Fundamentals of Spectroscopy

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Lecture- 36
Normal Mode Coordinates

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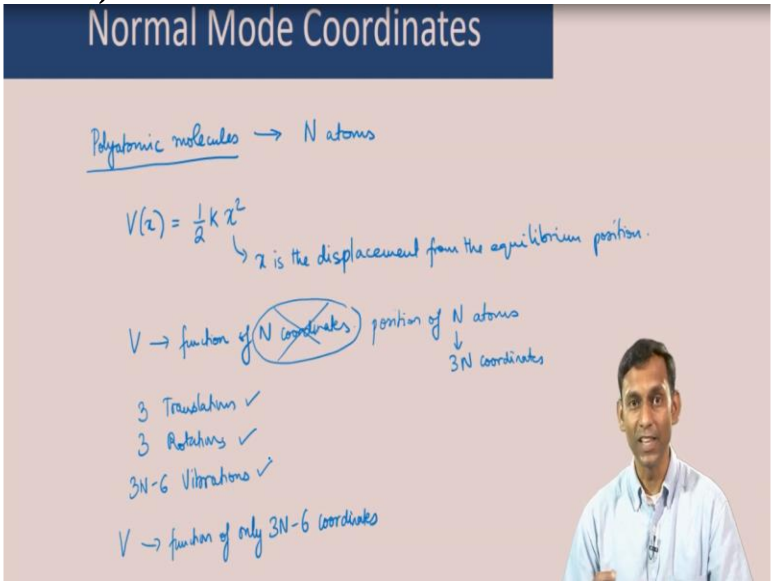

Normal Mode Coordinates

Polyatomic molecules → N atoms

$V(x) = \frac{1}{2} k x^2$

↳ x is the displacement from the equilibrium position.

V → function of (~~N coordinates~~) position of N atoms
↓
3N coordinates

3 Translations ✓
3 Rotations ✓
3N-6 Vibrations ✓

V → function of only 3N-6 coordinates

In this lecture, we will discuss the idea of normal mode coordinates. Normal mode coordinates are important in the context of understanding vibrational spectroscopy of polyatomic molecules. So this is important for polyatomic molecules were, let us say there are N atoms in the molecule in the case of diatomic molecules that is when there are just 2 atoms. We have seen in a previous lecture, that the vibrational motion of the 2 atoms is equivalent to the vibration of a single particle connected with a spring and performing simple harmonic motion.

The particle in that case moves with a potential energy which is quadratic in the distance of the mass displaced from the equilibrium position when the spring is undisplaced. So, the form of the potential energy for simple harmonic motion is V of x is equal to half some constant times x square where x is the displacement from the equilibrium position. Let us now see what happens in the case of polyatomic molecules when there are N atoms.

So, in this case the potential energy in general depends on the position of all N atoms. So, in other words, the potential energy V is a function of N coordinates. You may recall that in the case of a diatomic molecule, we showed that the motion of the 2 atoms can be decomposed into an overall translation of the molecule and additionally, the vibrational motion of a reduced mass. In a similar way, when we come to a polyatomic molecule with N atoms, using mathematics, we can show that the motion of these N atoms in the molecule can be decomposed into 3 motions.

Which are purely associated with the center of mass moving in the x, y and z direction and similarly, 3 other motions which are associated with the molecule overall rotating along the x axis, y axis and z axis. And besides these 6 overall motions, there are 3N - 6 internal motions or vibrational motions. So, 3 translations, 3 rotations and 3N - 6 vibrational motions the potential energy V is therefore, a function of only 3N - 6 coordinates.

Note that I have written that the potential energy is a function of N coordinates, but that should actually be the function of position of N atoms. And since each atom has an x y and z coordinate, this is a function of 3N coordinates. And then we just discussed that out of these 3N coordinates there are 3 translations, 3 rotations, and only 3N - 6, pure internal motions or vibrations. So the potential energy is a function of only the internal motions.

Because if does in overall translation of the molecule or overall rotation of the molecule, the potential energy does not change, or an overall translation can be associated with the kinetic energy, but there is no change in the potential energy. The potential energy changes only when there is relative motion between the atoms of the molecule.

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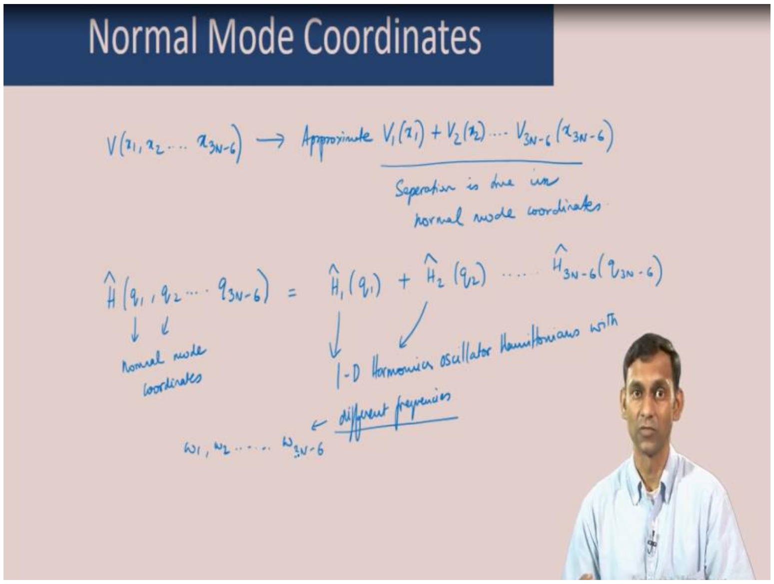

Normal Mode Coordinates

$V(x_1, x_2 \dots x_{3N-6}) \rightarrow$ Approximate $\underline{V_1(x_1) + V_2(x_2) \dots V_{3N-6}(x_{3N-6})}$

Seperation is true in normal mode coordinates

$\hat{H}(q_1, q_2 \dots q_{3N-6}) = \hat{H}_1(q_1) + \hat{H}_2(q_2) \dots \hat{H}_{3N-6}(q_{3N-6})$

normal mode coordinates

1-D Harmonic oscillator Hamiltonians with different frequencies

$\omega_1, \omega_2 \dots \omega_{3N-6}$

The potential energy of N atom molecule, which we have seen is a function of 3N - 6 coordinates can do a very good approximation be written as a sum of 3N - 6 one dimensional potential energies. By this, I mean this is approximately V 1 of only coordinate x 1 + V 2 of only coordinate x 2, and so on V 3N - 6 function of only coordinate x 3N - 6. The important point here is that, although the potential energy is actually a function of 3N - 6 coordinates.

It is approximately a much simpler form, which is just a sum of 3N - 6 one dimensional functions. And this simplification of the potential energy happens in a specific set of coordinates, the specific set of coordinates in which the potential energy separates into this simple form are called the normal mode coordinates. So, this separation is true in normal mode coordinates. Moreover, it can be shown that the total energy of the polyatomic molecule.

The kinetic and the potential energy can be written as a sum of total energies of one dimensional harmonic oscillator. And this can be done when the coordinates used other normal mode coordinates. So, I mean that the Hamiltonian which is a function of let us say q 1 q 2, q 3N - 6 where these q 1 q 2 are the normal mode coordinates. This Hamiltonian becomes a sum of one dimensional Hamiltonians q1, H 1 of q 1, H 2 of q 2, and so on H 3N - 6 of q 3N – 6.

Where each of these Hamiltonians are just one dimensional harmonic oscillator Hamiltonians with different frequencies we can denote these different frequencies by omega 1, omega 2, and so on up to omega 3N - 6, which are associated with the different one dimensional harmonic oscillator. Each of these one dimensional harmonic oscillators, in a normal mode coordinate has a specific frequency associated with it, and a very specific overall motion of all the atoms in the molecule.

The total vibrational motion of the molecule is a combination of these different normal mode motions. So, a normal mode coordinate in general is a combination of motion of all the atoms in the molecule. We will notice that these motions can be associated sometimes with specific motions of a bond or specific bending of an angle and these are used to name or given nomenclature to the normal modes.

Let us look at this with some examples, which will help us concretize the idea of normal modes in the case of polyatomic molecules. Let us start looking at some example of normal mode coordinates. And let us begin with a very simple example, which is of the triatomic molecule water.

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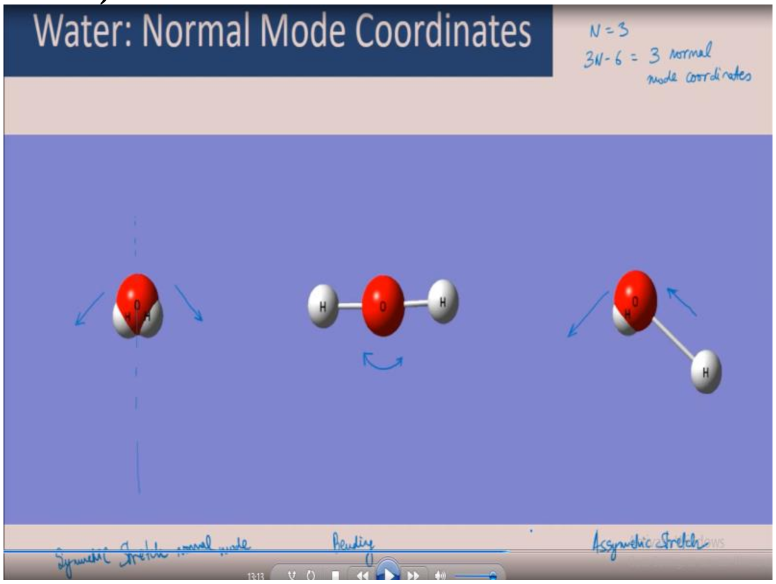

Water: Normal Mode Coordinates

$N = 3$

$3N - 6 = 3$ normal mode coordinates

Symmetric Stretch normal mode

Bending

Assymetric Stretch

So, this molecule has 3 atoms. So, N = 3 and there are 3N - 6 that is equal to 3 normal mode coordinates. We will look at how these 3 normal modes actually look like in the case of the water molecule. So, the first normal mode is what you see here. And you notice that the motion is primarily a stretch of the OH bond. So, the vibration is essentially the OH stretching and this vibration is symmetric about this axis.

So the C 2 V symmetry of the water continues to remain during the vibration. And you see that the primary motion is the OH stretch like this. But you also notice that as the OH stretches and goes down, as the H goes down, the oxygen moves up. And this is because the center of mass does not move during the vibration. This normal mode is called the symmetric stretch normal mode of water.

Let us look at another normal mode of water. And that looks like this. And here you notice that the primary motion is a bending of the HOH molecule. In other words, this angle HOH keeps on changing. And again, you will notice that as the hydrogen moves up, the oxygen begins to move down to conserve the center of mass. This motion is the bending motion. And it is a symmetric bend because the C 2 V symmetry of the water molecule continues to be conserved as the molecule bends in this fashion.

The third normal mode of water can be seen here. And here you notice that the motion can be classified as primarily a stretch. So here the hydrogen and oxygen bond in one case is increasing. And when that is happening, the other one is decreasing. And the oxygen is moving in such a way that the center of mass is again conserved. Now, this motion does not conserve the symmetry of the water molecule.

It is a stretching motion, which does not conserve the symmetry. And so this is called an asymmetric stretch normal mode of the water. So this is a asymmetric stretch. So the points to note are that the normal mode coordinates involve the motion of all the atoms and the atoms move in such a way that the center of mass does not move, and there is no overall rotation and in these various, specific coordinates the overall Hamiltonian of the molecule.

And in particular the Hamiltonian associated with the internal motion of the atoms of the molecule separate into one dimension harmonic oscillator Hamiltonians each of these one dimensional harmonic oscillator Hamiltonians are functions of the normal mode coordinates and overall motion of the molecule in this case of water can be decomposed into a sum of these 3 motions. And therefore, the water molecule will absorb radiation which will excite these 3 motions.

And because the vibrational levels are quantized the frequency of absorption will correspond to the frequency of motion corresponding to these 3 normal mode motions. Another thing to note is that the frequency of these motions is, in principle all different although they might appear the same in this animation that is simply because it has been animated that way. But the frequency of motion of the stretches are actually higher typically then of the bends.

So in this particular case of the water molecule, the symmetric stretch has a frequency of about 3700 wave numbers. And the asymmetric stretch also has a frequency of about 3700 wave numbers. The asymmetric stretch typically has a little higher frequency than the symmetric stretch, but I have just given you an approximate idea of what the frequency is here. The bend has a much lower frequency and is of the order of 1600 wave numbers.

This is indicative of the fact that the bend is a floppier motion associated with a spring which has a smaller spring constant and therefore, also a smaller frequency. Let us now look at one specific normal mode of a more complicated molecule. And in particular, we will look at a few carbonyl molecules, which are different, but the common thing in all of them is they all have a carbonyl or a CO bond. Each of these molecules as we have discussed has 3N - 6 normal mode coordinates and out of these 3N - 6 coordinates, there is one coordinate in which the carbonyl motion is the most significant motion of all the other motions.

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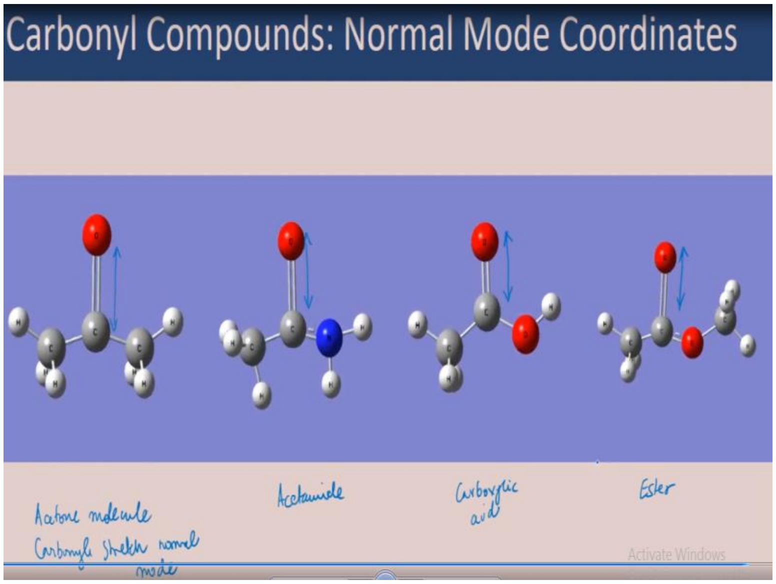

Carbonyl Compounds: Normal Mode Coordinates

So, let us look at that and this particular normal mode, we call as the carbonyl stretch normal mode. So, what we see here is the acetone molecule. And although all the atoms are moving in this normal mode coordinate, the most important or the most significant or the most prominent motion is that of the carbonyl stretch, which is the CO bond stretching and then contracting accompanying that is of course, motion of the other atoms the carbon and the hydrogen.

But primarily this is the CO stretch and that is why this normal mode is referred to as the carbonyl stretch normal mode. This normal mode associated with carbonyl stretching has a typical frequency it is around 16 to 1700 wave numbers. Now the point is that if we look at another carbonyl molecule other than acetone, so let us do that. And here we have acetamide which is amide with a carbonyl and a CN bond.

And now you see that this is also the carbonyl stretch normal mode. But here the normal mode is not quite the same as the acetone normal mode. The similarity is that most significant motion is still the carbonyl stretch. But the difference between the normal modes in these 2 molecules is that apart from the carbonyl stretch, there are different atoms which are moving to different extents. So acetamide carbon carbonyl stretch is different from the acetone carbonyl Stretch.

The frequencies associated with these are about similar, but clearly the normal mode is not just the carbonyl stretch and that is important points that although we refer to this as the carbonyl stretch normal mode, there are other motions also involved. And that depends very much on the exact molecule in question. So, if we look at another example, and here we look at an acid there you have a CO carbonyl bond and a COH.

So, this is a carboxylic acid. The carbonyl stretch is again the predominant motion in this particular normal mode. But then there are other motions also. And that constitutes the carbonyl stretch normal mode in this molecule. And if you take yet another angle Example, where we have an ester there again you have the carbonyl stretch as the major motion, which helps us call this normal mode as carbon stretch. But there are other motions also.

So to summarize, the normal mode coordinates are very specific coordinates. They involve the motion of all atoms of the molecule. And they are special because in those coordinates, the Hamiltonian of the molecule or the Hamiltonian associated with the internal motion of the atoms of the molecules separate into a sum of one dimensional harmonic oscillators. So, the Hamiltonian which is a function of 3N - 6 coordinates becomes a sum of 3N - 6 one dimensional harmonic oscillator Hamiltonians.

That helps us Simplify the solution of this problem quantum mechanically. But moreover, it also helps us interpret vibration spectra. Because the frequencies associated with excitation are the frequencies of these different 3N - 6 oscillators, written in the normal mode coordinates. The signatures of the harmonic oscillator frequencies are what we see in a vibrational spectrum of a polyatomic molecule.