Chemistry 1
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 34
Molecular Vibrations in Polyatomic Molecules -Qualitative Account

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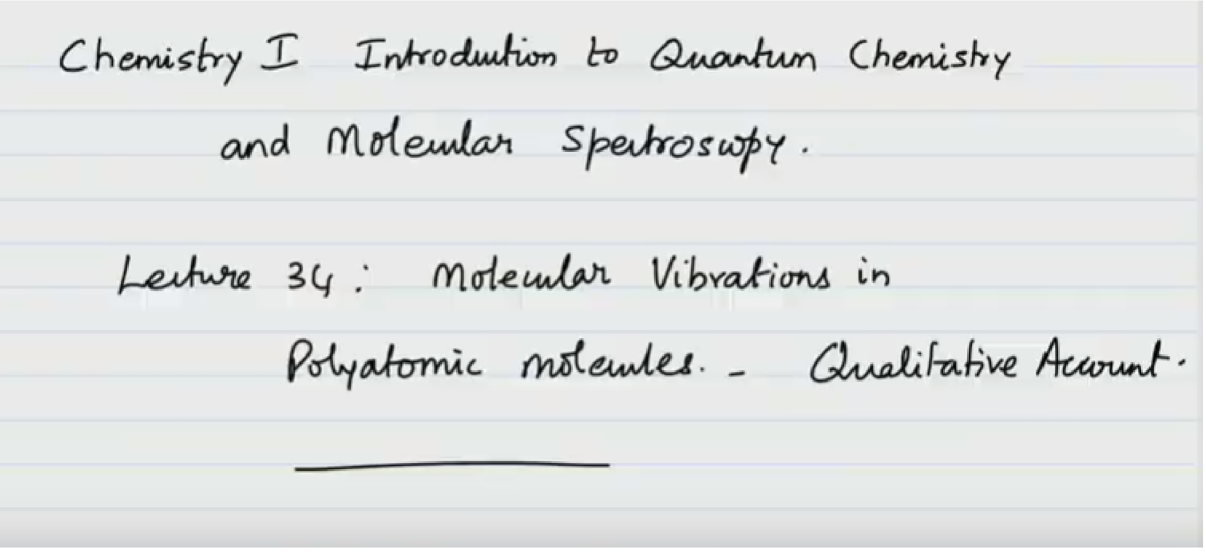

Chemistry I Introduction to Quantum Chemistry
and Molecular Spectroscopy.

Lecture 34: Molecular Vibrations in
Polyatomic molecules. - Qualitative Account.

Welcome back to the lectures in Quantum Chemistry introductory topic and also molecular Spectroscopy. The last two lectures we examined molecular vibrations, using two elementary models. One is known as the simple Harmonic Oscillator Model, the most elementary approach to studying Molecular Vibrations and the second one was to take into account anharmonocity using a special form known as the Morse oscillator form.

We looked at the energy levels, the wave functions, the transition frequencies and the fact that, Vibrational Spectrum of your Diatomic Molecule in the Harmonic Oscillator contained only one line. Whereas in the Morse Oscillator, you do get several lines and therefore you do get a spectra of lines. Both these models are elementary and they form the basis for understanding Molecular Vibrations of polyatomic molecules and that is the topic of this lecture.

We will take a brief tour on understanding the molecular motion based on the degrees of freedom. This whole lecture is a qualitative account. I will not be able to give you quantitative description of the molecular vibration of polyatomic molecules without getting into the mathematics of it and the mathematics of it in the classical mechanical level it involves normal modes of vibration.

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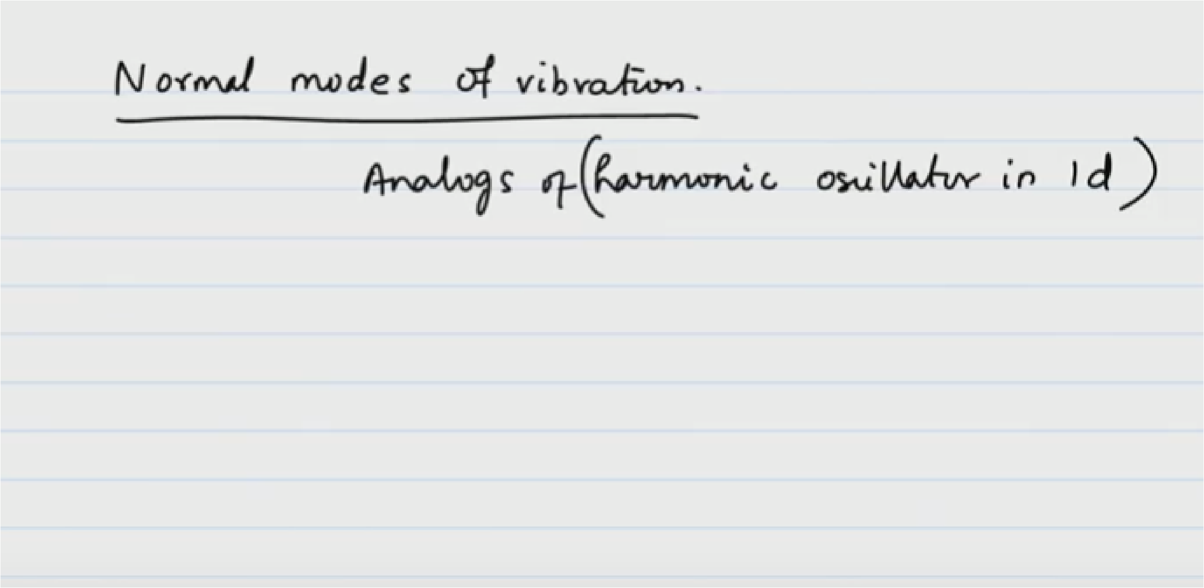

Normal modes of vibration.

Analogs of (harmonic osillator in 1d)

This is also the most elementary level in terms of or the most fundamental level in terms of understanding Molecular Vibrations. The normal modes are the analogs of the Harmonic Oscillator, in one dimension. These are approximations of small amplitude vibrations in molecular motion.

And at that level when the amplitude of vibration is very small and the molecular vibrational energies are such that, most of the molecular state is in the ground state are very few in the first excited state and if the potential energy supports many such vibrational states then the normal world approximation is a very important one in understanding what are the basic frequencies, that the molecules that molecules will absorb and which will be seen in the infrared spectrum. Therefore in that sense, normal Moore is the equivalent of the Harmonic Oscillator model.

Even to get to the normal mode approximation from the general formula or the general form for the molecular energy involving kinetic energy and potential energy, we have to do some elementary mathematics.

I will not do that at this point of time and that will be relegated to some other lecture in the future, in an advanced course in spectroscopy. So here, what we will look at, is the basic idea, namely that the degrees of freedom of a molecule, there are young atoms in a molecule in general two three four five, whatever is a fixed number and each atom in a true sense has 3 degrees of freedom of motion, in a three-dimensional world, which is what we live in.

The three degrees of freedom, basically relate to the fact that we have three orthogonal axis systems, three orthogonal axes and therefore we have three independent components of the position or the velocity or the momentum, whatever that may be. Therefore each atom has three degrees of freedom in general and therefore there are the three n degrees of freedom, which is the total degree of freedom park N atom molecule. We are not taking into account the electrons.

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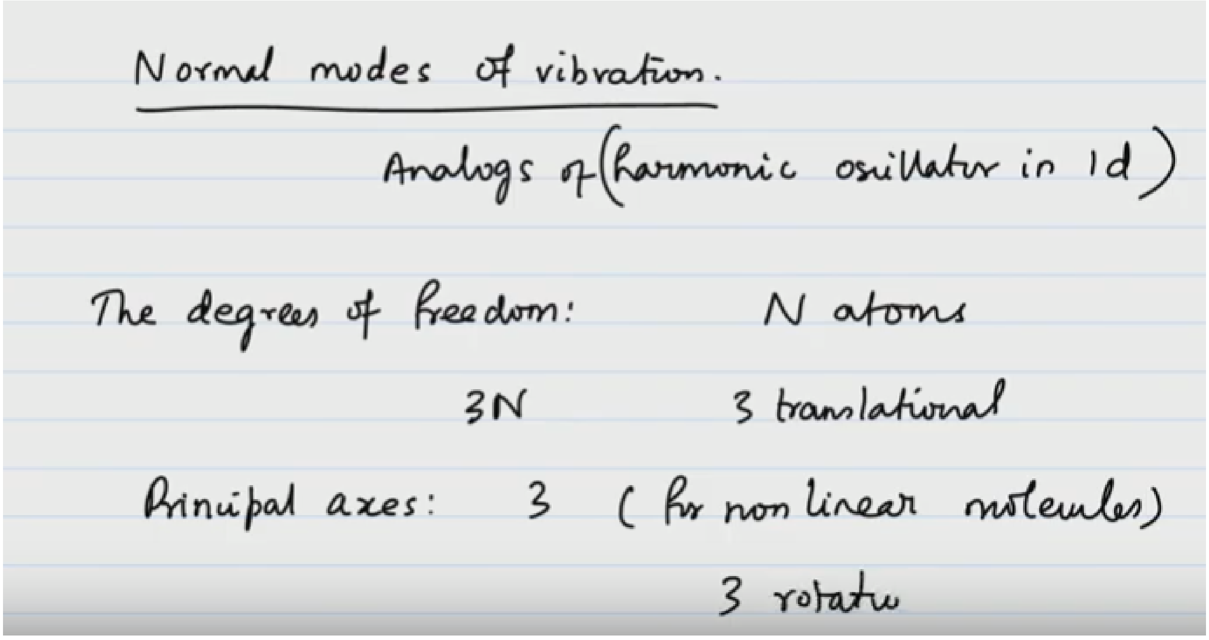

Normal modes of vibration.

Analogs of (harmonic osillator in 1d)

The degrees of freedom: N atoms

3N 3 translational

Principal axes: 3 (for non linear molecules)

3 rotatn

We will assume that it is the atom as a whole. After three and it is possible for us to immediately visualize that the molecule as a whole is moving in one direction or in another direction and obviously there are three different such directions, which are mutually independent of each other and this is what we call as the, ‘Three Translational Degrees of Freedom’. Essentially all the atoms move in the same direction and therefore this is a concerted motion and so let us take the three translational degrees of freedom, oh they are not relevant for this particular topic, in addition the molecules also have a concerted motion about an axis, which we call as an angular motion or a rotational motion. We will study more of it in the next lecture.

The rotational motion is usually visualized in terms of three, again three mutually independent axis known as, ‘The Principle Axis of Moments of Inertia, Principle Axis of Inertia or Principle Axis in Molecules’. Three of them for nonlinear molecules and therefore we have three rotational degrees of freedom and what is left over is the remaining, namely the 3 and minus 6 degrees of freedom are called the genuine vibrations of molecule by genuine vibrations. What we mean is that the molecule does not exhibit at the same time when it undergoes vibrational motion, which is the relative displacement of the atoms with respect to each other in a molecule the centre of mass of the molecule does not move.

That means the molecule is not translating or the molecule is not rotating at the same time we assume that these two are, these are all independent in principle they are not independent. But for certain approximations and for calculating energy levels at a very low level of approximation, we can treat these motions as friendly independent of each other and therefore the energies associated with the translational motion, the energy associated with the rotational motion and the energy with the vibrational motion, can be treated as independent in principle, they are not. No molecule is static, no molecule does not undergo I mean every molecule undergoes rotation at any temperature above zero Kelvin and even at zero Kelvin the molecule undergoes vibration and at any temperature above zero Kelvin the molecule or translates.

Therefore in principle, these degrees of freedom are coupled to each other, but for the level of approximation and to understand the basic features of spectroscopy, we assume that these are independent.

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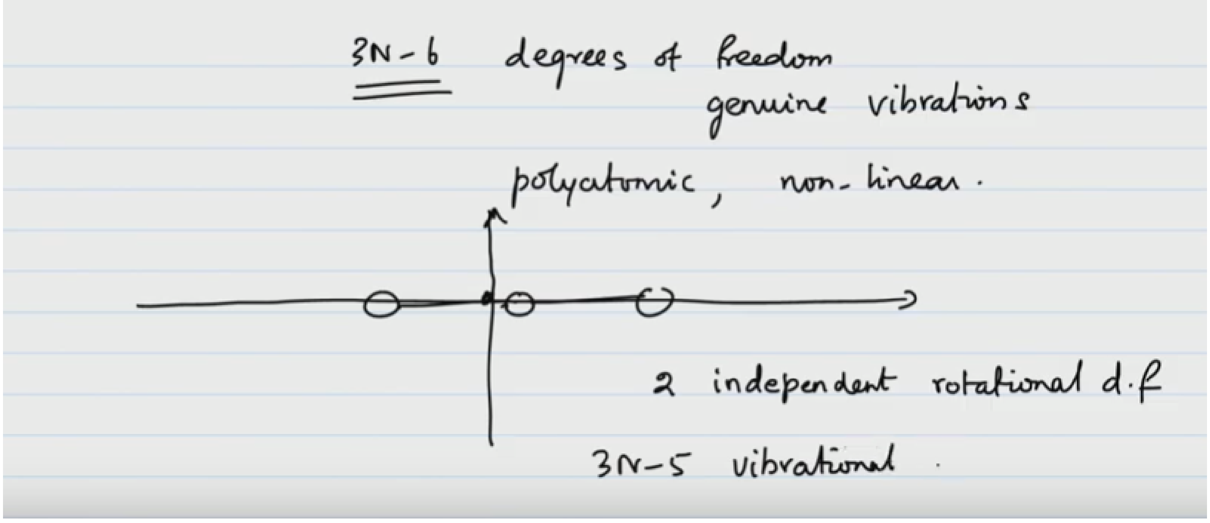

3N - 6 degrees of freedom
genuine vibrations

polyatomic, non-linear.

2 independent rotational d.f

3N-5 vibrational.

Therefore we have 3N minus 6 degrees of freedom genuine vibrations for a polyatomic molecule, which is nonlinear. Why? For a linear molecule, if you assume that the atoms are all collinear, for example, the rotation about this axis, the molecular access does not have any energy associated with it, there is no moment of inertia, there is no inertia associated with that motion, there is no energy requirement. The only axis that we can think about is suppose the centre of mass is somewhere here. The rotation about this axis, for example, if this axis is in the plane of the board, this if it is this axis, then the rotation is about up-and-down. It is about that axis. If the rotation if the axis is perpendicular to the plane of this board, then the molecule rotates in plane, that is on the plane of the screen.

These are the two independent degrees of freedom, two independent rotational degrees of freedom. Therefore for a linear polyatomic molecule, we have 3N minus 5 vibrational degrees of freedom. That is one more vibrational degree of freedom, then any polyatomic polygon which is nonlinear. Now these are all conceptual ideas. How do we visualize them? Let us take a very simple example of a Tri Atomic Molecule.

And even before that, if you think about a Diatomic Molecule, it is a linear molecule by definition, therefore, 3N and minus 5 there means only one vibrational degree of freedom, which is about the bond axis. Namely the displacement about the equilibrium of the two atoms and therefore that is what we have been studying as a small molecule, small amplitude vibration or as an enharmonic vibration in the last two lectures.

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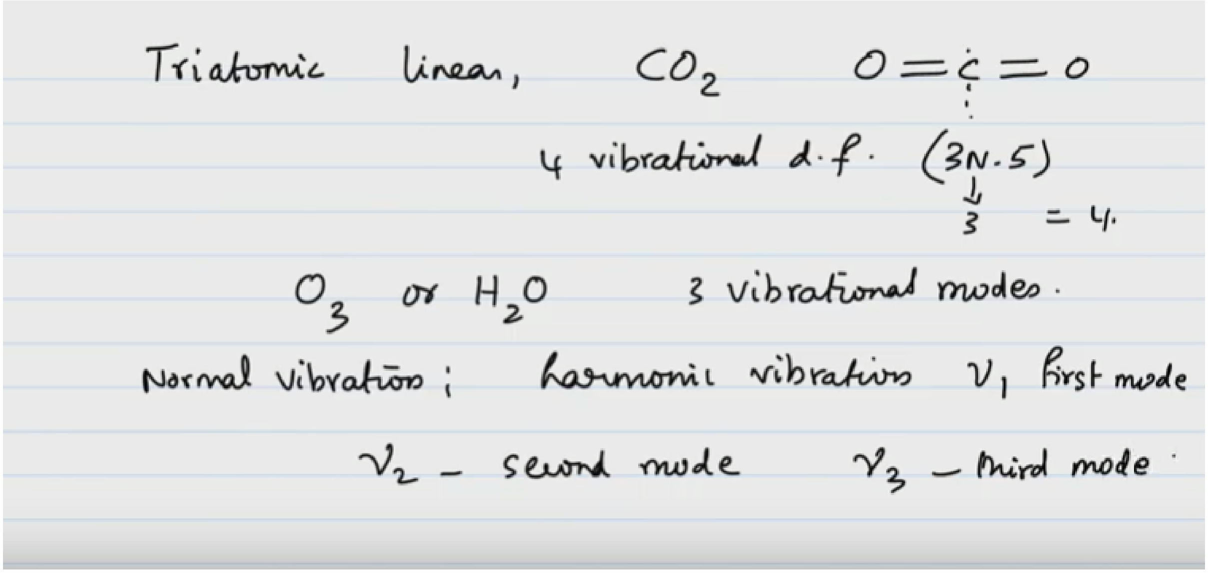

Triatomic linear, CO_2 $O=\underset{\vdots}{C}=O$

4 vibrational d.f. $(3\underset{\underset{3}{\downarrow}}{N}\cdot 5) = 4.$

O_3 or H_2O 3 vibrational modes.

Normal vibration ; harmonic vibration ν_1 first mode

ν_2 – second mode ν_3 – third mode.

Now if we look at this in the form of a triatomic molecule, for example to visualize, then a Triatomic linear molecule carbon dioxide for example, oxygen, carbon, oxygen, the centre of mass is right to the carbon and the this is one example, there are four vibrational degrees of freedom. 3N minus 5 and N is 3, so there are 4 and in the case of say ozone or water which are famous examples in molecular spectroscopy, for very detailed study of vibrational motion and rotational motion. You have 3 vibrational modes. Therefore I shall describe here what is called the normal vibration, which is essentially a harmonic vibration, about harmonic vibration, about equilibrium geometry and this harmonic vibration has a frequency say nu 1 for first mode, first harmonic mode nu 2 for the second mode and nu 3 for the third mode. These are in general different, except when the molecule has specific symmetries, like a threefold symmetry or in the case of a linear molecule, some of these vibrational frequencies can become degenerate. That is, they will have the same energy, but they will be different vibrational modes and therefore you have a mix of all kinds. So let us start with the simple example of water molecule.

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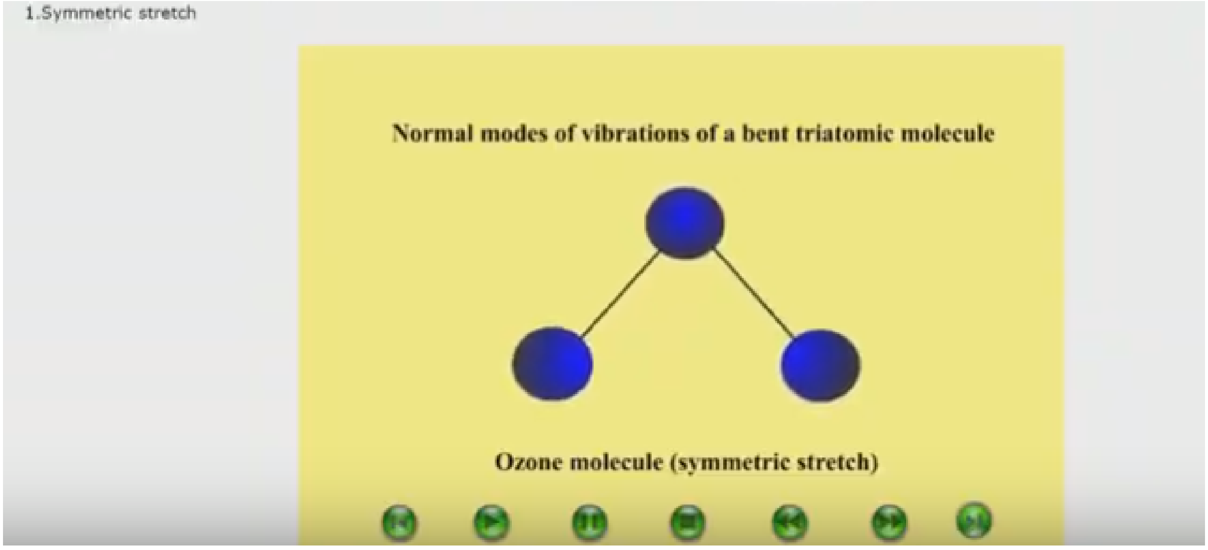

1.Symmetric stretch

Normal modes of vibrations of a bent triatomic molecule

Ozone molecule (symmetric stretch)

So sorry, we will go with the Ozone Molecule to begin with. So here is the first picture that you have of a normal mode of vibration of a bent Triatomic Molecule. Ozone has two oxygen, is oxygens with two different types. Namely, this the oxygen in the middle connected to the other two oxygens and you can see that, in this molecular motion, you can see that, this stretch, the oxygen-oxygen stretch, this bond happen in the same manner. They are symmetric. I mean the stretch happens on the same level and then it compresses, it goes back to the same. Therefore, there is one vibrational frequency. Of course, this is a very slow motion you are talking about a vibrational frequency of the order of 10 to that 11, 10 to the 12 13 Hertz. I mean that many vibrations in 1 second.
This is a typical picture to tell you what that mode is. Therefore what you see here is, there are two things that you have to and notice, one, the atoms vibrate or displace themselves about the equilibrium and go back to the equilibrium, at the same time all the atoms. Therefore the frequency with which each atom vibrates about its equilibrium geometry position, the frequency for all the atoms is 1 1 1 frequency, that is it,nothing more than. Second, since all the three atoms are identical in mass, all the 3 are oxygen; the vibrational amplitudes are also the same. That is a displacement of these two oxygen atoms, versus these two oxygen atoms. The displacement is about the same length, in fact it is exactly the same, the amplitude of vibration is the same. Third, the centre of mass does not move the centre of mass is right here, right in the middle, the therefore this is why it is called a genuine vibration, that we have already removed from this picture, the overall translation of the molecule. Suppose we go with the molecule at the same speed at which it is translating, then you do not see the molecule move you, only see the vibrations, like you are in a train. You move inside the train. If you close the windows, you do not see the translational motion. You come to know that the train is actually moving, when it is decelerating or when it is accelerating. Otherwise you are in a constant speed frame and if we go into the frame of the constant speed of the molecules, then we will see only genuine vibrations. Therefore, this is one example of a one normal mode of a Triatomic Molecule. What is the other normal mode?

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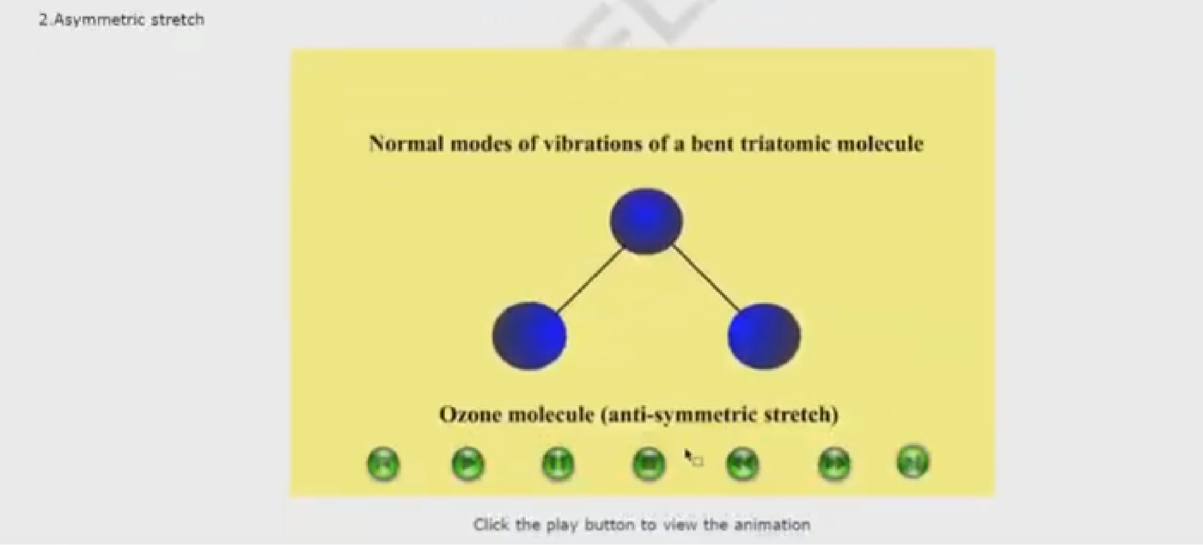

The other normal vibration of a polyatomic molecule, in this case was all again, is an anti-symmetric stretch, you can see immediately that these two atoms that is the bond length, is shortened; while the bond length here is lengthened it stretched. Therefore the stretching is anti to each other. That is why it is called anti-symmetric stretch, this is another normal vibration again since the atoms are of the same mass, and the amplitudes of vibration are the same. The frequency, with which this anti-symmetric stretch happens, will be different from the frequency with which the symmetric stretch happens. Therefore, the symmetric stretch is one normal vibrational frequency say called, a new one. The anti-symmetric stretch is the second normal vibrational frequency, probably called a new two. It does not matter, which label is there are conventions for putting these labels right.

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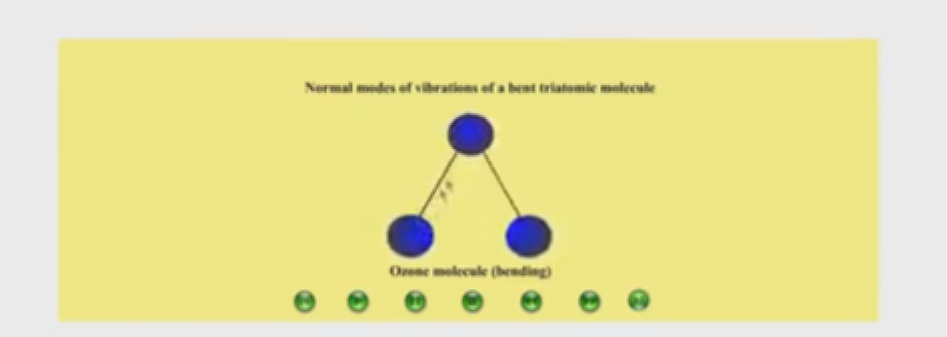

Normal modes of vibrations of a bent triatomic molecule

Ozone molecule (bending)

But the point is the frequencies are different and the third motion which is of a much lower frequency, than either of those bending symmetric and anti-symmetric stretch is the bending vibrational motion. You can see that in the bending vibrational motion. It is the oh-o-oh bond angle, which gets changed. It does not do so here; in a stretch you do not see any change in the bond angle, Okay? The bond angles remain the same. Whereas the bending motion, which is an independent mode, actually changes the bond angle, of course that is there, appears to be a stretching, but it is not. The these three modes, are the three normal vibrations of any bent Triatomic molecule, whether it is ozone or whether it is water or whether it is Sulphur Dioxide or Nitrogen Dioxide, it does not matter any Triatomic molecule, which is not linear. These are the three normal modes that you can have and all three will have different frequencies. No matter what, because all of them have, when we study group theory at a later time, all of them correspond to what is known as the C toV symmetric point group and the C 2 V symmetry point group also tells us the molecule vibrational modes will not be degenerate, they will all be non degenerate, okay? So this is for the nonlinear molecule. What about the nonlinear molecule involving water?

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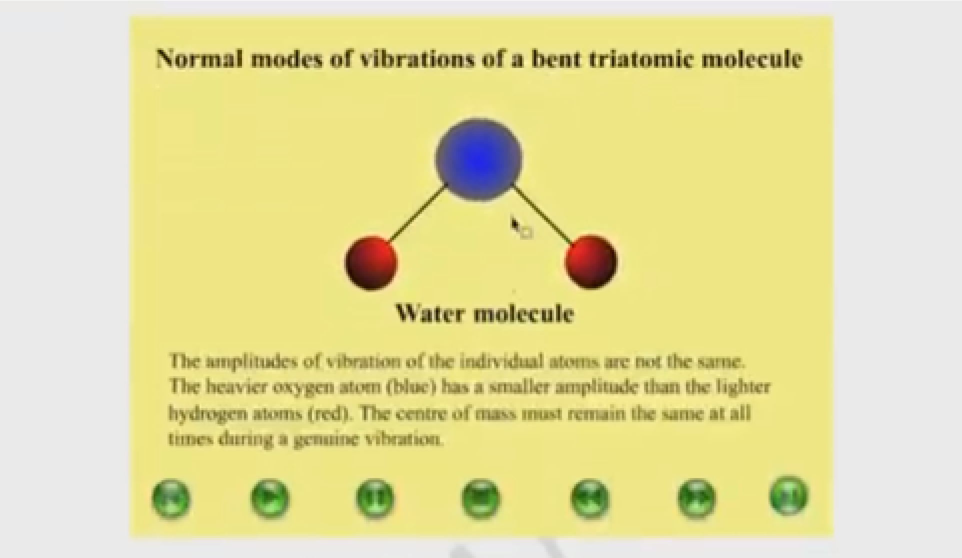

Normal modes of vibrations of a bent triatomic molecule

Water molecule

The amplitudes of vibration of the individual atoms are not the same. The heavier oxygen atom (blue) has a smaller amplitude than the lighter hydrogen atoms (red). The centre of mass must remain the same at all times during a genuine vibration.

It is the same, you can see that there is a symmetric stretch, there is an anti-symmetric stretch and then there is this bending. The thing that is to be noticed here, even if it is not visible clearly in this picture, is that for any given vibrational frequency, the displacement of the hydrogen atoms from the equilibrium will be much farther. Than the displacement of the oxygen atom from its equilibrium position, oxygen is heavier, therefore it undergoes a very slight displacement, but at the same same frequency. Therefore obviously, it travels a smaller distance in a lot, in the same amount of time, while the the hydrogen atoms, travel a larger distance or the same amount of time, which means that the amplitudes of vibration are more. In fact it is inversely proportional to the square root of the mass, I think, it is. Therefore, the amplitudes are different for different atoms and are dependent on the masses, but the frequency with which the atoms vibrate, in a given normal more is identical for all the atoms and in principle, all the atoms will move, if you want to keep the centre of mass at one position, the vibrational positions have to be adjusted in such a way, that, you have that, the all the atoms have to vibrate, they have to be displaced. This is the feature of a normal vibration. Okay?

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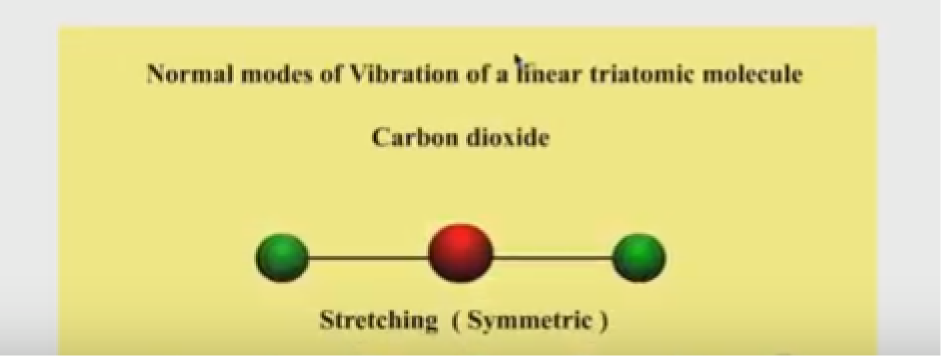

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

Stretching (Symmetric)

Now what about a linear molecule? Let us take carbon dioxide as an example. Carbon dioxide being a linear molecule of a three at a molecule, it is a the number of vibrational degrees of freedom is 3N and minus 5, which means that there are 4 vibrational degrees of freedom, 1 in addition to what you see in a bent Triatomic molecule and here is an example of the here is a picture, of the normal vibration of a symmetric stretching. Now, the symmetric stretching here if you look at it, carbon dioxide with the carbon in the middle and the two oxygen's at the end. The bond lengths are stretched identically on both sides and carbon and oxygen having different Electro negativities, there will be a dipole moment in the direction from the positive carbon, to the negative oxygen in this direction. But that dipole will be compensated or it will be cancelled by the dipole in this direction, because the dipoles are charged into distance vectors and the two vectors cancel each other. Therefore during this vibration, there is no dipole moment, either formed or present. Equilibrium structure of carbon dioxide does not have a dipole moment and during this particular vibration, there is no dipole moment and we cannot detect this kind of molecular motion in traditional infra red spectroscopy.

To detect this motion, we need to study what is known as, 'The Raman Spectroscopy', which takes into account, these scattering properties, light scattering properties of the molecule. So Raman spectroscopy is able to do complementary detection, to infrared spectroscopy. We will see that, when we need to study Raman spectroscopy later.

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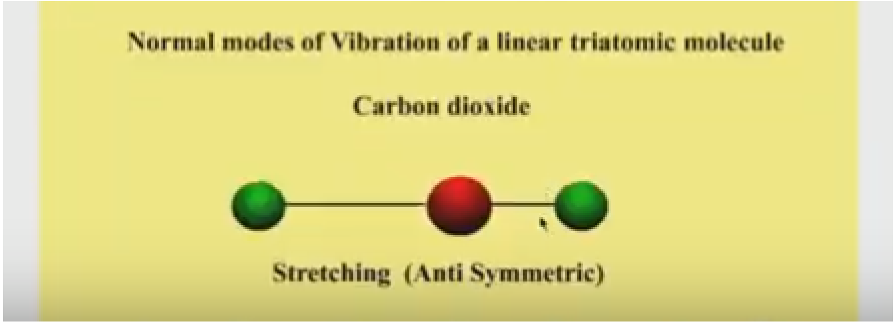

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

Stretching (Anti Symmetric)

This is one stretching mode. The anti symmetric stretching of carbon dioxide is such that, the carbon oxygen bond one of them is shortened and while the other is lengthened. But here obviously the carbon has to move in order to see that there is no overall translation. I mean the molecule does translate, but we are not considering them, we are in the frame in which the molecule is translating. Therefore what we see is the relative displacement of the atoms and here clearly that there is a dipole moment, which is not cancelled by the dipole moment in this direction. Because the charge difference is the same, between these carbon and this oxygen, as well as this carbon and this oxygen, but the distances are different. Therefore the dipole moment in one direction is more at times, than the dipole moment in the other. Therefore the dipoles do not cancel each other, therefore this has an oscillating dipole moment and this is detected using infrared spectroscopy, it is easy to detect that. Surprisingly, in Raman spectroscopy, this cannot be detected. This any molecule which has a centre of symmetry, has either Raman's detection modes or the Infra red detection modes, these are things that we will learn more in detail when we study Spectroscopy in detail. Okay.

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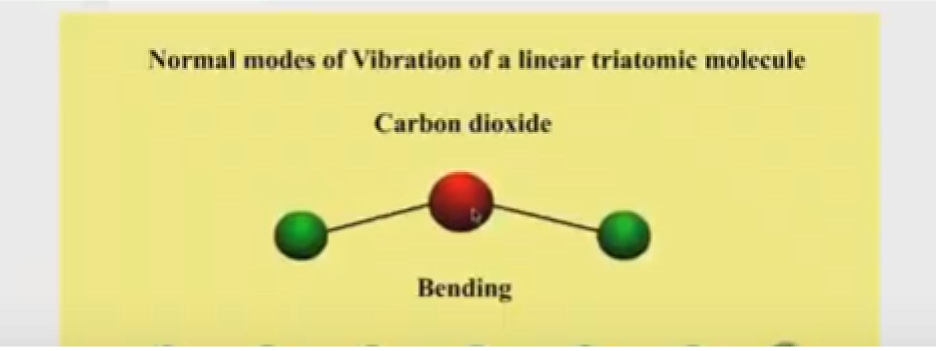

Normal modes of Vibration of a linear triatomic molecule

Carbon dioxide

Bending

The third is the bending vibrational mode of carbon dioxide. It is a tri atomic linear molecule, therefore if you take the plane of the screen, as the plane of the molecule, then you see in the plane itself, the molecule bends to introduce obviously dipole, this dipole moment and this dipole moment will not cancel each other, in fact they will act as the dipole is increased, the dipole moment will be in this direction. Let me see. This is carbon to oxygen so if the dipole is this way e oh and C oh the dipole moment usually is written this way

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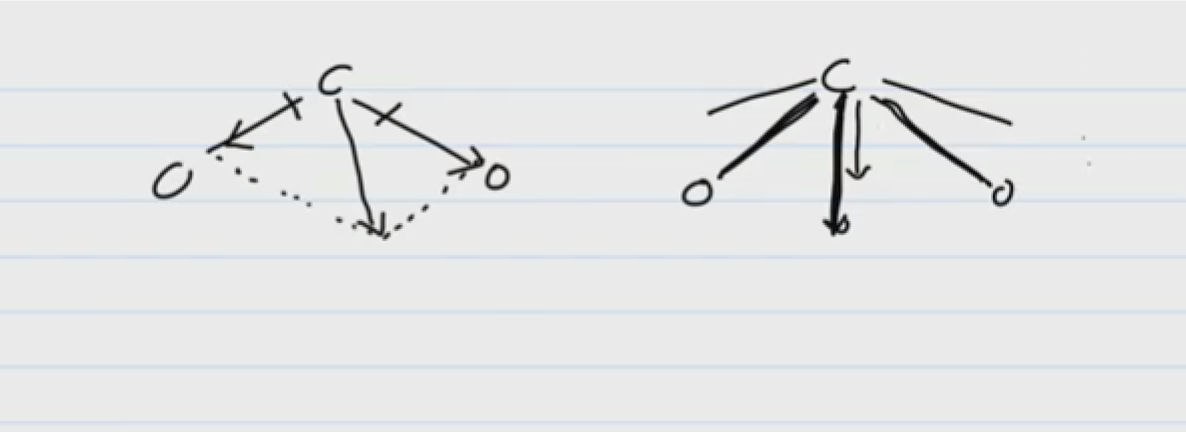

and therefore the net dipole moment will be in this direction. In fact the net dipole moment is the sum of the two vectors, therefore you can get that vector by simply drawing the diagonal of the parallelogram, that is formed with these vectors.
Sorry, the way this picture is drawn it is like this, but no, you know the vibrations would be in fact the bending will be so symmetric that it will be, dipole moment will always be in this direction. It will increase and it will decrease, increase and decrease, as the bond lengths as the bending becomes more versus the bending becomes less in this case the dipole moment will be only this. Therefore, there is an oscillating dipole moment and this is detected of course by infrared spectroscopy. The additional feature is that there is a fourth mode, we have seen the three modes, the stretching, the anti symmetric stretching and then the bending. The fourth bending is obviously in a direction or in a plane independent of this plane, which is orthogonal to this and you can see that right here. This is in and out of the screen if you can imagine that the screen is the plane of the molecule, then essentially the carbon atom goes behind the screen, the oxygen atoms come up in front of the screen and then it goes back and so on and this movement again produces a dipole moment during the process of the vibration, yeah growing or a changing dipole moment.

So this is also detected using infrared spectroscopy and this motion can be observed to undergo transitions. So these are the four vibrational modes, but since the plane of the molecule or a plane perpendicular to the molecule is irrelevant, except for what is called the cataloguing different types, the two frequencies the bending frequencies are identical and therefore the vibrational frequency the new of the bending mode in this form, in the bending mode in this form, they are both degenerate. Which does not happen in the case of a Triatomic molecule, which is not linear.

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The spectra of benzene, toluene and m-xylene are given here to show how the structural similarities and differences between them are present in their correponding IR spectra.

The normal mode description is one way of describing the molecular vibration.There are also what are called, ‘The Group Modes or Local Modes of Molecules’. The local modes often refer to the vibrations of a group of atoms, in a molecule, relative to the other and the group frequencies, which are usually listed in the infrared spectroscopy tables of an organic chemistry or an inorganic chemistry textbook, basically tell you that those frequencies are also the ones by which we characterize molecular systems. An example of a group frequency and a traditional infrared spectrum, you see here is that of toluene has many absorption frequencies.

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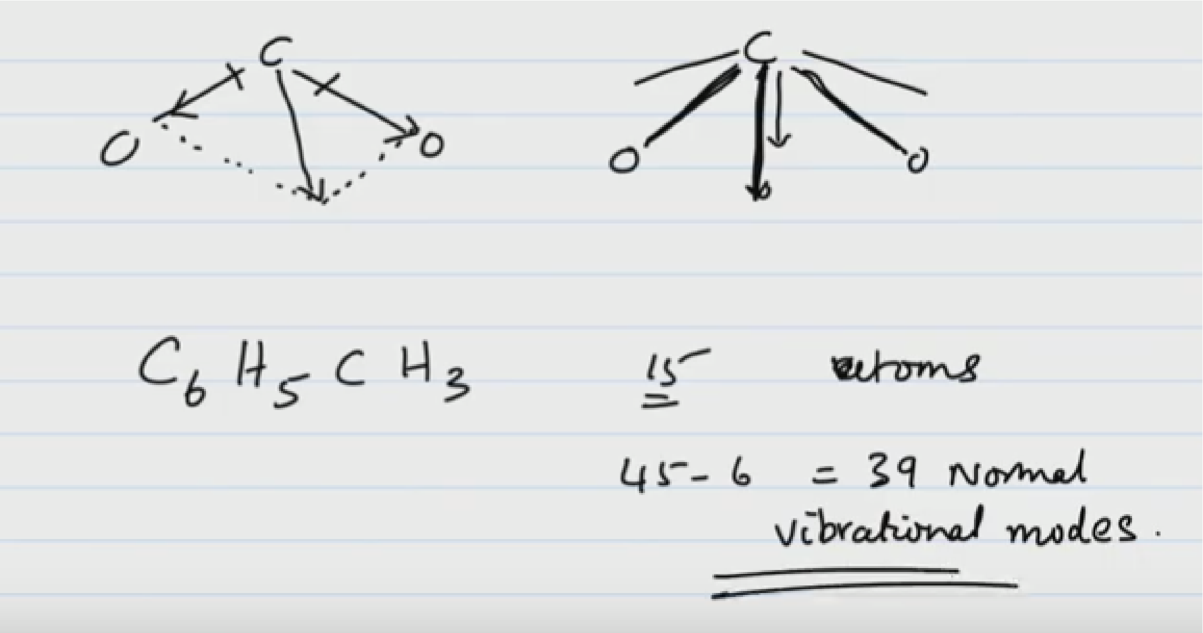

$C_6H_5CH_3$ 15 atoms

45 - 6 = 39 Normal vibrational modes.

It is not as surprising that you have many of them, if you recall Toluene has C6H5 CH3 so it is C 6 H 5 CH 3 what is this how many atoms that we have. C 6 H 5 CH 3, 6 plus 5, 15 atoms and it is a nonlinear molecule. Therefore it is 45 minus 6, you have 39 normal vibrational modes, quite obviously visualizing each one of these vibrational modes, is possible with the current day computational technologies that we have the techniques, that we have, the 39 normal vibrational modes of Toluene, can be visualized by solving this problem in in a computer using Basic Quantum Chemistry methods and those 39 vibrational frequencies will be listed somewhere. You can basically search for them in the internet also.
But I have looked at many of these vibrational frequencies, here.

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The spectra of benzene, toluene and m-xylene are given here to show how the structural similarities and differences between them are present in their correponding IR spectra.

You have 15, 39 normal vibrational modes, so you can see what is called, ‘The Bending Rocking Scissoring type of vibrations’, at very low frequencies molecular motion and then you have what are called, ‘The Absorption Frequencies’, for the symmetric and anti-symmetric stretch, as well as this is also part of the bending frequency motion for the Toluene and then at very high frequencies you have got what is called, ‘The Symmetric and Anti-Symmetric’, stretch frequencies. So this is a typical Toluene spectrum in solution in in some of the in Toluene 99%, I mean it is as pure as you can. This is one example of what are called grouped frequency identifications for molecules tables and tables of spectra are recorded and listed, tens of thousands of lines are known or maybe maybe hundreds and thousands of lines are known and these tables basically provide us the fingerprints for identifying molecules, if they have already been detected and so on. Therefore this is a truly experimental spectroscopy phenomenon which allows us to characterize molecules. Now if you go to the another spectrum, for example, this is Benzene instead of Toluene, we have the Benzene spectrum and you can see similar lines that you see in Toluene, but toluene of course has more lines. So, Benzene Toluene and Metozyling. For example, One more, CH3 group, one less CH3 group if you go through.

Therefore you can characterize these molecules into groups of molecules, which are very similar to frequencies and then additional ones and this is very very well recorded and the tabulated and these frequencies are used by experimental spectroscopies, all the time this is about the group frequencies. In the next lecture we shall see in detail some of the normal vibrations of many atom polyatomic molecules and with some very very notable examples such as, the normal mode spectra of methane, ethane and probably Benzene. Benzene has 30 vibrational modes and it is one of the classic molecules for which the spectroscopy, has been me has been carried out, the spectroscopy investigations, have been carried out in detail and Benzene is also a very very beautiful molecule, with 30 degrees of vibration, classified according to the molecular symmetry group in a beautiful manner, by a very early paper in 1934 or around that time, by Professor E Bright Wilson jr. at Harvard University. We will see more of such molecular spectra in a qualitative manner in the last lecture, on the vibrational spectroscopy for this course.

Until then, thank you very much.