Chemistry II: Introduction to Molecular Spectroscopy

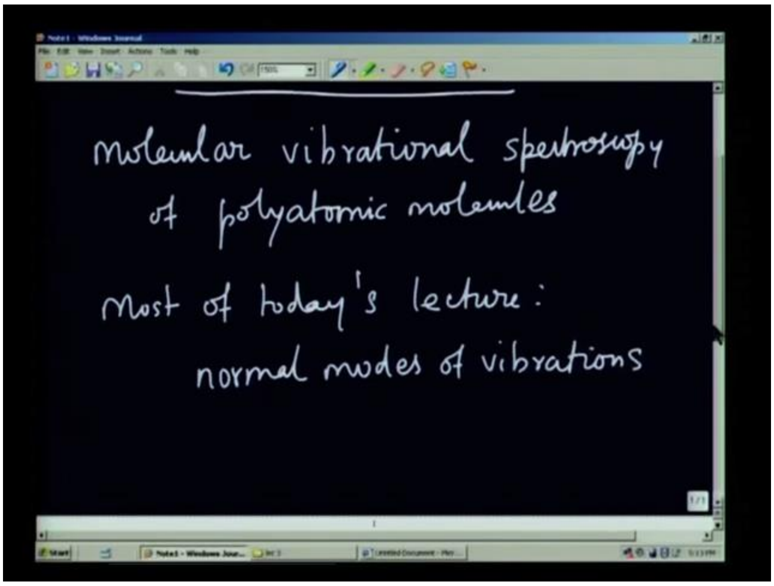
Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture – 12

Normal Vibrational Modes Triatomic Molecules

Today's lecture continues on the spectroscopy module that I have been giving for the last few lectures today we will talk about the polyatomic molecular vibrational spectroscopy fairly elementary and we will show a large number of animations on the vibrational motions as perceived by the spectroscopies. Let me recollect a bit of the diatomic molecular spectroscopy that we did in the last lecture. Let us start today this is lecture 6 on Spectroscopy Molecular.

(Refer Slide Time: 01:13)

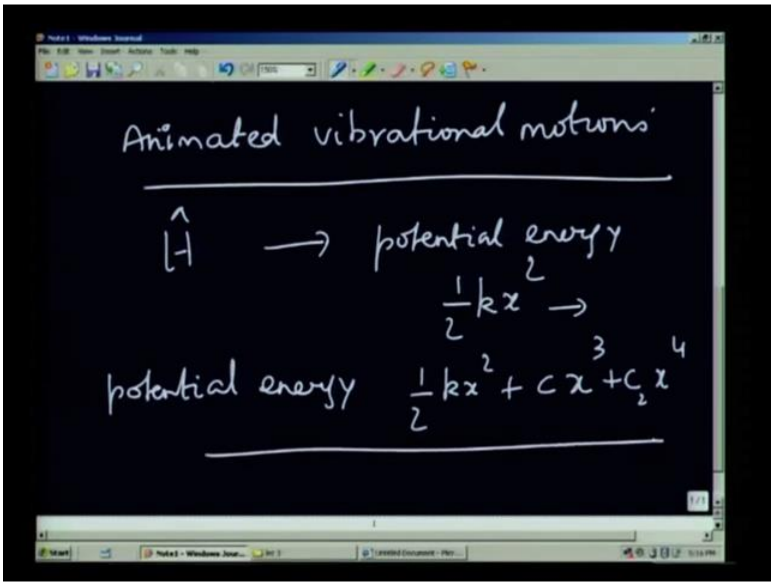


Molecular vibrational spectroscopy
of polyatomic molecules

Most of today's lecture:
normal modes of vibrations

And we want to talk about the molecular vibrational spectroscopy of polyatomic molecules linear or non-linear there is going to be slight difference and what we will be concern for most of today's lecture is on normal modes of vibration this is the theme of today's lecture vibrations.

(Refer Slide Time: 01:52)



Animated vibrational motions

$\hat{H} \longrightarrow$ potential energy

$\frac{1}{2}kx^2 \longrightarrow$

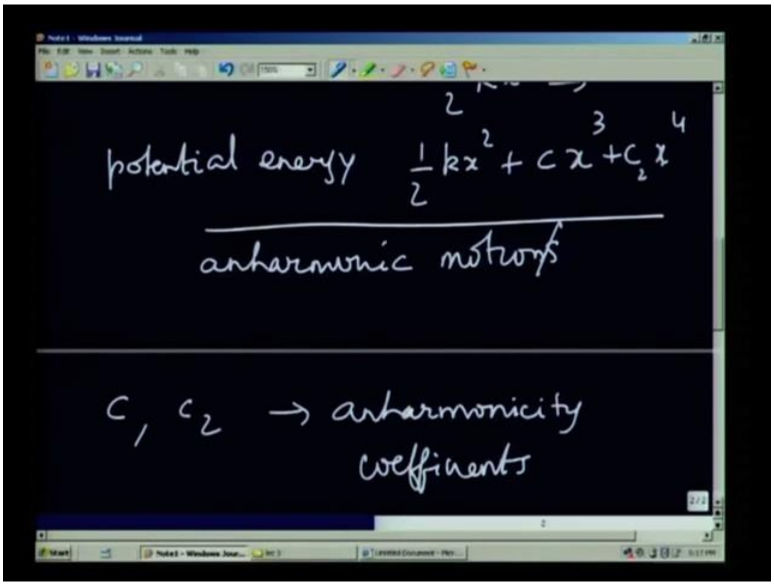
potential energy $\frac{1}{2}kx^2 + cx^3 + c_2x^4$

And I shall use a program to show some of the animated vibrational motions. Let me recollect the essential points of last lecture remember that when we discuss the diatomic molecular spectrum vibrational spectrum we started off with the simple harmonic oscillator model.

It is a very useful model and nevertheless it has, it is difficulties and it is not applicable for molecules when they are in an excited energy state or when they are heated up to 5 temperatures and so on. The reason being that molecular motions under the assumption of the harmonic oscillator approximation the motion is restricted to small amplitude vibrations now, think about the cases of simple molecules which have very strong bond no problem with such cases like hydrogen chloride carbon monoxide these are examples that I have given several diatomic molecules practically any hetronuclear atomic molecule that you talk about I also told you that homonuclear diatomic molecule do not show infrared spectrum because there is a no change in the dipole moment of the molecule as they vibrate.

The hetronuclear diatomic molecules which have a strong bond it is very appropriate for us to consider the first few excited energy states as confirming to the simple harmonic oscillator model. And when this model is not really applicable we also looked at the alternatives by allowing in our own theory the consideration of unharmonic motion recall me harmonic motion was half KX square in the Hamiltonian the potential energy being half KX square where K is the force constant of the diatomic molecule was the harmonic approximation and when we change the or when we include in the potential energy of the molecule terms like half KX square plus some constant times X cube plus some other constant times X raise to 4 and so on.

(Refer Slide Time: 04:40)



potential energy $\frac{1}{2}kx^2 + cx^3 + c_2x^4$

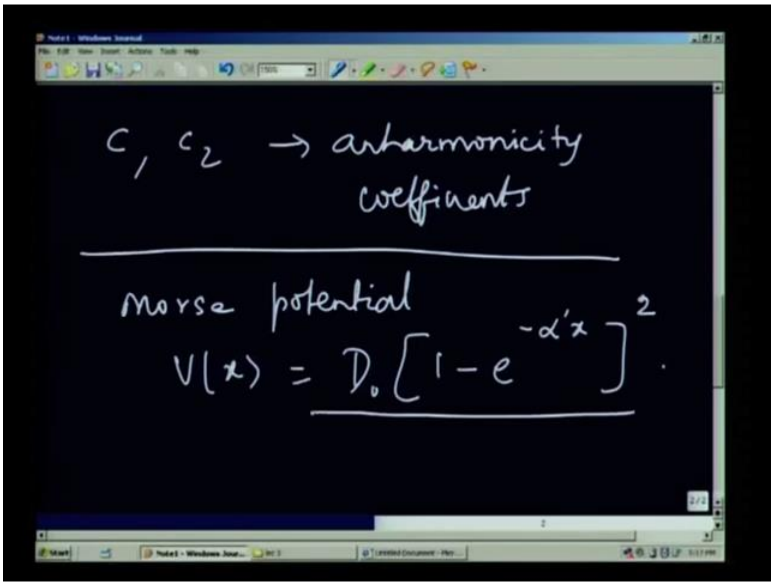
anharmonic motions

$c, c_2 \to$ anharmonicity coeffinents

These permit us to study the molecular motion as unharmonic and the coefficients unharmonic motion the coefficient CAC2 etcetera. Harmonic motion the CC2 etcetera they are called anharmonicity coefficient.

Specifically, we motion see the coefficient C corresponding to the X cube term is called the cubic anharmonicity the coefficient C2 corresponding to X raise to 4 is called quartic anharmonicity and so on.

(Refer Slide Time: 05:27)



$c_1, c_2 \rightarrow$ anharmonicity coeffients

Morse potential

$$V(x) = \underline{D_0\left[1 - e^{-\alpha' x}\right]^2}.$$

We also looked at a general potential in which all this anharmonicity coefficients are included and this potential that we looked was known as the Morse potential. The potential energy for that is given by some constant D naught into 1 minus E to the minus alpha prime X whole square the used to this formula and we looked at the anharmonic vibrational energy levels and so on this is for the diatomic molecule.

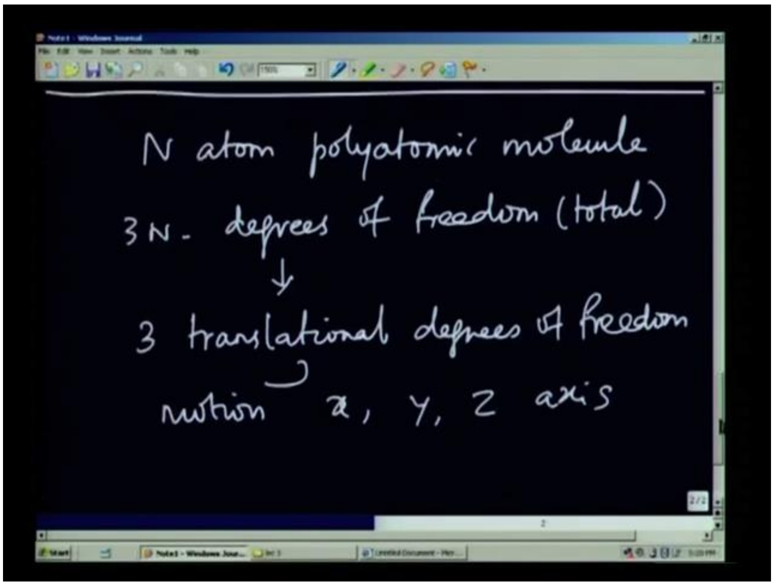
Now, today's lecture is to worry about the polyatomic molecules where there are more than obviously, 2 atoms and there is a very simple formula for determining the number of the vibrational modes in the polyatomic molecule this is a very easy method to think about it you can imagine that there are N atoms in a polyatomic molecules each of the atom is free to moving any one of the 3 dimensions the total degrees of freedom that the polyatomic molecule has is three M.

But you know that the atoms cannot move in entirely freely of each other they are constrained because they are bonded to each other therefore, out of the 3 N degrees of freedom if we remove the constrained motion two types of constraint, constraint corresponding to the overall translational of the molecule that is all the atoms move in the same direction at the same time then it is a concerted motion and it is a translational of the center of mass the molecule that is one way to look at it and there are 3 translational degrees of freedom corresponding to the 3, mutually perpendicular directions in a 3 dimensional world in which we live.

There is also the motion about 2 or 3 mutually perpendicular axes that pass through the molecule and these axes are known as the principle moments of inertia principle axes of inertia and the moments of inertia calculated about these 3 principle axes of 2 depending on whether the molecule is non-linear or linear.

A simple diatomic vibrational the diatomic molecule has only one degree of rotational sorry has 2 rotational degrees of freedom, so considering these for a 3N degree of freedom.

(Refer Slide Time: 07:53)



N atom polyatomic molecule

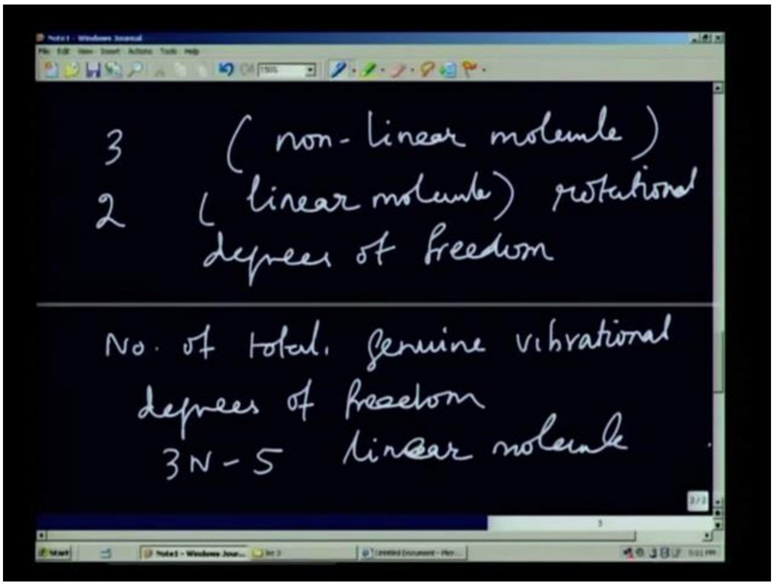
3N - degrees of freedom (total)

3 translational degrees of freedom

motion x, y, z axis

In N atom polyatomic molecule or 3N degrees of freedom totally total you can remove 3 translational degrees of freedom corresponding to the motion about the three different mutually perpendicular axes mutually we denote them XYZ axes.

(Refer Slide Time: 08:33)



3 (non-linear molecule)

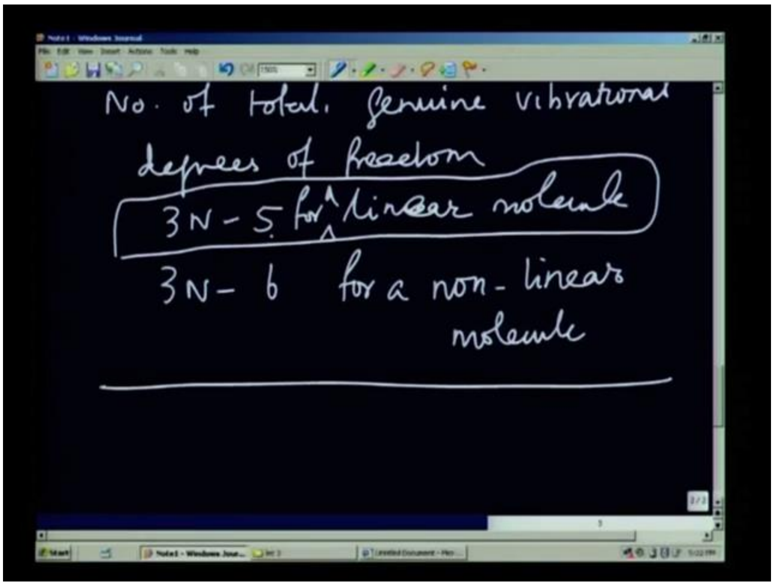
2 (linear molecule) rotational degrees of freedom

No. of total. genuine vibrational degrees of freedom

3N - 5 linear molecule

And then there are 3 for a non-linear molecule or 2 for linear molecule rotational degrees of freedom. Therefore, the number of vibrational degrees of freedom in a polyatomic molecule, number of total genuine vibrational degrees of freedom - vibrational degrees of freedom is 3N minus 5 for a linear molecule and 3N minus 6 for a non-linear molecule for a linear molecule and for a non-linear molecule. Now diatomic molecule comes under the category of a linear molecule obviously.

(Refer Slide Time: 09:32)



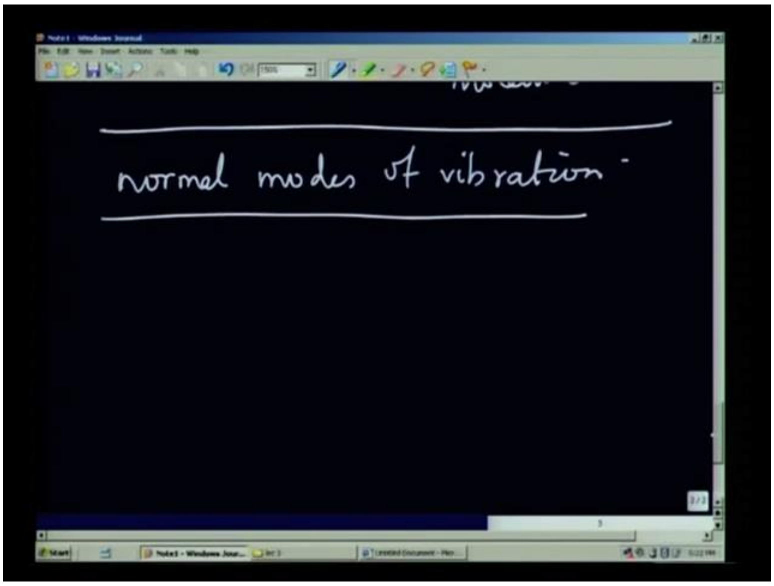
No. of total. genuine vibrational degrees of freedom

$\boxed{\text{3N - 5 for a linear molecule}}$

3N - 6 for a non-linear molecule

And when N is 2 there is only one vibrational degrees of freedom, 3N minus 5 and that is, what we went through in the previous lecture on the harmonic and the unharmonic motions of a diatomic molecule.

(Refer Slide Time: 10:16)



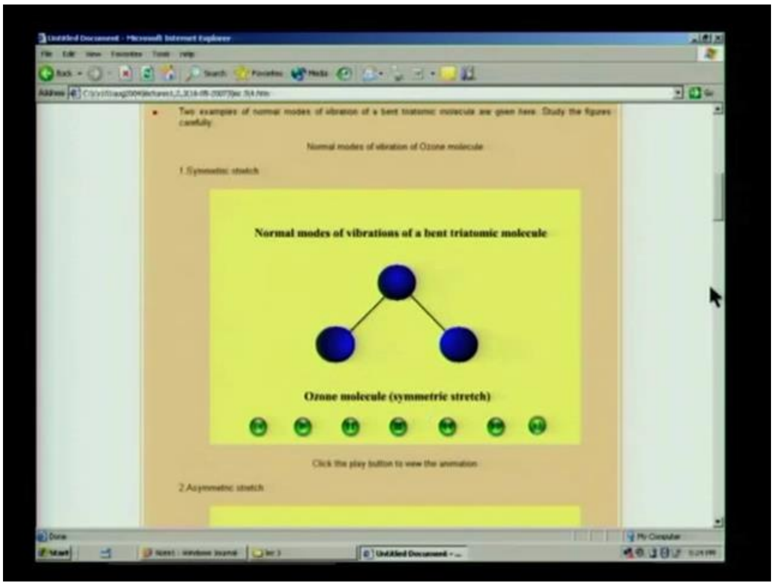
normal modes of vibration -

Today when we talk about the polyatomic molecule the 3N minus 6 degrees of freedom will be described in the form of normal modes of vibration. Let me illustrate the normal modes by some pictures and then we will explain what these things are and how do we understand them qualitatively it is not possible for me to give you a quantitative description of the normal modes requires a little bit of mathematics and some basic familiarities with classical mechanics I do not want to do that here.

But I would like you to appreciate that the qualitative picture of how we visualize the normal modes of vibration as we see in the animations today. Please understand that within the approximations of harmonic motion this is a very useful and is a very accurate picture of the molecular motion, we will also look at what are called group vibrational modes or vibrations of groups of functional groups or certain sections of the molecules relative to the other known as the local modes of vibration.

Again qualitatively I will illustrate this through the spectra that you must be familiar with when you look at the vibrational spectrum of polyatomic molecules. So, today's lecture is qualitative and will contain a large number of animations about we will try and visualize at least about 5 to 10 different molecules small to large and let us look at examine what are called the normal vibrational degrees of freedom.

(Refer Slide Time: 11:56)



- Two examples of normal modes of vibration of a bent triatomic molecule are given here. Study the figures carefully

Normal modes of vibration of Ozone molecule

1.Symmetric stretch

Normal modes of vibrations of a bent triatomic molecule

Ozone molecule (symmetric stretch)

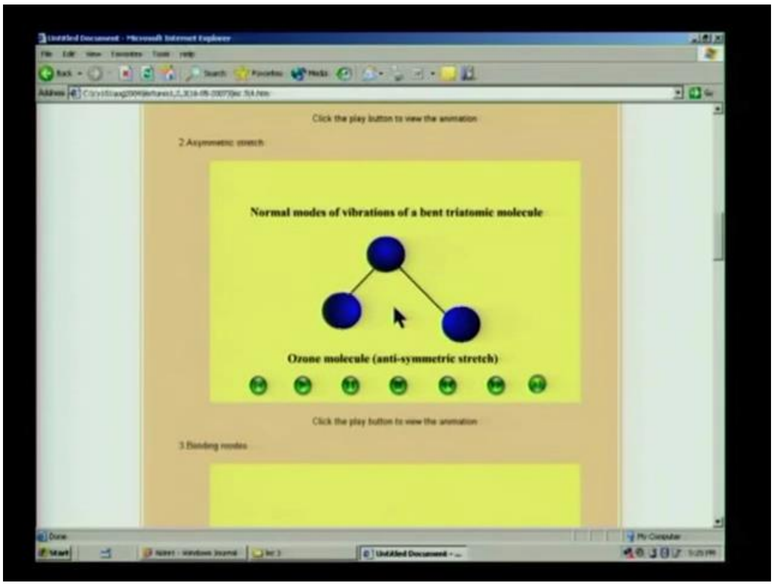
Click the play button to view the animation

2.Asymmetric stretch

Let us first start with the simple triatomic molecule we will play the animation for the O zone molecule there are 3 vibrational modes this is one of the 3 normal modes O zone is non-linear it is triatomic bent and therefore, what you have is the symmetric stretch you see that both the bonds are stretched equally about the equilibrium both the O O and the other O O bond this motion is known as the symmetric stretch.

If you look at the vibrations carefully you see that the molecule does not translate it does not see into rotate, but the center of mass remains where it is white in the middle a genuine vibration normal mode of vibration is one in which the center of mass does not move and the atoms are displaced relative to each other in a certain fashion.

(Refer Slide Time: 12:58)



Click the play button to view the animation

2 Asymmetric stretch

Normal modes of vibrations of a bent triatomic molecule

Ozone molecule (anti-symmetric stretch)

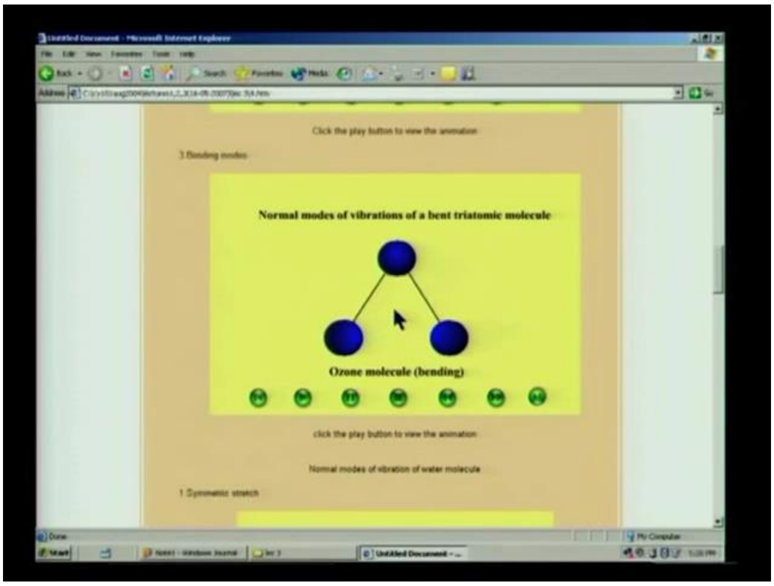
Click the play button to view the animation

3 Bending modes

Symmetric stretch is one of the 3 normal modes let us look at the other normal mode this is anti symmetric stretch you see that one bond is lengthened while the other is shortened.

Therefore, in this mode like the previous mode of course, this is spite being O zone that the atoms are identical, but you see that the bonds are this oxygen is different from this oxygen this is the other normal mode in which the vibrations are stretched the bonds are stretched due to the vibration unsymmetrically it is called anti symmetric stretch.

(Refer Slide Time: 13:38)



Click the play button to view the animation

3 Bending modes

Normal modes of vibrations of a bent triatomic molecule

Ozone molecule (bending)

click the play button to view the animation

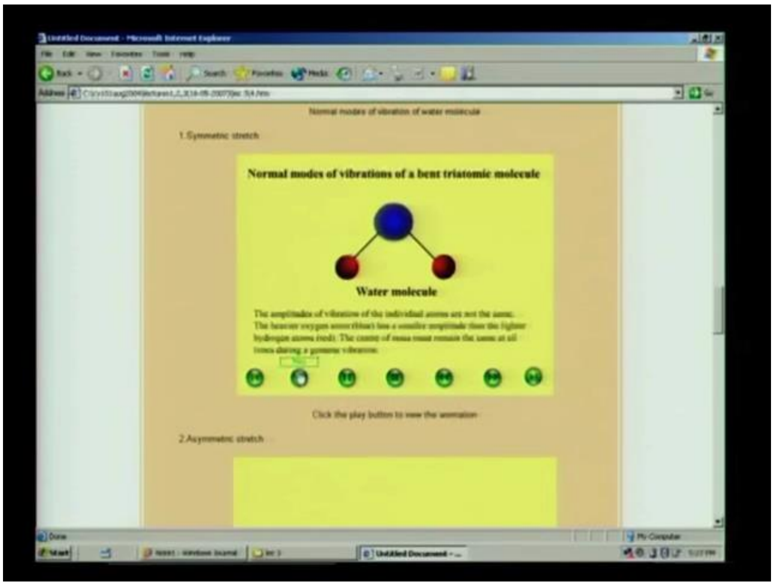
Normal modes of vibration of water molecule

1 Symmetric stretch

The third vibrational mode is a bending mode again center of mass will not move what you see that is that the molecular the bond angle between O O O the bond angle is shortened and back to normal and so on, an oscillation about the equilibrium bond angle this is called the bending vibrational mode of a triatomic molecule.

Here, this is O zone all the 3 molecules are identical and therefore, one thing that you must note in all these 3 pictures is that from with respect to the center of mass each atom is displaced by the same extent that is, if you think about the amplitude of vibration of each atom from it is equilibrium position. If one atoms moves away by a little bit identical atoms also move by the same distance the amplitudes of vibrations are all the same and the frequency of all these vibrations for a given motion all the atoms vibrate with the same frequency here, the atoms being the same all of them vibrate with same amplitude and this is an example of a normal mode.

(Refer Slide Time: 15:04)



Normal modes of vibration of water molecule

1. Symmetric stretch

Normal modes of vibrations of a bent triatomic molecule

Water molecule

Click the play button to view the animation

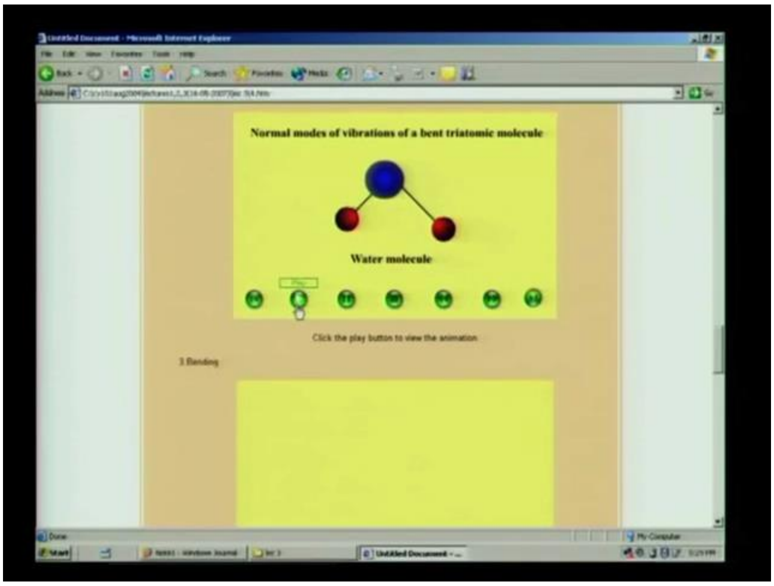
2. Asymmetric stretch

In the case of O zone there are 3 normal modes let us look at the example of water let me stop the motion for the time being. So, water with 2 hydrogen atoms lighter atoms and heavier atoms the center of mass somewhere closer to the somewhat closer to the oxygen atom here brighten the middle where the, it bisects it is on the line which bisects the bond OH.

It quite here and the center of mass will not move, but you must see even if the picture is not entirely clear if the animation is not entirely clear you must see that the oxygen atom moves a little less than the 2 hydrogen atoms. These are lighter and the amplitudes of vibration of these atoms are different and they are inversely proportional to the square root of the masses. See the oxygen atoms moves a lot less than the 2 hydrogen atoms text what here says that is the amplitudes of vibration of the individual atoms are not the same the heavier oxygen atom has smaller amplitude than the lighter hydrogen atoms.

But what is important that the center of mass of molecule should not move during the genuine vibration this is the again this is the symmetric stretch since both the bonds are stretched equally.

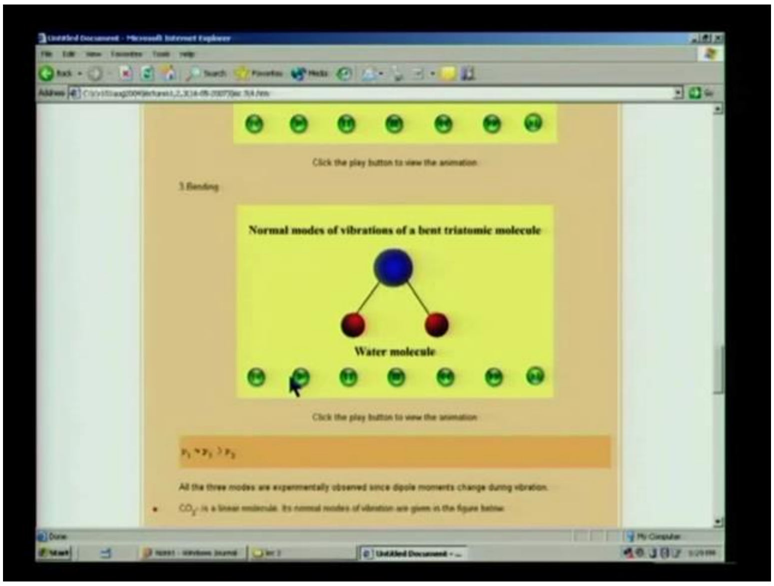
(Refer Slide Time: 16:22)



Click the play button to view the animation

And this is an example of the anti symmetric stretch for the water molecule where one bond is shortens while the other is lengthen and third is of course, the bending motion of the water molecule.

(Refer Slide Time: 16:34)



Click the play button to view the animation

3 Bending

Normal modes of vibrations of a bent triatomic molecule

Water molecule

Click the play button to view the animation

$\nu_1 \sim \nu_3 > \nu_2$

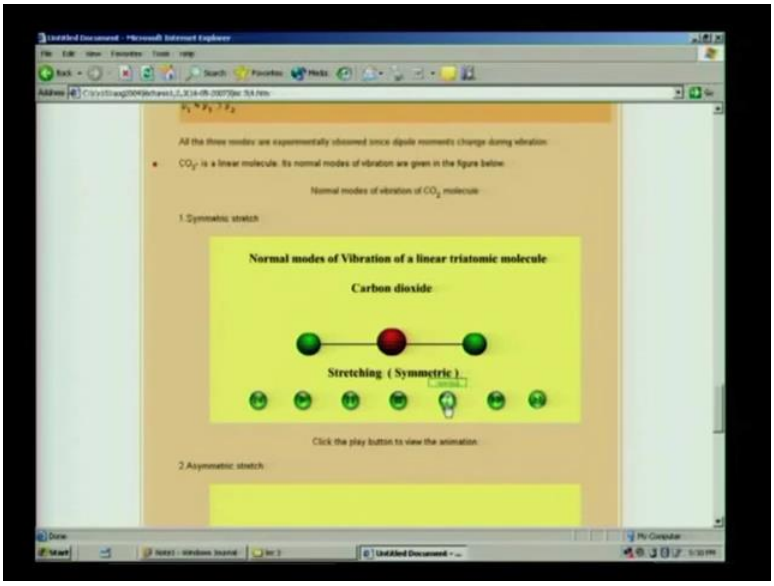
All the three modes are experimentally observed since dipole moments change during vibration

- CO_2 is a linear molecule. Its normal modes of vibration are given in the figure below

With respect to this the bond angle changing during this motion and then coming back to equilibrium and so on. So, this is these are 3 different modes of the water molecular vibrations this is for non-linear molecule bent triatomic. Now we there will be lots of illustrations for many other polyatomic molecules during this lecture.

But let us think about a linear molecule again as a slight variation from this the normal modes of vibration for a simple linear molecule like carbon dioxide all of us are familiar with that, that it is a linear structure with the C O O C O bond angle being 180 degrees.

(Refer Slide Time: 17:30)



$\nu_1 \sim \nu_3 > \nu_2$

All the three modes are experimentally observed since dipole moments change during vibration

- CO_2 is a linear molecule. Its normal modes of vibration are given in the figure below

Normal modes of vibration of CO_2 molecule

1 Symmetric stretch

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

Stretching (Symmetric)

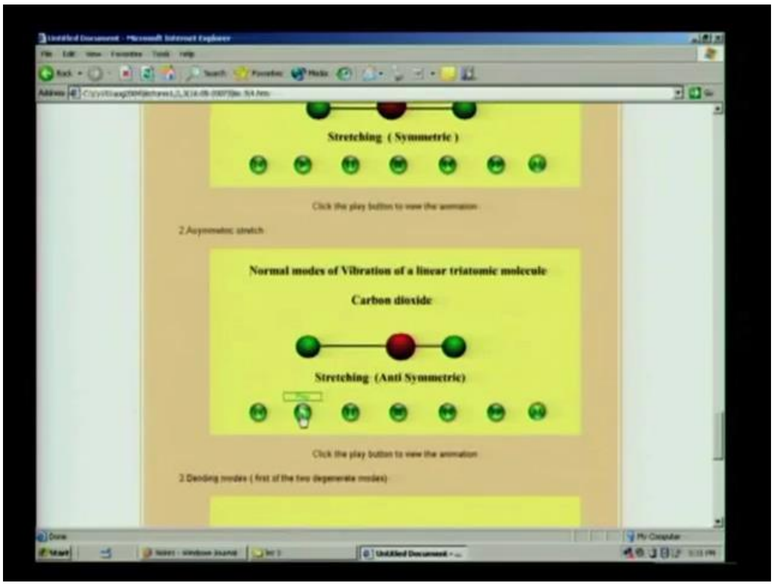
Click the play button to view the animation

2 Asymmetric stretch

Let us look at what the vibration modes are like the normal modes are like let me stop that the no we will go back to that is a fully stretched motion and then what you have is the equilibrium bond length. So, the vibration about the equilibrium position with both the oxygen atoms being stretched with respect to the carbon by equal amounts notice that, the during any stage of this vibration there is no dipole moment created that is carbon dioxide in equilibrium has 0 dipole moment.

Because the dipole vector this direction and the dipole vector are in this direction cancel each other, but in this symmetric stretch cancel each other, but in this symmetric stretching since both the bonds are extended by the same amount that any instant of time there is no dipole moment for this molecule and therefore, there is no change in the dipole moment as well from it is initial value of 0. This mode is not detectable by the infrared spectrum technique infrared spectroscopy cannot detect this mode because there is no change in the dipole moment of the molecule it remains 0 all the time this is a symmetric stretch.

(Refer Slide Time: 18:50)



Stretching (Symmetric)

Click the play button to view the animation

2.Asymmetric stretch

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

Stretching (Anti Symmetric)

Click the play button to view the animation

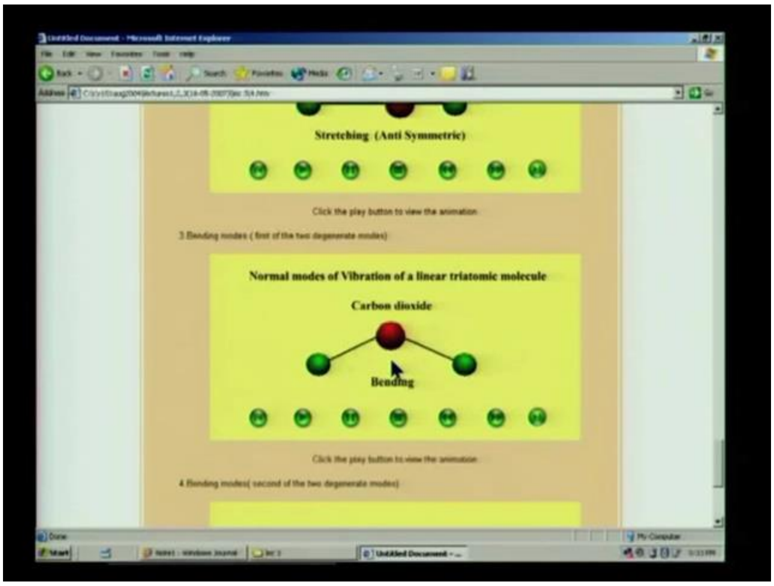
3 Bending modes (first of the two degenerate modes)

Let us look at the symmetric stretch again the molecule should not move from it is equilibrium position the center mass remains where it is the stretches such that one of the carbon oxygen bond is stretch while the other carbon oxygen bond is shortened such that the center of mass remains where the white where carbon was in equilibrium position.

And in this position you see that the stretch due to this thus not give you a dipole vector which is equal to the dipole vector here the charge separation between these 2 atoms will be different from the charge separation here therefore, there is a net dipole moment during this stretch and the dipole moment increases to a certain value and then it decreases to 0 it increases decreases and therefore, the dipole moment sort of oscillates between 0 and a certain value there is a continuous change in the dipole moment during the vibration this is detected by the infrared spectroscopy.

Therefore, carbon dioxide despite being linear molecule with 0 dipole moment has one normal mode of vibration which is detected there are two other modes which will tell you the molecule cannot be detected by microwave spectroscopy for it is rotational spectrum because it does not have a permanent dipole moment. In the limit of rigid router if the molecule is not rigid router, but it is a semi rigid router with a vibration is taking place you see that moments of inertia keep changing dipole moments are created and therefore, we have problems. Pure carbon dioxide in the limit of rigid router an approximation does not have the microwave spectrum, but one of it is vibrational degrees as you see here has you see here has a vibrational spectrum it how is the dipole moment is created and destroyed it oscillates between different values.

(Refer Slide Time: 20:41)



Stretching (Anti Symmetric)

Click the play button to view the animation

3 Bending modes (first of the two degenerate modes)

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

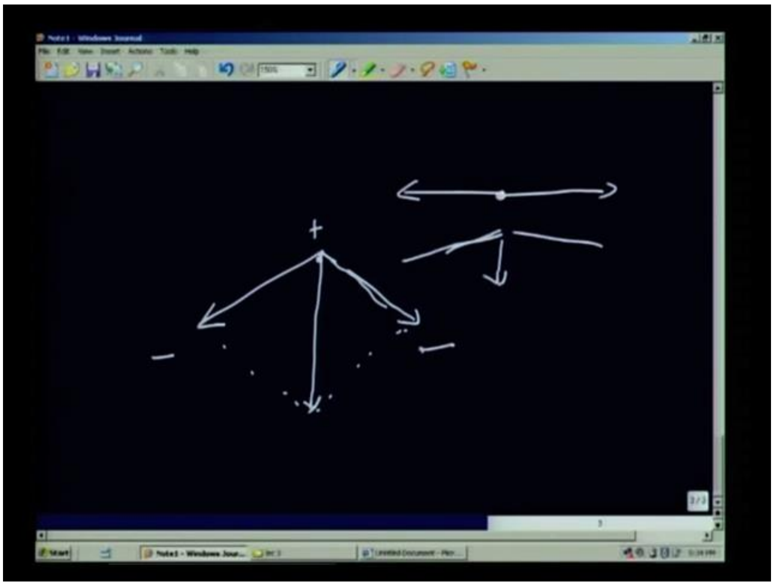
Bending

Click the play button to view the animation

4 Bending modes(second of the two degenerate modes)

There are other 2 other modes for carbon dioxide it is a linear molecule 3N minus 5 for N equal to 3 linear is 4. Two of them you have seen it is a third one which is the bending in a such a way that the carbon balances the bending of the 2 hydrogen atoms such that the symmetric the center of mass remains where it is and again in this bending the dipole moment vector as you see it.

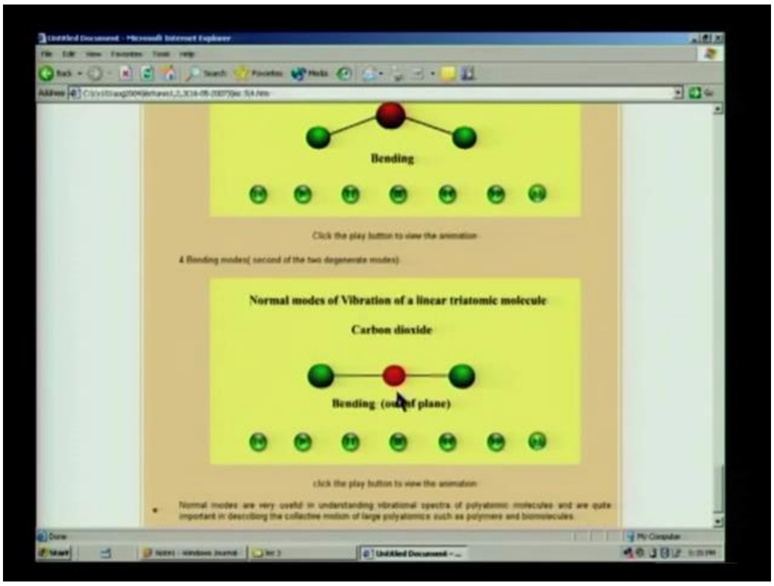
(Refer Slide Time: 21:10)



In this bending dipole moment vector is created with a plus charge and the minus charge here plus and minus here and therefore, the sum of these 2 dipole moment vector is that it is not 0 actually it should be exactly the same as the diagonal of the parallelogram that you have sorry let me erase that. If these are the 2 dipole vectors then you draw a parallelogram the total dipole moment vector or the sum is that.

Therefore that dipole moment is 0 when the bond is like that when the bond is like that when the bond is like that the dipole moment is small and when the bond is bent to it is full extent possible under the small amplitude motion when you see that the dipole moment keeps increasing and then it decreases to 0. When it goes up therefore, there is a change in the dipole moment. So, this is an oscillatory motion bending mode for which the dipole moment changes it can be detected by IR spectroscopy.

(Refer Slide Time: 22:26)



Click the play button to view the animation

4 Bending modes(second of the two degenerate modes)

click the play button to view the animation

- Normal modes are very useful in understanding vibrational spectra of polyatomic molecules and are quite important in describing the collective motion of large polyatomics such as polymers and biomolecules.

There is one more bending more which has the same energy it is called the degenerate bending mode that this bending is that the molecule is going into the plane of screen and out back on to the screen. So, it is going to I mean if you are watching in the television screen it is like going to the back of the television screen and then coming back to the front. So, this is another bending mode again in this bending mode dipole moments are created and it is value keeps changing during the oscillation therefore, this is an oscillating electric dipole that is present in the molecule this is also detected by the infrared spectroscopy.

What is important to note that this bending or this bending is only in 2 different planes here the plain is plain perpendicular to the plain of the screen here the plain of the motion is the plain of the screen. Therefore, they are the both degenerate the molecule, does not know what the plain it is oscillating it is a triatomic molecule and other association of axes is for us to visualize various different possibilities energetically. Both these motions of the same energy and therefore, they are degenerated these are the 4 normal modes of vibration for carbon dioxide molecule. Now, let us go and define the normal vibrations a little more quantitatively.