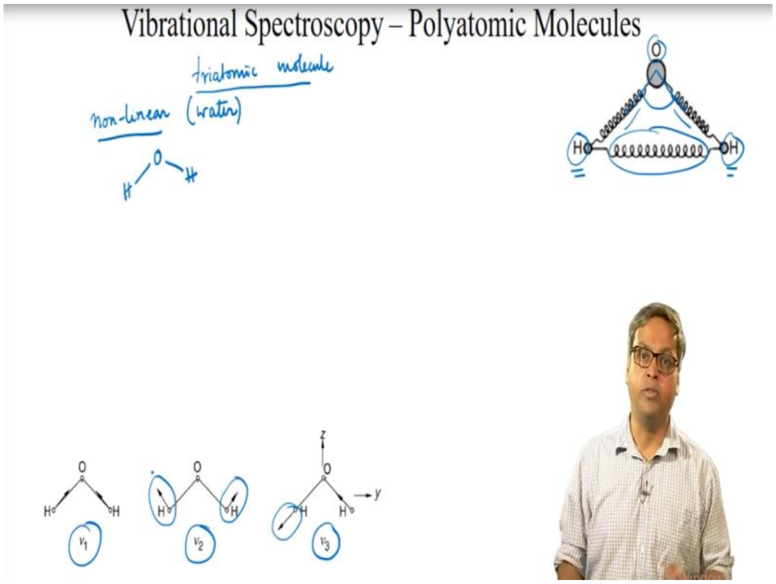

Vibrational Spectroscopy – Polyatomic Molecules

So, let us look into triatomic molecules to start with and see how many fundamental bands are present. So, let us start with a non linear triatomic molecule. So, the nonlinear triatomic molecule which we will look at is water or H 2 O classically we can think of the vibrational motions of a molecule as being those of a set of balls representing the nuclei of various masses connected by Hookes law springs representing the various forces acting between the nuclei.

So, such a model of water is shown here in this figure. So, the stronger forces between the bonded oxygen and the hydrogen nuclei are represented by strong springs, which provide resistance to stretching of the bond or stretching of the OH bonds. The weaker force between the non bonded hydrogen nuclei is represented by a weaker spring which provides resistance to an increase or decrease of the HOH angle.

Even with this simple model, it is clear that if one of the nuclei is given a sudden displacement, it is very likely that the whole molecule will undergo very complicated motion consisting of a mixture of angle bending and bond stretching. This motion can always be broken down into a combination of the so called normal vibrations of the system, which are super imposed in varying proportions.

A normal mode of vibration is one in which all the nuclei undergo harmonic motion, they have the same frequency of oscillation and they move in phase, but generally with different amplitudes. So, examples of such normal modes for water are shown here. So, we have 3 modes, nu 1, nu 2 and nu 3, the arrows attached to the nuclei, the arrows that are marking now, so, these arrows are vectors representing the relative amplitudes and the directions of motion.

The form of the normal vibrations can be obtained from a knowledge of the bond lengths and angles of the bond stretching and angle bending force constants, which are a measure of the strengths of the various springs in the ball and spring model in an approximation, which is analogous to that, which we have used for a diatomic molecule, each of the vibrations of a polyatomic molecule can be regarded as harmonic.

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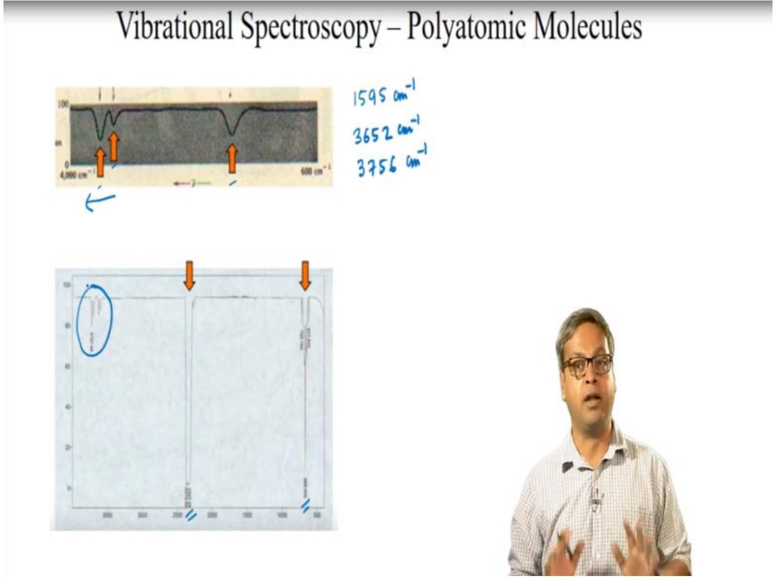

Vibrational Spectroscopy – Polyatomic Molecules

So, going back to water, let us look in the IR spectrum of water. So, in this spectrum as we can see, there are 3 peaks marked by these arrows. So, we have 3 peaks, one peak is that 1595 wave numbers and the 2 other peaks are at higher wave numbers because the wave number is increasing to the left here, and these higher wave number peaks appeared at 3652 wave numbers and 3756 wave numbers.

Now, if we look into carbon dioxide spectrum, we can see 2 peaks. So, the high frequency peaks that we see here are due to the presence of water which we can neglect now. So we can see that despite water and carbon dioxide, having the same number of atoms and bonds, they exhibit different number of peaks.

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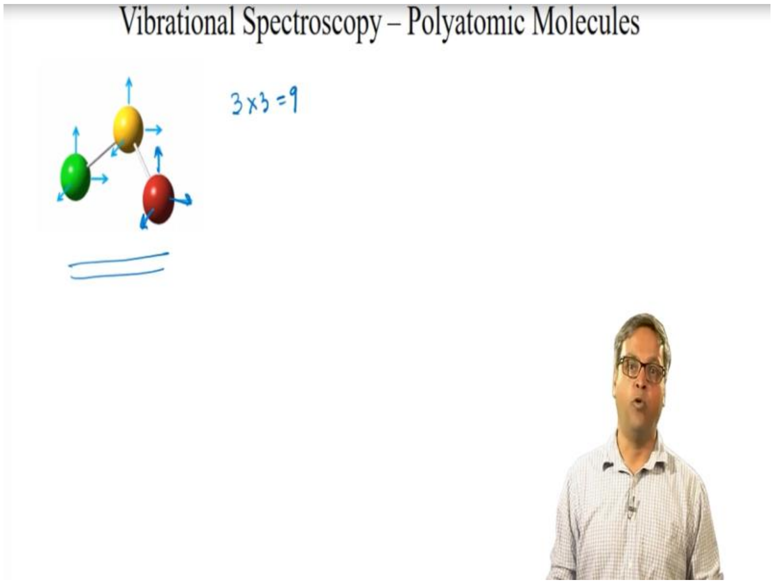

Vibrational Spectroscopy – Polyatomic Molecules

So, we will see later that what determines the number of peaks is not just the number of possible vibrations in the molecule, but also some vibrations are degenerate. That means they are of the same energy and some are intrinsically infrared inactive. So, let us revisit the degrees of freedom and normal modes. Let us look into our triatomic molecule we describe the position of an atom in the molecule with 3 coordinates.

This means, in order to describe the motion of each atom, we also required 3 coordinates we can say that each atom has 3 degrees of freedom. If we had a single atom in the system, then each of these 3 degrees of freedom would be purely translational in nature. If we had a diatomic molecule, then we need 3 times 2 that is 6 coordinates to describe the motion of both atoms and there would be 6 degrees of freedom.

The motion of 3 atoms in a triatomic molecule would require 3 times 3 that is 9 coordinates and there would be 9 degrees of freedom. A polyatomic molecule of N atoms has 3 times N that is, 3N degrees of freedom. When we have more than 1 atom, these degrees of freedom can be written as combination of atomic coordinates that describe translations, vibrations or rotations.

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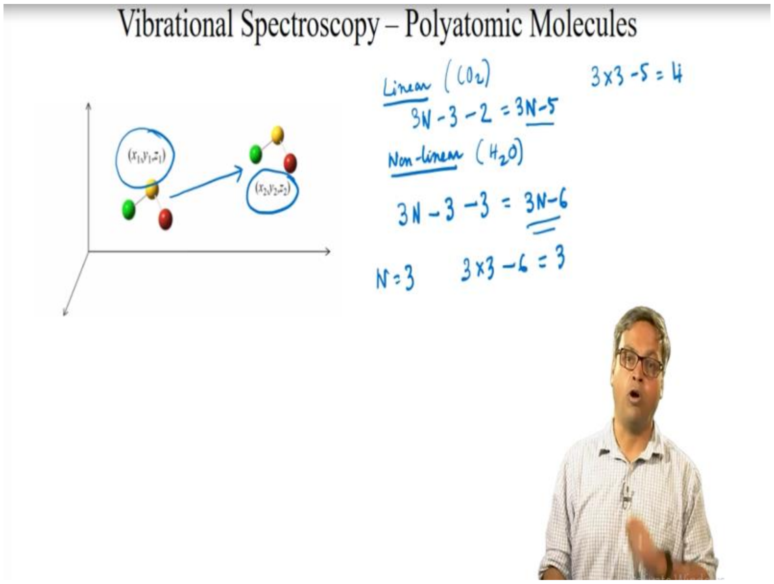

Vibrational Spectroscopy – Polyatomic Molecules

Linear (CO_2)

$3N-3-2=\underline{3N-5}$

$3\times3-5=4$

Non-linear (H_2O)

$3N-3-3=\underline{\underline{3N-6}}$

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

So, first, let us look at translational motion to describe the position of molecule. We need to specify its center of mass. With 3 coordinates, we can describe the translation of a molecule from one position of the center of mass, let us say x 1 y 1 z 1 to another by identifying the change in the 3 coordinates of the center of mass. So let us say after the translation, the new coordinates are x 2 y 2 and z 2. Therefore, every molecule has 3 translational degrees of freedom.

A purely translational motion is one where during the motion, there is no relative change in the internal coordinates of the molecules, that is no rotation, or no vibration takes place. So of the 3N degrees of freedom for polyatomic molecules consisting of n atoms, 3 of these degrees of freedom can be identified as pure translations. To describe the rotation of linear molecules required 2 angular coordinates, we have 2 rotational degrees of freedom.

This enables us to determine the number of vibrations, the number of vibrations is simply the number of degrees of freedom that is 3N minus the number of translational and rotational degrees of freedom. So it will be 3N - 3 because 3 comes from the translational and - 2 for a linear molecule, which comes from rotations. So, we will have 3N - 5 degrees of freedom or 3N - 5 vibrations.

In a nonlinear molecule, we required 3 angular coordinates to describe rotation. We have 2 angles as before, as we had in the linear molecule, but we also need another angle to describe the molecules internal rotation. Therefore, for nonlinear molecules, we have 3 rotational degrees of freedom. So, 3N - 5 was for linear. And now, we are talking about nonlinear molecules. The 3 rotational degrees of freedom means for nonlinear system, number of vibration.

Once again, can simply be the number of total number of degrees of freedom that is 3N minus the number of translational and rotational degrees of freedom. So this will be 3N - 3, 4 translational - 3 for the rotations. So we will have 3N - 6 vibrations. So therefore a nonlinear molecule will have 3N - 6 vibrations. This means that nonlinear systems have one fewer vibrations than linear systems with the same number of atoms.

So let us revisit the 2 triatomics water and carbon dioxide. So water is nonlinear. So water falls in this category that is nonlinear. So it has 3N - 6 vibrations. For water, N = 3. So water should have 3 times 3 – 6 that is 3 vibrational degrees of freedom. The IR spectrum has 3 bands. So, all the bands are IR active and non degenerate carbon dioxide is a linear molecule. So carbon dioxide falls in this category, because carbon dioxide is a linear molecule.

So we expect 3N - 5 vibrations. So this means that carbon dioxide has 3 times 3 - 5, that is 4 vibrational degrees of freedom. However, the IR spectrum of carbon dioxide shows only 2 bands, we need to explain this, but before that, we will formally define what is meant by normal modes of vibration. Any arbitrary set of displacement of atom can they expressed as a superposition of 3N - 6 or 3N - 5 normal modes of vibration. So, the 3N - 6 is for the nonlinear case and 3N - 5 is for the linear case.

A normal mode of vibration is one in which all atoms move in phase with the same frequency also, the center of mass remains fixed, so that there is no core translational motion, the vibrational energy is quantized. The motion is approximately harmonic and each normal mode is independent and unaffected approximately by others. And finally, if molecule starts vibrating in a normal mode, it will continue to do so. It would not transform to another normal mode.

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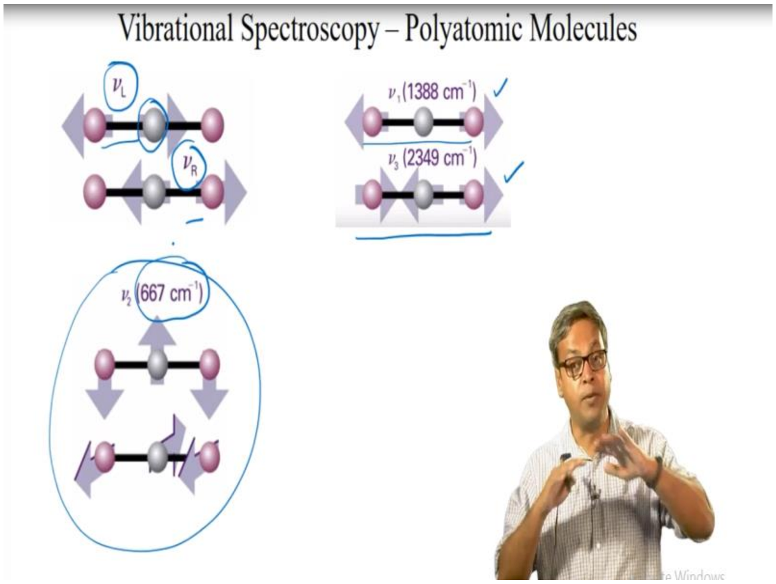

Vibrational Spectroscopy – Polyatomic Molecules

So, let us see, if you understand this in terms of carbon dioxide vibrations involve stretching a bond. So, let us consider the CO bond in carbon dioxide vibrating separately. So, we have a left bond which is shown here and a right bond is shown here. So, we have a left bond vibration a live right bond vibration. However, these bond vibrations are not independent. If we excite the left vibration, then because it involves the motion of the central carbon atom, the right bond will be affected and right vibrations will be excited.

The normal modes of vibration associated with stretching are in fact a linear combination of the left and the right vibrations. If we add the left and right vibrations together in phase, we get the symmetric stretch which is shown here. And if we add the left and right vibrations together out of phase, then we get the asymmetric stretch, which is shown here. So, symmetric stretch is nu 1 and the asymmetric stretch is nu 3.

So, this time exciting, the symmetric stretch does not lead to the excitation of the asymmetric stretch. There are also 2 bending modes which are shown in this figure. So, this bending modes have exactly the same frequency that is 667 wave numbers. These bending modes are thus degenerate, the bending modes are related by symmetry, we can transform one mode into another by rotating about the inter nuclear axis.

The fact that the blending modes are degenerate, explains why one band is missing from the IR spectrum. And why we have 2 bands that mean, another band is missing, we will talk in the next lecture. So, if you excite the fundamental transitions of either bending mode, it occurs at exactly the same energy and so the spectral lines will lie on top of one another. If you superimpose all the modes that means, we simply add all the modes together the nu 1 nu 2 and nu 3. That is exactly what we are expected to see at the molecular level.

It is important that although we discussed the vibrational mode separately, we appreciate that the motion of the atom is described by a linear combination of all the vibrational modes. So, as we have mentioned earlier, each of the vibrations of a polyatomic molecule can be regarded as harmonic quantum mechanical treatment in the harmonic oscillator approximation shows that the energy in wave number associated with each normal mode of vibration. That is I taken that all these normal modes and non degenerate is given by.

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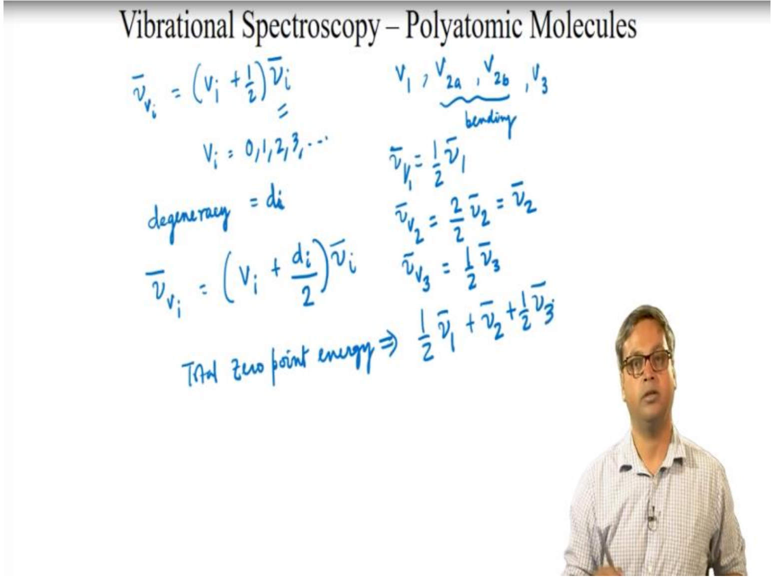

Vibrational Spectroscopy – Polyatomic Molecules

$\bar{\nu}_{v_i} = \left(v_i + \frac{1}{2}\right)\underline{\underline{\bar{\nu}_i}}$

$v_i = 0, 1, 2, 3, \ldots$

degeneracy $= d_i$

$\bar{\nu}_{v_i} = \left(v_i + \frac{d_i}{2}\right)\bar{\nu}_i$

$v_1, \underbrace{v_{2a}, v_{2b}}_{\text{bending}}, v_3$

$\bar{\nu}_{v_1} = \frac{1}{2}\bar{\nu}_1$

$\bar{\nu}_{v_2} = \frac{2}{2}\bar{\nu}_2 = \bar{\nu}_2$

$\bar{\nu}_{v_3} = \frac{1}{2}\bar{\nu}_3$

Total zero point energy $\Rightarrow \frac{1}{2}\bar{\nu}_1 + \bar{\nu}_2 + \frac{1}{2}\bar{\nu}_3$

So, nu bar v i = v i + half times nu bar i. So, here this nu bar i is the classical vibrational wave number and v i is the vibrational quantum number and v i can take values of 0 1 2 3 and so on. So, if the degree of degeneracy so let us say if degeneracy is given by di read where i is a subscript then we can write this nu bar v i = v i + d i divided by 2 times nu bar i. So each normal mode has its own set of vibrational energy levels, each with their own set of vibrational quantum numbers.

In carbon dioxide, there are 4 vibrational quantum numbers given by v 1, then v 2a and v 2b. So these are the bending modes. And we have v 3 and if all these quantum states are 0 we can identify the zero point energies associated with each of these modes, note that the total zero point energy of the molecule will be the sum of the individual zero point energies. So, it is the total zero point energy that molecule will have at 0 Kelvin.

So, that is when v 1 v 2a v 2b and v 3 are all equal to 0. So, if we want to calculate the zero point energies, for the v 1 quantum number, so this v 1 is 0. So, all we have is this nu bar v 1 should be half, nu bar 1. Similarly, because the bending states are degenerate, we can write nu bar v 2 equals the degeneracy is 2. So this is 2 / 2 nu bar 2 that is given by nu bar 2. And the nu bar for v3 is given by half, nu bar 3. So in this case the total zero point energy will be equal to half. Nu bar 1 + nu bar 2 + half nu bar 3.