Chemistry I
Introduction to Quantum Chemistry And Molecular Spectroscopy
Lecture 35
Polyatomic Vibrations-Illustrative examples of normal vibrations

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Welcome back to the lectures in, ‘Quantum Chemistry and Molecular Spectroscopy’. In the past lecture we saw a few examples of normal vibrations of a linear and nonlinear tri atomic molecule. At the end of that lecture, I also mentioned that I would show some examples of normal vibrations, as computed using quantum chemical methods and visualized in other polyatomic molecule. Many atom polyatomic molecules, such as, benzene and the methane, ethane and many others.

So this lecture is a visual presentation of some of these normal modes, the classification of them by the approximate nature such as bending torsional or scissoring or ring puckering ring torsion out of plane, out of plane bending. All these things mean, they are some things that you have to see the motion and then classify them. Most important to the lecture is that these normal modes have been calculated abinitio using quantum chemical packages and I use one of the softwares, which we use in our classrooms in IIT Madras, the software is goes view which allows us to visualize molecular structure as well as the coordinates of the molecules and in this particular lecture, I show the molecular vibrational modes, so the lecture is on poly atomic vibrations and there are illustrative examples of normal vibrations.

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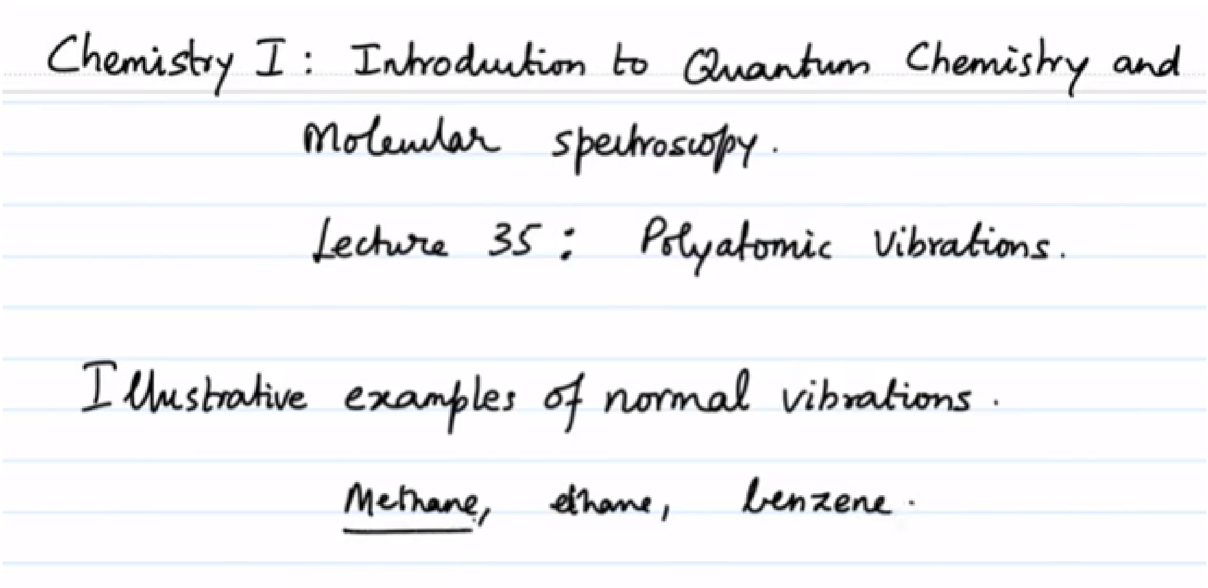

Chemistry I : Introduction to Quantum Chemistry and
Molecular spectroscopy.
Lecture 35 : Polyatomic Vibrations.

Illustrative examples of normal vibrations.
Methane, ethane, benzene.

We shall see simple polyatomic modes of methane 18 benzene to name a few okay,

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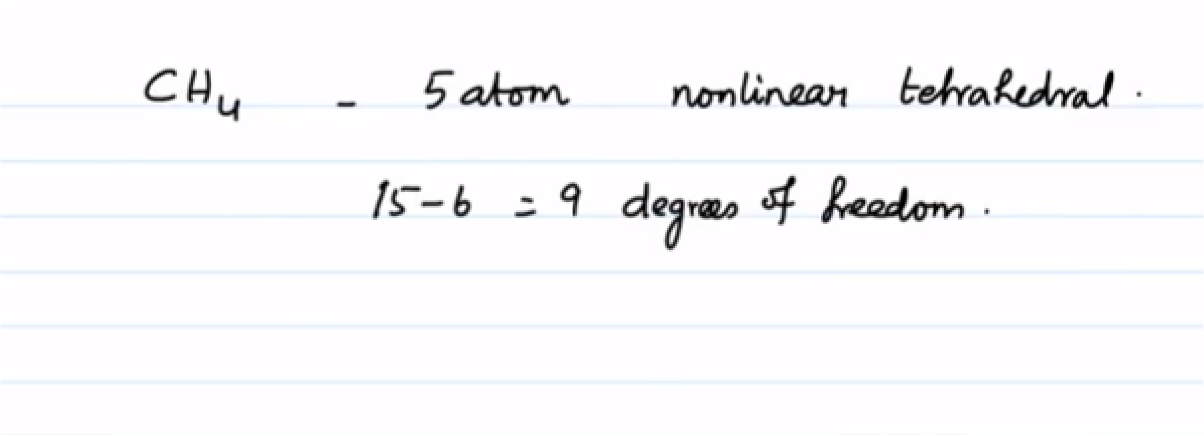

CH_4 - 5 atom nonlinear tetrahedral.

$15 - 6 = 9$ degrees of freedom.

methane CH4, it is a five at a molecule nonlinear, it is a tetrahedral structure, it has a tetrahedral structure and there are 15 minus 6 9 degrees of freedom.

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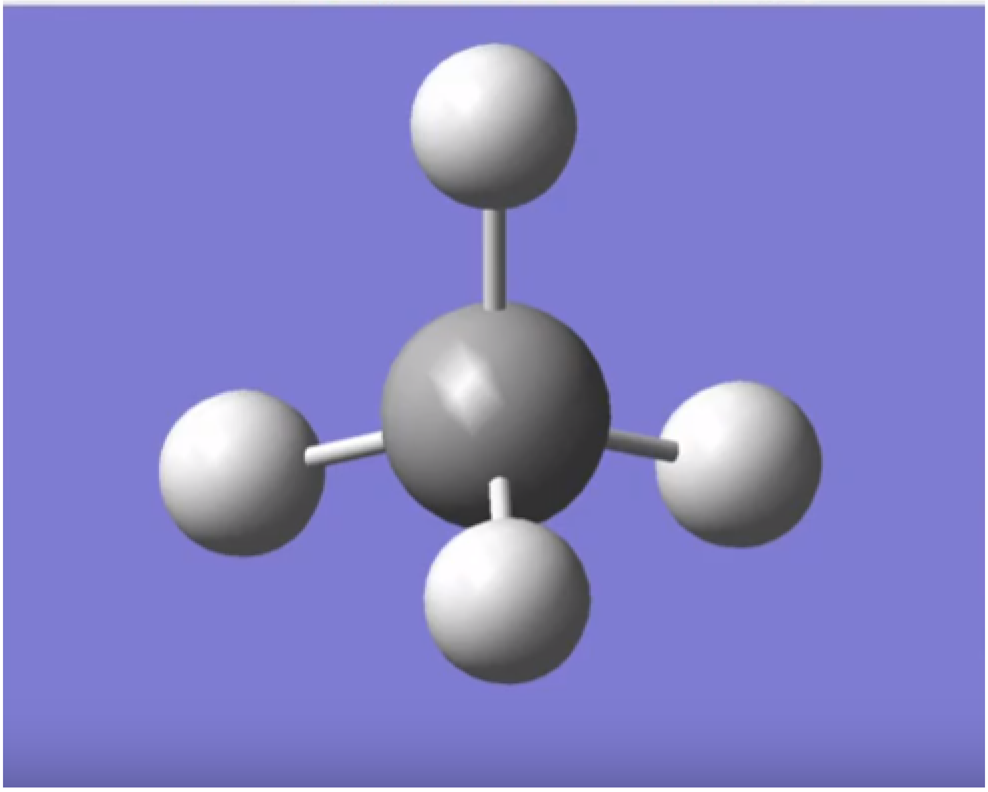

So we shall look at the methane molecular structure. Okay, this is a three dimensional perspective I think by now you can see that the tetrahedral structure is clear in this form and let us also look at the vibrational modes of this molecule now what we have in the small table you may not be able to read this, but let me give you the gist of it. There are nine normal vibrations 1 to 9 calculated according to the harmonic model, namely the force field, harmonic force field model, meaning that the vibrations are of small amplitudes and the frequencies are in centimetre inverse that you see from here roughly starting from 1413 centimetre inverse to about 3248 centimetre, inverse there are nine of them and you can see

that this molecule is a very highly symmetric molecule, tetrahedron is a molecular system which has 24 symmetry elements, according to the point group structure of the molecular structure and the presence of a three-fold axis 3 fold, rotational accessed about any carbon-hydrogen bond and there are four such threefold axis, introduce us be generous ease in the vibrational frequencies I mentioned this in the last lecture and so you can see that three of the vibrational modes are degenerate with the frequency 1413 centimetre inverse two others have a different frequency of 1624 centimetre inverse and then three others have degeneracy with three thousand two hundred and forty seven forty eight centimetre inverse and these are the stretching modes the symmetric and anti symmetric stretching mores that you see here three thousand one hundred and eleven and the 3248 centimetre inverse these are the high frequency modes and these are basically born stretching vibrations and all the others are bending and torsional vibrations let us see the vibrational motion of the first frequency 1413 centimetre inverse you can see that this is a bending mode or you can also call it and to see how it works so you can see that this is typical a pair of the plane of the bend hch is constantly changing now since you have four atoms you can pick two pairs.
But then these two pairs can be picked in three different ways. Therefore whatever you see here, has one pair, doing in the other degree of freedom, you will see another pair, doing the same thing.

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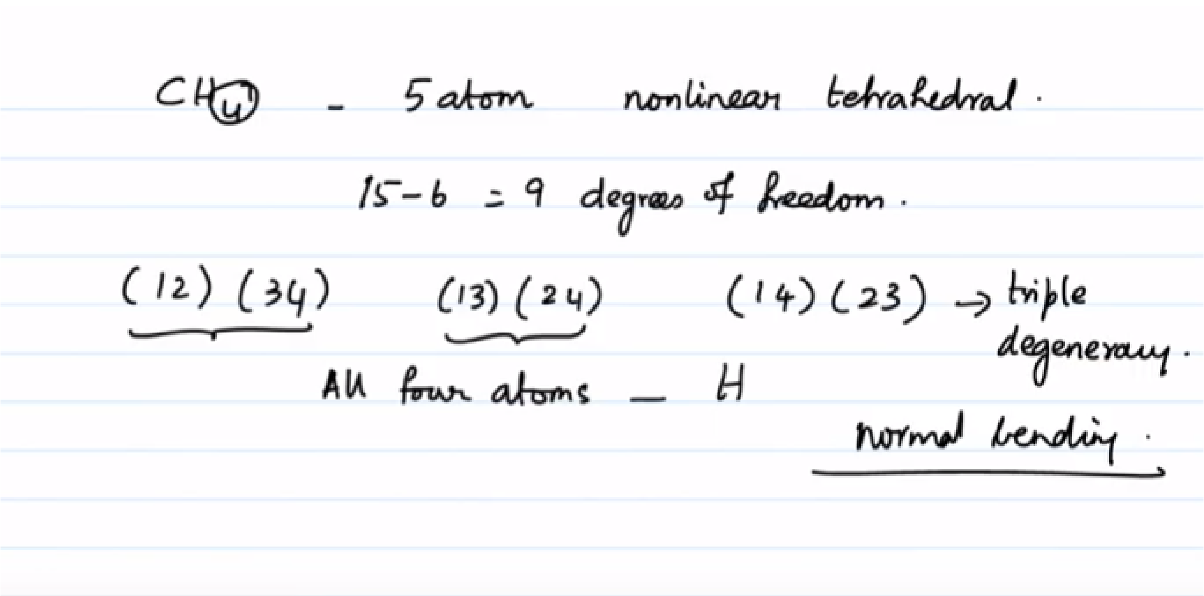

CH_4 - 5 atom nonlinear tetrahedral.

$15-6=9$ degrees of freedom.

$\underbrace{(12)\,(34)}$ $\underbrace{(13)\,(24)}$ $(14)\,(23)$ → triple degeneracy.

All four atoms — H

normal bending.

You see that it is like one two as one pair 3 4 as another pair, the motions are some things like this 1 2 3 4 the motion associated with this is identical to the other pair 1 3 2 4 and it is also the same thing as 1 4 2 3 it is so in this case because all four atoms or hydrogen atoms identical, these four hydrogen atoms, therefore the motion of these four atoms in pairs there are three pairs and therefore you have three frequencies this is what is called, The Triple Degeneracy.’ Normal vibrations normal, it is a bending more now let us go to the the other one also. Okay, let us look at to the sixteen hundred and twenty yeah you can see the fourteen, thirteen, the next one you see, the other two pairs do exactly the same degree of same motion so look at the sixteen twenty-four now this is a very different motion and this is doubly degenerate you can see that.

So these are the only two different ways by which this particular bending motion can be created. Now the high frequency vibration little more three thousand, one hundred, centimetre inverse is what is called,’ The Symmetric Stretching Mode.’ Let me just show that. Okay, you see if I can see that in something, yeah I think this is there more clear exactly a perspective view, you can see all the four bonds, stretch identically and quite of course meet in does not have a dipole moment and in this motion throughout the motion eteor, also will not have a dipole moment created at any point of time. Because any dipole created in one direction is going to be compensated by the dipoles, the collective dipoles created opposite to that and therefore this motion is dipole free motion and you can see the zero associated with the dipole free essentially means, that this cannot be detected by the infrared spectroscopy infrared spectrum cannot contain this, this can be detected only using Raman spectroscopy. Okay, this is a symmetric stretch and then you have anti-symmetric stretch you can see that two of, yeah you see that two of the bonds stretch and tied to each other one bond is shortened while the other bond is lengthened. This clearly introduces dipole moment during the vibration and the rest of the atoms move to ensure that the centre of mass of the molecule does not move away and there is no translation.

Therefore this is a genuine vibration and since you have a pair of these molecules undergoing the symmetric and anti-symmetric, that is stretching and the shortening while the other pair undergoes the the balancing act, again this can be three different ways of doing it. So if you call this as 1 2, if you call the the two atoms which undergo stretching as 1 2 and the other as 3 4 then you will have 1 2 3 4 1 3 2 4 and 1 4 2 3 and those are the three different vibrational frequencies, that you can see and in this case you can see the stretching and the anti symmetric stretching or clearly seen by all the others. Okay and the third one, is in a similar way. Okay therefore this is an example of the nine normal modes that can be visualized using a simple three-dimensional program and a three-dimensional viewer.

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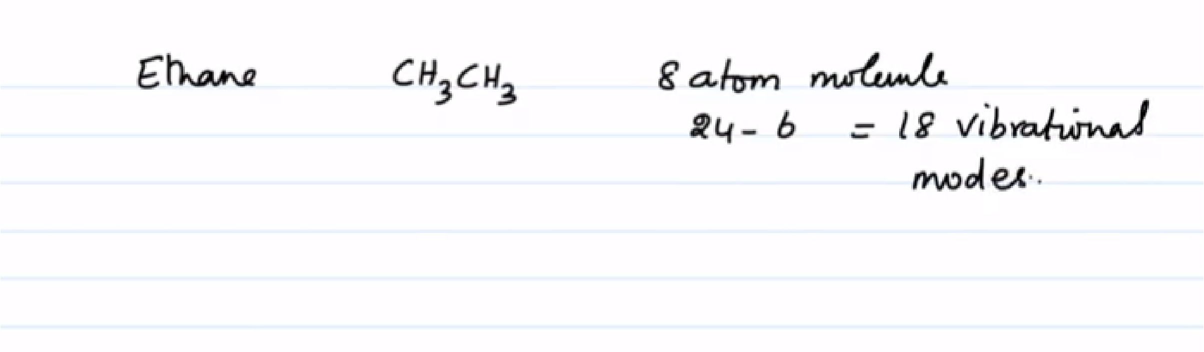

Ethane CH_3CH_3 8 atom molecule

24 - 6 = 18 vibrational modes.

Okay let us move on to the next molecular system eighteen CH3 CH3, it is eight atom molecule and it has 24 - 618 vibrational modes. This also has the three-fold axis symmetry, so this model this is the vibrational the spectrum of attained that we will see. Okay, so in this form you can see that two tetrahedrons.

Okay, from here of course you see what is called the staggered configuration, not the eclipsed configuration. This is a staggered configuration and you can see that the two **tetrahedral.** There are 18 frequencies, which you can see numbered from the 1 to 18 here and attained also does not have a dipole moment, 0 dipole moment molecule. But some words of 18 during the vibration will create the dipole and then the dipole will go to 0, dipole moment will go to 0, increase to some value go to 0 and so on. So those modes are **infrared** active and the other modes which are not internet active, will be common active, so here is the low frequency mode of 330 centimetre inverse these energies which are calculated from quantum chemistry packages, are approximate. There is an error of between 5 to 10% depending on the level of accuracy, that you have the level of approximation, that you have one of the goals of quantum chemistry is to simulate and obtain the vibrational frequencies very very precisely by including on harmonic motion. Also we will not worry about that in this lecture. We want to see qualitative picture of what are called the collective vibrational modes or normal vibrational modes.

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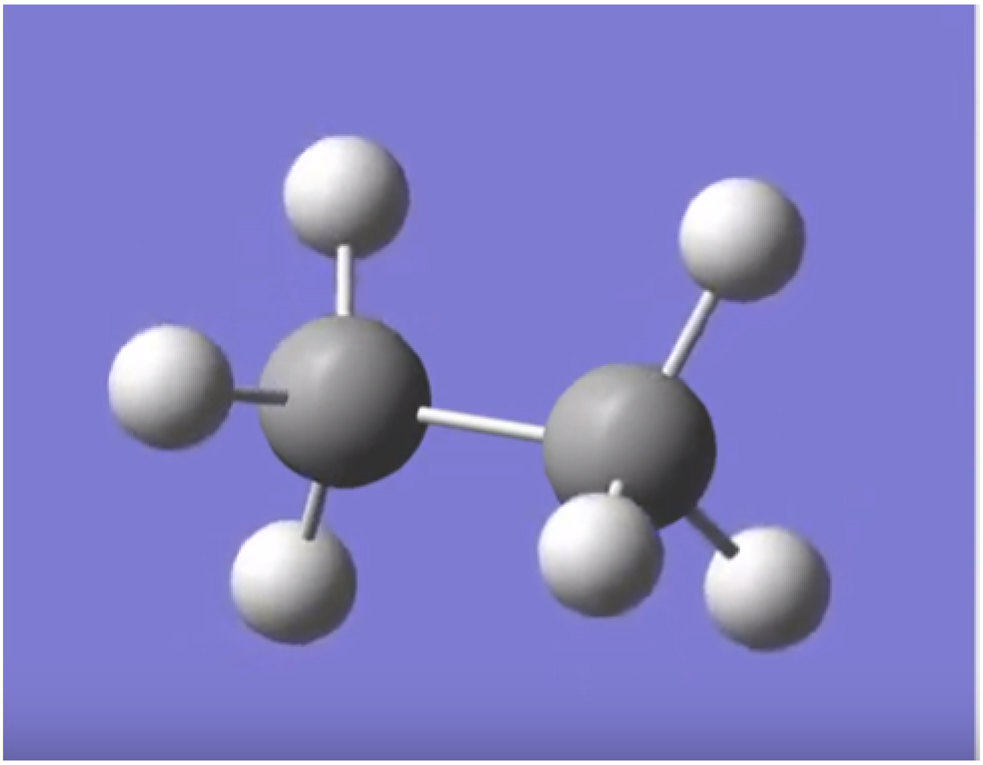

So let us start with the lowest frequency vibrational mode 3 31 centimetre inverse, you can see that the Rings rotate relative to each other. This is what is called generally called, ‘A Torsional Motion’. Okay they the motion is the Rings, the two three three three four, what is this the two fragments, the metal fragments, rotate relative to each other.
Okay, let us take the next one ,which is a doubly degenerate bore 849 8 and 50 centimetre inverse. Now you can see that this is more like the-- the two benzene are the two metal fragments. The bending motion generally creates a dipole moment in that process, because the dipole moment is probably in this direction and then it goes to zero in this direction and then it goes to zero you can see that and now the other thing that you have to see that the motion of carbon atoms. The amplitude of carbon atom vibrational motion you and see that is much smaller, than the amplitude of the vibrational motion of the hydrogen atom, which is also something that I said in the last lecture that in normal vibrations atoms vibrate with amplitudes which are inversely proportional to the square root of the masses and you can see that carbon is much much heavier, 12 times heavier than the hydrogen atom and therefore 1 by square root of 12 its amplitude is roughly one third of the slightly more than one third of the slightly less than one third of the amplitude of vibration of the hydrogen

atom or the bending motion the other motion 843 9 is basically the other plane it is in the other plane perpendicular to that plane.

Okay now let us see the next degree next motion namely 1049 very easy it is a symmetric but it is a carbon-carbon stretched CC bond stretch no dipole, because the dipole moment is zero throughout in this process the dipole created by this carbon this carbon carbon bond is cancelled by the dipole created by this carbon-carbon bond and therefore the other things don't move for to this 1200 and 1270. Let us see so this is again. Bending involving as well as the carbon and the hydrogen atoms there are two such motions. Both are degenerate, so you can see that it is in the other plane, you can see that the next vibrational more is the 1464 centimetre inverse the methyl groups if you look at it. If you look at these methyl groups, they are opening and closing, like the umbrella will close. For example, this is closing of the umbrella, while this is opening up and you can see that they are in the opposite directions and therefore there is a net dipole moment created during the motion and then it goes to zero and again the amplitudes of carbon are much less relative to the amplitudes of the bending hydrogen atoms and this has a large dipole moment and therefore this can be detected by the **infrared** spectroscopy techniques then let us go to the next one 1491 centimetre inverse this is also very similar and to see no they here they are opposite, sorry, it is not similar the one umbrella closes, while the other umbrella opens you see that as this goes up this also goes up, the therefore wait no as one umbrella closes, this also closes.

Therefore these two modes cancel each other, so there is no dipole moment in this process. Yeah, the motions are opposite to each other therefore this is the bending motion like the umbrella. In version 15 1568 you can see that it is also doubly degenerate modes. So what is happening here? Let us see. Yeah, you can see the motion of the two hydrogen atoms relative to the in the opposite extent moving, this is another normal mode, let us go to the more energetic one the the bond stretching and the symmetric and anti-symmetric stretching. Okay, this is the anti symmetric stretching of the carbon hydrogen bonds you can see that that one bond stretches, while the other born then shortens. What about this? Yeah, this is also anti symmetric stretching, then you will have a no this is also two of the bonds are shortened, while the other board is lengthened. So this is also anti-symmetric stretch. Okay, so there is no symmetric stretch here oh there is, okay, all the three are symmetrically stretched you can see that all these three are symmetrically stretched, while all these three are also symmetrically stretched and that frequency is 3112 centimetre inverse and you can see that these stretches are in the opposite direction, for this one and this one. Therefore, there is a net dipole moment as a result of which, this mode is also infrared active.

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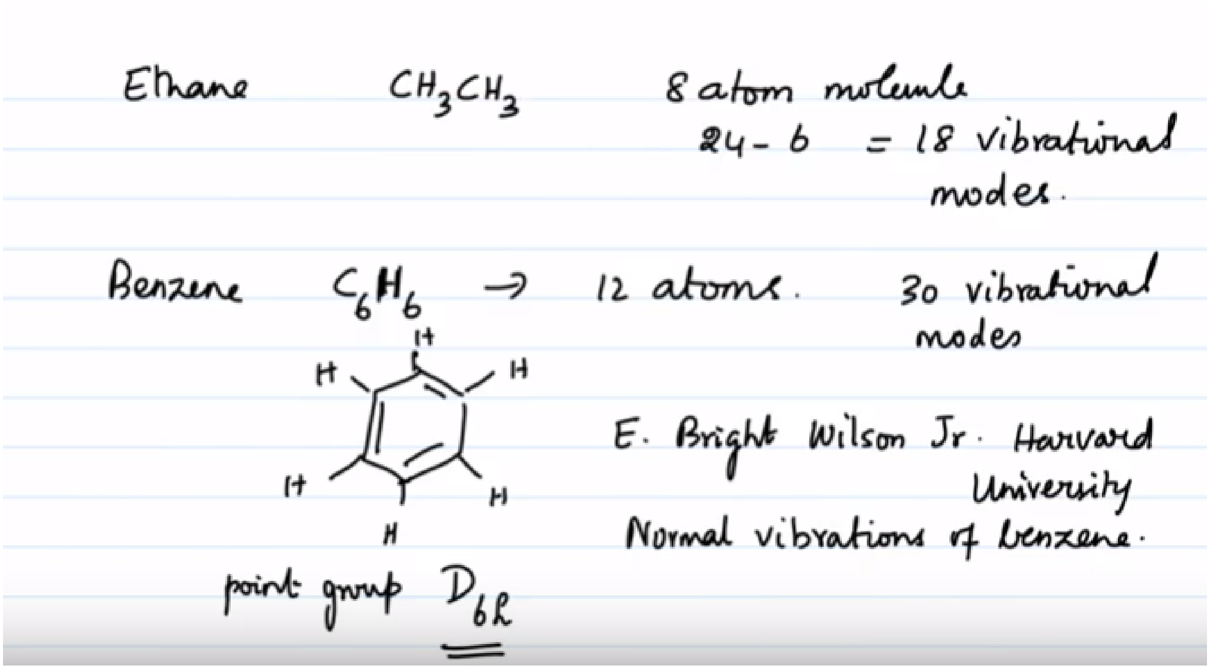

Ethane CH_3CH_3 8 atom molecule

$24 - 6 = 18$ vibrational modes.

Benzene C_6H_6 → 12 atoms. 30 vibrational modes

E. Bright Wilson Jr. Harvard University

Normal vibrations of benzene.

point group D_{6h}

Okay, this is 418 let us go to the last example of this lecture namely benzene c6h6 most important organic molecule among the most important organic molecules, 12 atoms a plane or molecular configuration, with all the hydrogen atoms, in the hexagon symmetric perfect hexagon. This is not, but the molecule is a perfect hexagon and so twelve atoms there, are thirty vibrational mores very beautiful paper in the early thirties by professor E bright Wilson jr. in Harvard University. He is also credited with having guided many many students more than 10 or 15 of his students have won Nobel prizes in chemistry for their contributions in many different areas. There was one of the best-known vibrational spectroscopy and Wilson and Hobart produced the best the most important simplification on the molecular rotational vibrational Hamiltonian in 1936. So it is a very well-known name right Wilson jr. Studied the normal vibrations of benzene and provided some classifications on the symmetry classifications of these benzene benzene is the it belongs to the molecular point group. When you study group Theory, you will see this belongs to a point group known as d6h it has a six-fold axis of symmetry very highly symmetric system and therefore many of its vibrational modes, are also regenerate.

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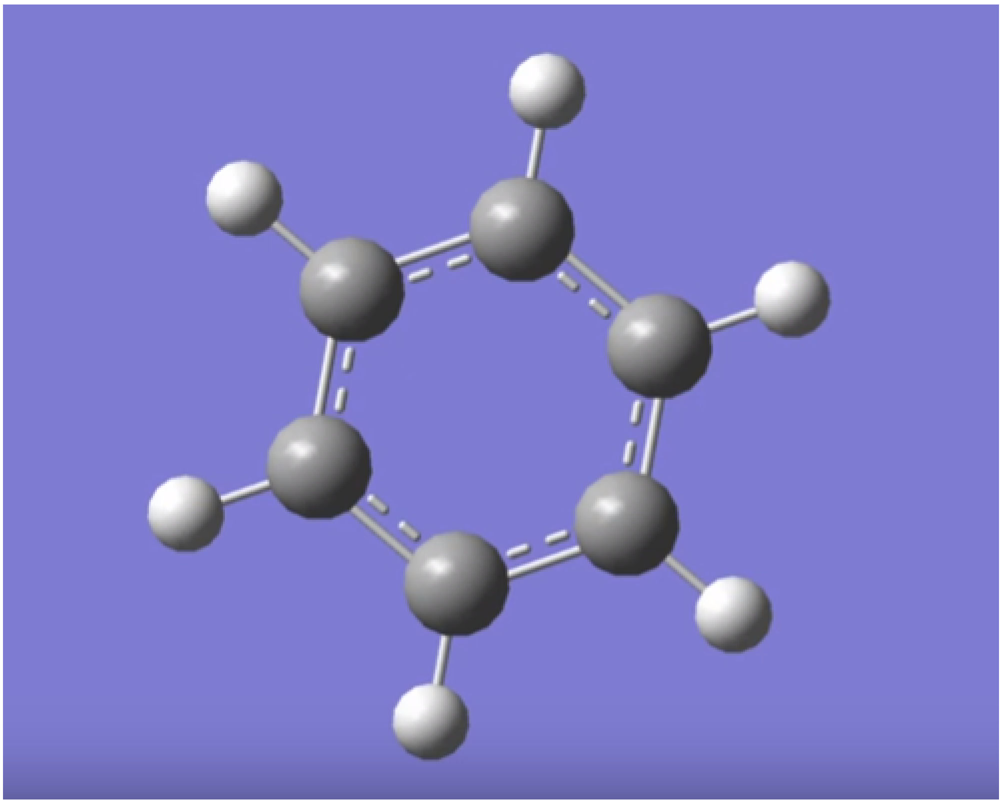

Let us look at the vibrational frequencies here so there are 30 vibrational modes as you can see 1 2 30 and the lowest vibrational frequency is 413 414 centimetre inverse and what it does, ok it is not seen from here and you rotate you can see how the plane oddity of benzene is lost. So this is a the motion that destroys the planar structure of benzene, due to the vibrational motion of the carbon atom, the two carbon atoms in and out of the plane and the carbon of course as a CH entity as a CH entity most the CH entity and the CH entity move in such a way, that the rest of the frame moves in the opposite direction. There is no dipole created in this process and this is not infrared active the other 414 is now the the ring. Whatever that was not moving very fast now it is moving in that direction with the to the CH fragments moving very slowly compared this with that you see that so this is one in plane out of plane Bend and this is the other in plane out of plane motion. Okay, then there is the next one at 600 621 centimetre inverse Wow the ring is distorted it is no longer a symmetric six-fold ring, but it stretches and then comes back to equilibrium. It is also emotions, such that, there is no dipole produced, because you can see for any one particular motion for example, of this fragment the opposite fragment and the other side moves in the opposite direction you can see that if this goes away this goes in and if this moves away this moves in so that there's no net dipole movement the next one is of course. It is a similar motion, except that this is about the other plane you can see this is about one plane one set of axis and this is about the other then you have a very large infrared active more 693 centimetre inverse. You can see that the whole of all the six hydrogen atoms move out of plane and their amplitudes is much higher much larger than the amplitude of the benzene ring, the all the carbon rings which move very slowly to compensate the centre of mass remains exactly where they where it is throughout the motion, but in this mode of course a dipole is created significantly during the motion because if all the six hydrogen atoms move in one direction your dipole is created along this axis and then it goes to zero and so on so you see that this is infrared Actium it is easy you have to rotate to see the perspective view of these normal modes. Okay, then there is the 717 centimetre inverse, in which you can see that the a group this entire group of CH this whole moves in, one this is in one direction, this is in the opposite and then likewise for the other. I mean all of these motions destroy the symmetry of the plane of benzene; however the dipole moment is not there 863 centimetre inverse there are several of them. There are two of them and you can see that one it is the pair of one set of hydrogen atoms and it is the other in the other motion.

So let us go to the last example of this namely the 3215 centimetre inverse the whole ring is breathing in and breathing out, this is symmetric stretch of all the six hydrogen atoms identical extent and the ring closes in, just to ensure that there is no translational motion so this is the other the most symmetric of the normal modes and this mode obviously has the highest symmetry that it is not changed by any of these symmetry operations, that you can perform on the benzene ring the anti-symmetric stretch is given by this 3200 centimetre inverse you can see that, yeah this is anti-symmetric the two hydrogen atoms when they stretch these two hydrogen atoms close him and opposite and you can obviously have one more mode in which the similar thing happens with the other hydrogen atoms and this these modes are highly intra and active the three thousand 188 centimetre inverse it is also anti-symmetric stretch. But please note that this does not produce any dipole moment freeze it for a moment. See that the atoms are moving in the opposite directions and therefore you see that there is no dipole in this process, this is the ring is I do not know, that it is called, the puckered ring puckering motion or it is it is definitely the distortion of the ring in a very very serious way. It is approximately half the frequency of the complete least stretch symmetric stretch frequency no there are hundreds of molecule there are thousands of molecules, probably tens of thousands of molecules, that people have explored using this program called the Gaussian and enables us to calculate many molecular properties from ab initio quantum chemistry and vibrational motion can also be studied more carefully using some of the more accurate components of the Gaussian program.

The purpose of this lecture is to visually illustrate, that there are what are called the collective motions of the atoms, in the form of normal boards and that these normal more follow an exact mathematical description, that we are familiar from classical mechanics and it is possible for us to measure these things, experimentally and correlate molecular degrees of freedom with the properties, whether they are infrared active, whether they are Raman active, whether one can study the bond length and bond angles, which the torsional angers and therefore, whether there are internal potentials for molecule fragments, rotating relative to each other and so on. So your whole lot of molecular properties, can be understood using vibrational spectroscopy. However, we have to come to a close on this topic, for this course. The next two or three lectures will be on molecular rotations and we will look at microwave spectroscopy of a simple diatomic molecule followed by a few symmetric top molecules, with that we will come to an end of this course, we until the next lecture on rotation spectroscopy starts.

Thank you very much .