# Chemistry II: Introduction to Molecular Spectroscopy

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## Lecture – 13
## Normal Vibrational Modes Polyatomic Molecules

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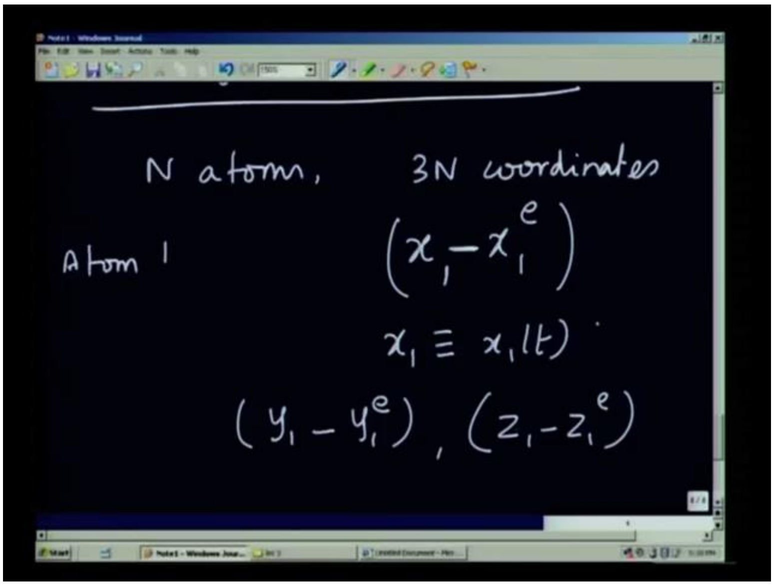

N atom, 3N coordinates

Atom 1 $\left(x_1 - x_1^e\right)$

$x_1 \equiv x_1(t)$

$\left(y_1 - y_1^e\right), \left(z_1 - z_1^e\right)$

A bit of quantitative consideration, we will not derive it, but let me explain what it means. Recall that that a polyatomic molecule has n atoms 3 n coordinates, and during the oscillation, or during the vibration each 1 of the atoms is expected to go away from it is equilibrium position. So, if you think atom 1, as having a coordinate x 1, equilibrium, and it is instantaneous atom 1, x 1 equilibrium and at any instant of time, it has a position, amplitude, x 1, the difference between the two, x 1 minus x 1 equilibrium is the amplitude of the oscillation. x 1 is a function of time x 1 equilibrium is not, x 1 is x 1 of t, it is a function of time, therefore, during the oscillation the x 1 changes, and as a changes the amplitude there is a vibrational amplitude, which is increased and it goes to 0 and it increases and so on.

So, this is for the x coordinate of the first atom, and likewise for the y coordinate of the atom y 1, y 1, e, and z coordinate is z 1, minus z 1 e. Now when you ask me what these coordinates are, if you have to ask me, how do we define the axis system, let us assume that these axes system the x y z axes remains fixed at the center of mass of the molecule, this is a classical picture, please remember that. In quantum mechanics there is a problem in fixing the center of mass to a particular point, if the total momentum of the molecule is conserved there is a problem, let us not worry about that.

Let us worry about the fact that we have the axes system fixed at the center of mass of the molecule and we talk about the 3 coordinates of atom 1, then with respect to the polyatomic molecule, if I may draw the picture.

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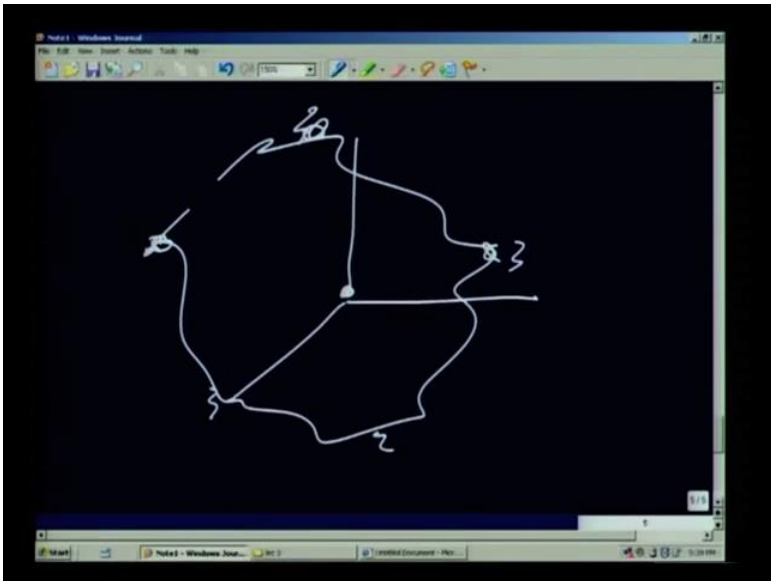

So, let us assume that some 3 dimensional blobs, of a polyatomic molecule with various atoms in positions, bonded to each other and let us assume that the center of mass is somewhere here, we will draw 3 axes system, there are reasons there are specific methods for assigning these axes system, do not very about it.

Let us assume, as a first drawn picture that we can assign an axes system and we can find out that how this atoms goes away with respect to it is equilibrium position, during the vibration, that vibrational vector amplitude is projected on to this axes system into 3 components, x component, y component, and z component and let us call those as a 3 coordinates for atom 1, and likewise, if we write for atom 2, similarly x 2 minus x 2 of e, as the x coordinate, y 2 minus y 2 of e, z 2 minus z 2 of e, and likewise we can do this for all the n atoms, n atoms.

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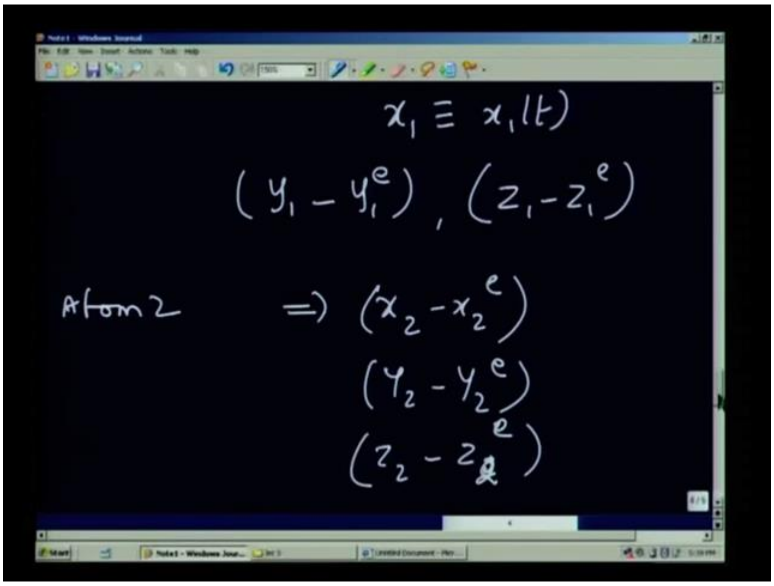

$$x_1 \equiv x_1(t)$$

$$(y_1 - y_1^e)\ ,\ (z_1 - z_1^e)$$

Atom 2 $\Rightarrow (x_2 - x_2^e)$

$$(y_2 - y_2^e)$$

$$(z_2 - z_2^e)$$

So, we have 3 n coordinates, which are likely to change during vibrational motion of this molecule 3 n coordinates.

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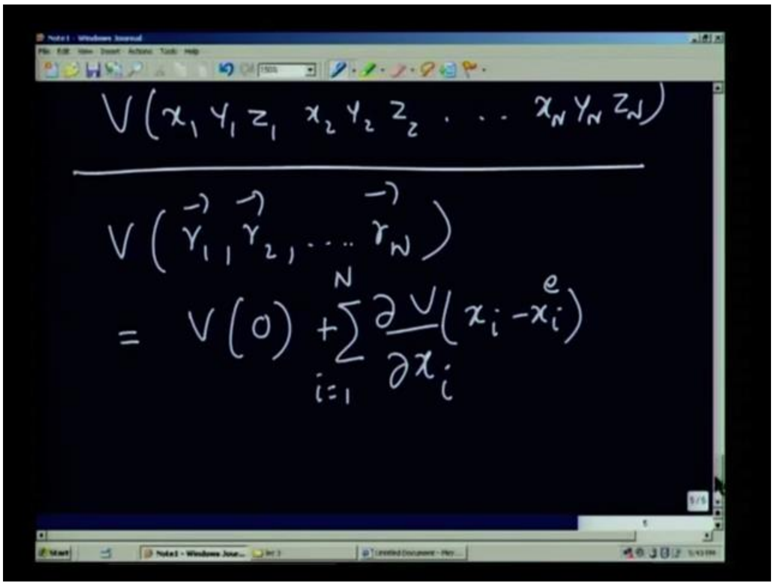

$$V(x_1\, y_1\, z_1\ \ x_2\, y_2\, z_2\ \ldots\ x_N\, y_N\, z_N)$$

$$V(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)$$

$$= V(0) + \sum_{i=1}^{N} \frac{\partial V}{\partial x_i}(x_i - x_i^e)$$

Therefore the potential energy of the molecule, during the vibration, is a function of all these coordinates x 1, y 1, z 1, x 2, y 2, z 2, x n, y n, z n. Remember this was not a problem for the diatomic molecule, because in the case of diatomic molecule we consider only the relative displacement of the atoms with respect to each other, 1 coordinate, now we have got 3 n coordinates. The potential energy in the case of a diatomic molecule depended on that 1 coordinate in the form of k x square, where x is the amplitude of the vibration.

Now when you have a polyatomic molecule with 3 n such coordinates, you see that the potential energy is going to be a function of all these 3 n coordinates, therefore, it is a much more difficult function to write and this were the approximation of a harmonic oscillator like approximation, comes out very handy, comes in very handy, right, the normal modes as you will see in a few minutes, are nothing other than the extension of the harmonic oscillator diatomic molecule to harmonic motions of all the 3 n minus 6 degrees of freedom of a polyatomic molecule restricted to quadratic in the amplitudes. k x square is the quadratic in the amplitude x and if you do that in the case of a polyatomic molecule, as a quadratic to every such atomic amplitude, then what you get out these the solution called normal mode solution. This is all known in classical mechanics.

And in quantum mechanics again, you take this picture directly and then you construct the vibrational Hamiltonian, and solve for the quantum mechanical normal modes of vibration for a polyatomic molecule. So, if we have to write the potential energy as a function of all these coordinates and, let me write them as simply r 1, vector r 2, r n, if we write this as n vectors, you see that for amplitudes of vibration, the potential energy is nothing, but a constant value corresponding to this amplitudes all being 0, what is meant by that? Every difference x 2 minus x 2 e, y 2 minus y 2 e, z 2 minus z 2 e, likewise all the amplitudes are 0, v 0, corresponding to equilibrium concentration, equilibrium geometry, then we have sum over, let me not specify what they are.

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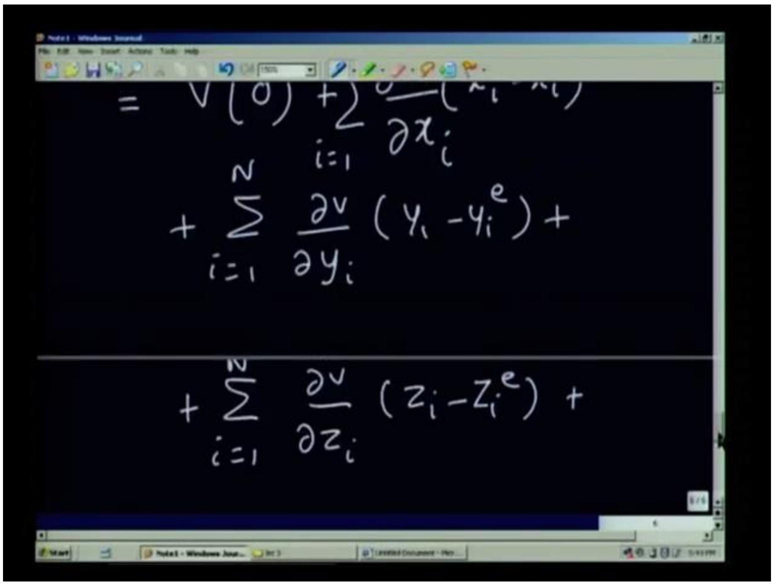

$$= V(0) + \sum_{i=1} \frac{}{\partial x_i}$$

$$+ \sum_{i=1}^{N} \frac{\partial v}{\partial y_i}(y_i - y_i^e) +$$

$$+ \sum_{i=1}^{N} \frac{\partial v}{\partial z_i}(z_i - Z_i^e) +$$

But sum over, every coordinate dou v by dou x I, x I minus x I e, sum over I equal to 1 to n, plus again I equal to 1 to n, dou v by dou y I, y I minus y I e, this is a Taylor series, plus, some over I equal to 1 to n, dou v by dou z I, times z I minus z I e, and what you have is nothing, but the first derivative in the Taylor series of a multidimensional function, dou v, dou v and if you extent this to the quadratic term, which you have is 1 by 2, sum over I, not equal to j, dou square v, by dou x I, dou x j, x I minus x I e, x j minus x j e, and you can write 5 more such products, corresponding to y I y j, z I z j, then x I y j, x I z j, y I z j.

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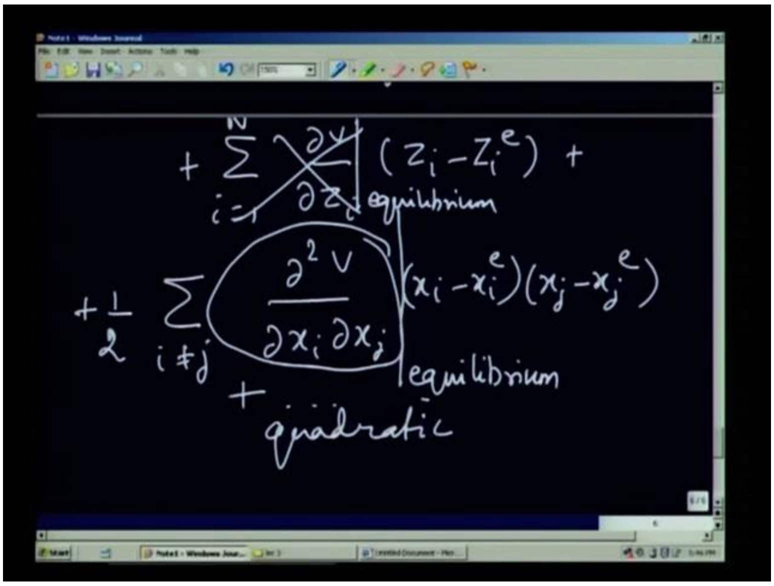

$$+ \sum_{i=1}^{N} \cancel{\frac{\partial v}{\partial z_i}}(z_i - Z_i^e) +$$

equilibrium

$$+ \frac{1}{2} \sum_{i \neq j} \frac{\partial^2 V}{\partial x_i \partial x_j}(x_i - x_i^e)(x_j - x_j^e)$$

equilibrium

+ quadratic

There are 6 such terms and this is called the quadratic term. It is quadratic. Because you see this is a constant evaluated at equilibrium. This is evaluated at equilibrium therefore, these are all constants, this is evaluated at equilibrium.

Now, if the potential is a minimum, is an absolute minimum, we have a way of saying let us ignore the potential, these equal to 0. This is again goes back to the harmonic oscillator model. We remember the force as minus k x, we integrated the force by writing them as a negative derivative of the potential, and then we set the potential at x is equal to 0, to be 0, as a scale, that is our minimum. And in the same way if we assume that the equilibrium geometry, has the smallest potential energy lest assume that to be the minimum therefore, with respect to the minimum, you remember, the minimum is defined by the requirement, of all the derivatives of the potential with respect to the first coordinate, as you have here, this one, all the derivatives will also be 0, radiant is 0 at the minimum with respect to that coordinate, therefore, if we write the potential energy, using the small amplitude approximation as a Taylor series, this goes to 0 by our scale, this goes to 0 by the requirement that the potential is minimum, this goes to 0 by the requirement that the potential is minimum, and also this, and therefore, the very first term that is non-zero, is the quadratic term.

The quadratic term unfortunately contains the x coordinate of 1 atom and the x coordinate of the other atom, it contains the x coordinate of 1 atom, and z coordinate of the other atom, therefore, quadratic is the mixed quadratic. The normal approximation or the procedure is a procedure by which we are able to rewrite this, in the form of new coordinates, which will contain only the squares of the individual atoms.

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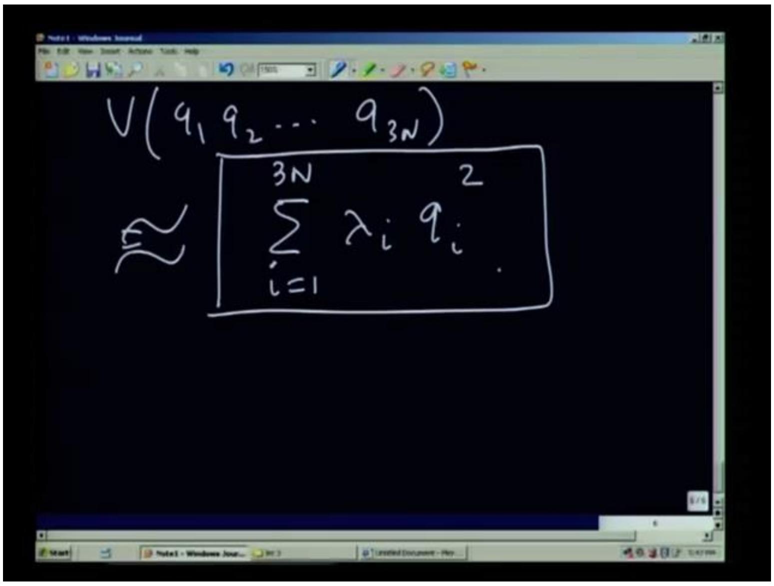

$$V(q_1\, q_2 \cdots q_{3N}) \approx \boxed{\sum_{i=1}^{3N} \lambda_i\, q_i^{2}}$$

When you write this v, in the form of new coordinates q 1, q 2 q 3 n, such that the potential energy is to first approximation, nothing other than, sum over I, a constant lambda I, q I square, I equal to 1 to 3 n, as opposed to what you have here, what you have here is a constant, which is the function of the 2 labels, atom I and atom j, this is a lambda I j equivalent, but now if you are able to do an analytical procedure. So, that this is changed into this new coordinate. So, that the potential energy is nothing other than lambda I, q I square, where now q I are defined as a new amplitudes. This procedure is something that one can do analytically, there is no problem with that, and if you cannot do analytically for large molecules, we can subject the procedure to a computer program and we can get the results numerically, you will see all the animations that I will show you in the next few minutes, are based on a procedure of converting them into this form.

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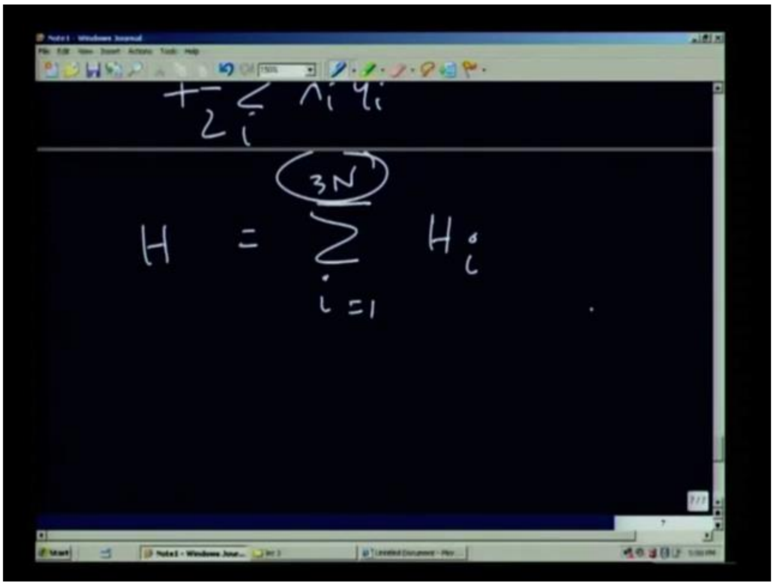

$$+ \frac{1}{2} \sum_i \lambda_i q_i$$

$$H = \sum_{i=1}^{3N} H_i$$

And so, what you have is h, is nothing, but some over all the atoms of the individual harmonic oscillator, I equal to 1 to 3 n, except that now we have 3 n coordinates, and therefore, what we have is, of these 3 n coordinates, if we remove the 6 degrees of freedom for a linear, for a non-linear system we get 3 n minus 6 normal coordinates, corresponding to the q I, this is a very, very gross way of explaining things, but mathematically if we have to do it, it gets somewhat complicated, the procedures are well known.

Now, let us see for some real molecular cases, what this will lead to, for vibrational motions of the polyatomic molecule. Let us see it one by one, and with a few examples.

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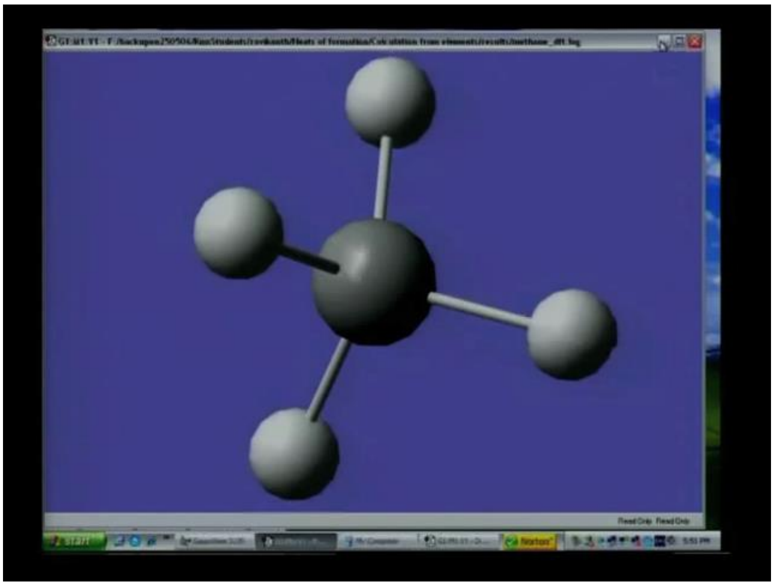

So, what I have here in this program, I am I am using a program known as Gaussian in chemistry, it is 1 of the most important programs in computational chemistry, for the discovery of this program, Professor John Porter from Carning (Refer Time: 13:14) university, when he did most of this work, got the Noble prize. He shared it with Walter Corn for computational chemistry. Walter Corn devised the procedure what is called density functional theory, for computing the energies, and the, the quantum mechanics of atoms and molecules.

This is a program which provides you the animations, and calculations that are shown, that use to provide you the animation, the calculations are all, they are all numerically very accurate calculations. So, here, what I have is the tetrahedral molecule of methane. Again you see that methane, as is does not have a dipole moment, but there are going to be some vibrational modes in which, the atoms change unsymmetrically, and therefore, dipole moments will be introduced. Let us see that, by way of simple definitions, that this a 5 atom molecule therefore, there are 15 degrees of freedom, 6 degrees these are non-linear molecule, tetrahedral, therefore, 6 degrees of freedom go towards rotation and translation, there are remaining 9 degrees of freedom.

Now, molecule is highly symmetric, and therefore, some of these vibrational degrees of freedom have the same energies, and same frequencies. Let us look at this table which is not very clear to you, but in this table there are 9 vibrational degrees of freedom, each with the vibrational frequency given here, and what is here is the first 3 vibrational frequency are the same, the next 2 vibrational frequencies are the same, this is different, and then there is another vibrational mode for which all the 3 frequencies are degenerate, but the vibrational motions will be different.

Let us take the first one, 1373.5 centimeter inverse. We will start the vibrational motion and see what it looks like. So, this is a, clearly the way you look at it, this is the bending motion, look at it from angle, you see that what you have here is the bending of 2 atoms, these 2 atoms in 1 plane, and those 2 atoms in the other plane, just look around, this is clear in this view, the pair of atoms in a plain perpendicular to the pair of atoms in the other plain, undergoing the bending motion. This is one of the normal vibrational modes for methane. Let us stop this, and there is another vibrational mode with the same energy, now it is easy for you to remember that there should be at least 2 other modes.

Let us look at, why it should be. See what kind of bending that takes place, which modes are bent here, see that these 2 atoms are bent, and this is the other vibrational normal mode, let us look at what is the third one, is this is the third vibrational normal mode. So, the bending about various axes, there are 3 such equivalent bending modes, in this case. What about the next one, the frequency is now 1593 centimeter inverse, and again this is a bending vibrational mode, you see that these 2 bonds are bent, and there are relative variations positional angle variations and all of this.

The bending motion is generally of a lower energy than the stretching motion, the stretching means you are stretching a given bond like a c h, which is a fairly strong in energy, therefore, let us look at one of the stretching motions, and see what it is, with a very high energy, you can see that this bond is being stretched, and likewise the other bond is being stretched, and there is a certain amount of synchronization, look at it very carefully, all the 4 atoms are displaced from the equilibrium, by the same, during the same time, by the same amount, because all 4 are hydrogen, same mass, and the positions of the atom instantaneously at any point is such that, you see that there is a dipole moment created during the motion. There is a net dipole moment, which gets created, increases and then decreases to 0 and so on. Therefore, this is an infrared active mode, that it can be detected using infrared spectroscopy.

Now, let me look at another such bending mode, sorry another such the stretching mode, and what you see here is again, the stretching of the atoms in a different way, there are very specific rules for determining these oscillations, these amplitudes, and these were given elaborately by professor Herzberg in his most famous the monograph on molecular spectroscopy, professor Gerhard Herzberg did most of his research on this in Canada, let us look at one vibrational mode which is very interesting namely, the symmetric stretch. Let us looks at that, all the atoms vibrate about the breath in and breath out with respect to the equilibrium position, and in this motion of course, there is not a single instance where there is a dipole moment, therefore, this there is no dipole moment during the motion, and there is no dipole moment for equilibrium structure of methane, and therefore, this is not infrared active, this cannot be detected. This is for benzene, this is for methane.

Let us look at some interesting case like the slightly more numerous atom molecule. Let us look at the normal modes of vibration of benzene. It is a very classic example, one of the most important aromatic molecules of course, c 6 h 6, 12 atoms, 36 degrees of freedom, 3 n, 3 n minus 6, benzene is a non-linear molecule, planer in it is equilibrium geometry, and what you have is 30 vibrational degrees of freedom. Also benzene has a very symmetric structure and therefore, by the rule of nature, by the law of nature, benzene also has several vibrational modes which are degenerate. The important thing to note is that, benzene does not have any vibrational mode, which is more than w degenerate, the previous molecule that I talked about, the ben, the methane molecule, has 2 degrees of freedom which are triply degenerate, because of certain types of symmetry, the molecular symmetry and molecular vibrations are intimately connected to each other, is not about, this lecture is not about it, but let us look at the benzene vibrational modes to see a little bit more about what normal modes are.

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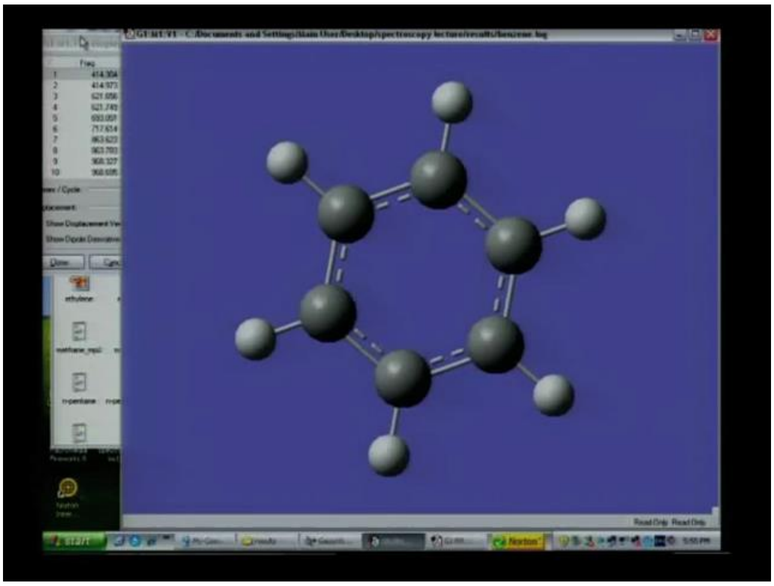

So, let me first locate a very low energy vibration 4 1 4, 304, 0.304, that is 414 centimeter inverse, this is theoretically calculated numbers, there are 30 vibrational degrees of freedom. Let us look at the first one, and start the animation to see how they look like. Nothing seems to be happening on the screen, but if I just move the plane of the molecule, to a slightly better perspective view, you can see that the atoms are vibrating; this is nothing but the ring the benzene ring getting distorted. See that 2 of the atoms come out of the plane, and other 4 atoms remain, and this motion is such that, a there is no net dipole moment created, because whatever is the dipole that is created by these 2 groups, is annulled by the other 4 groups. There is no dipole moment; therefore, this cannot be detected by infrared spectroscopy.

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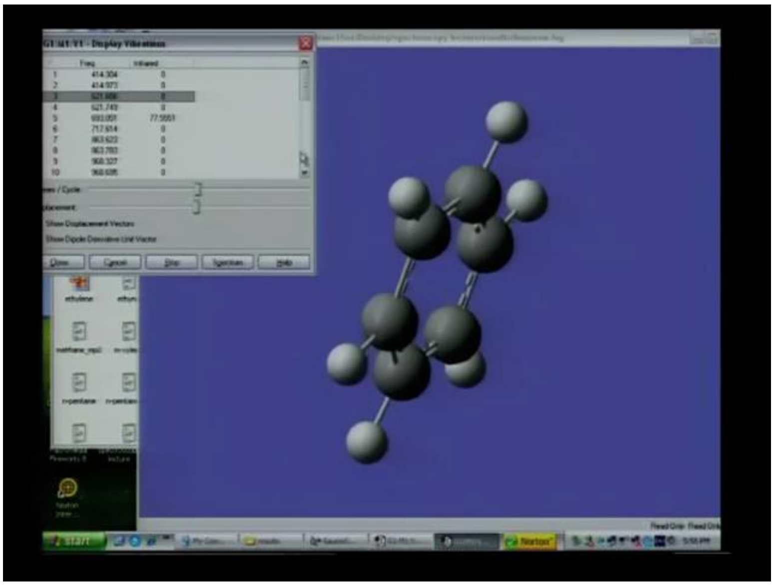

Now, let me look at another benzene vibrational degrees of freedom, degree of freedom and here is another one, this is also such that, the, you can see that the rings are getting distorted, almost like the benzene is dancing into the tune of a molecular motion.

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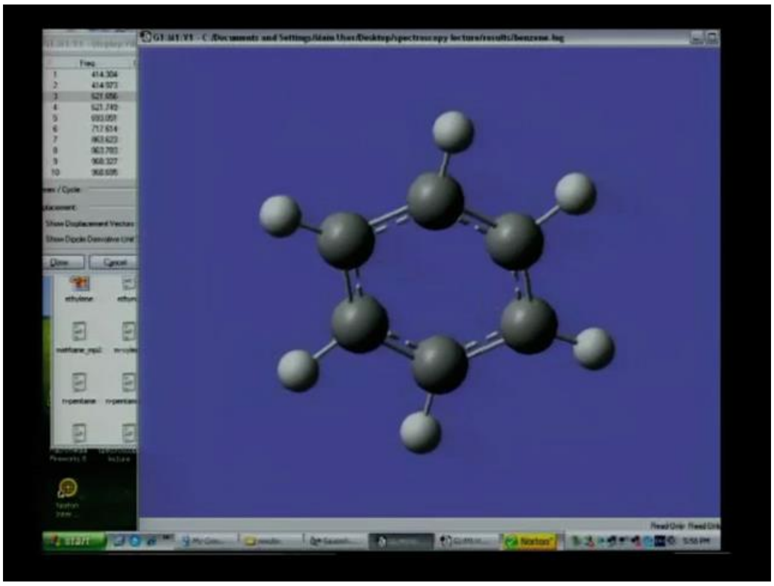

Again if you are look at carefully, there is no dipole moment at any instant of time, because the atoms are exactly oppositely placed, as the molecule vibrates, for this atoms position this is compensating, for this atoms position this is compensating, and for this,

this is compensating, there is no net dipole moment, during the vibration therefore, this is also infrared inactive.

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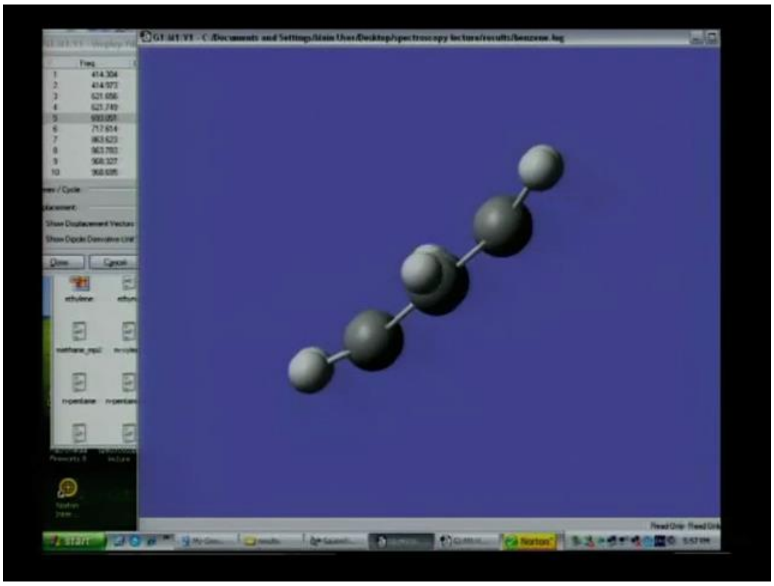

Let us look at another motion where, which has a large dipole moment, the all of the hydrogen atoms, come down on the plane, but to keep center of mass of the molecule constant, you see the benzene atom, the carbon atoms, go up the plane. Look at it very carefully this way, you can see it, let me just rotate the molecule in such a way that you can actually see it yes, you can see that that with respect to this, that there is a very slight displacement of the carbon atoms, above the plane while there is a large displacement of the hydrogen atoms below the plane, above and below the if you look at it, that is simultaneously a large dipole moment is created in this motion, because there is no compensation between, the dipole moment is created and destroyed, it oscillates between zero and some value, therefore, this is infrared active.

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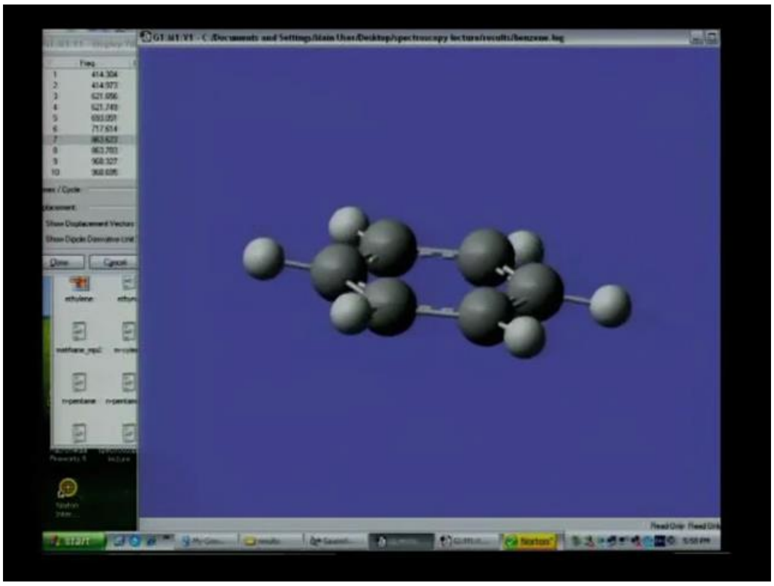

Let us look at another infrared inactive motion here, this is also a sort of a benzene ring, which in which some of the atoms, you see it clearly that, one this 1, 2, 3 the 3, the carbon atoms, move up while the other carbon atoms move down, and as this carbon atoms moves up, the hydrogen atom moves down, these normal mode, there is a very clear mathematical procedure for drawing these normal mode arrows, and how they should oscillate, and the fact that this is a 3 n minus 6, or 3 n e is not magical, you know there is mathematical structure for doing that, therefore, vibrational motions, at the level of very elementary, what is called harmonic approximation, give you a little bit about the molecular motion. Benzene in a highly excited state, of course, throws away all of these things, this is not going to be the picture, but that is a slightly more advanced part of spectroscopy, since we are concerned with the basic or the elementary aspects, we will restrict ourselves to the normal modes. So, let us look at this, and all of these are some sort of bending mode, as you see it they are low frequency modes.

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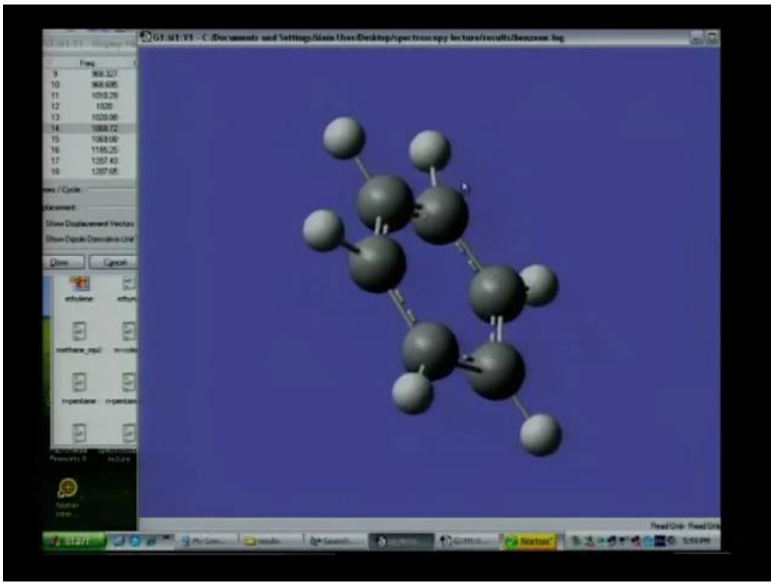

Let us take somewhere in the middle, go to again, slightly different frequency, and what you see is now the bending of groups 1, 1, 2, 3, 4 groups, with respect to 1. 2, 3, 4 you see that, this slightly more energetic, note the, you can see it using any perspective angle that you want take, this is probably better, to see how the individual atoms are, it is, it is like nodding it is head, this way and that way.

Let us look at this motion; this is one of the normal modes. Clearly you see these two, they seem to compensate for any dipole changes, these 2 seem to compensate for any dipole changes, and these 2 seem to compensate for any dipole change, do they move? They do not seem to move, there is very little of that, but this is clear that, this is unlikely to be infrared active - yes, it is not detected by infrared spectroscopy.

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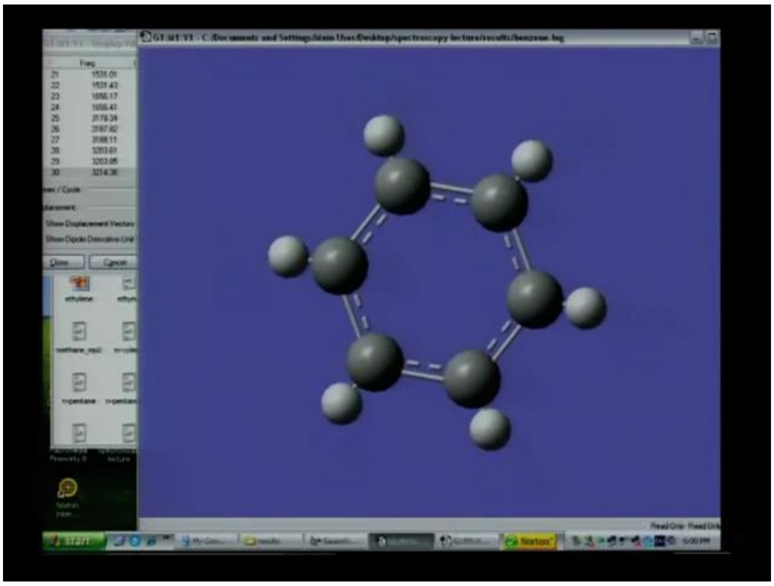

And let us look at a very high energy, one of the most beautiful oscillations of benzene, the symmetric stretch of benzene about it is equilibrium position. This is easier to see, this is like all the oxy the carbon atoms shrink, while all the hydrogen atoms get extended, and there has to be because this is the center of mass, and the center of mass cannot move in a genuine vibration.

We have already removed the translational and the rotational motion of the molecule, therefore, what you see, that is why this is called the genuine vibration; there is no other contamination by translation and the rotation in this kind of motion. So, what you see here is; obviously, molecular motion in which, which is very symmetric, throughout this motion there is no dipole moment, therefore, this cannot be detected by infrared spectroscopy. How do we do this? The great Sir C V Raman, found a procedure for determining all the missing vibrational modes of infrared spectroscopy, through his procedure of spectroscopy through scattering, and you would see that, his is a very complementary spectroscopy to the infrared spectroscopy, that was known till then, and every mode that is not infrared active, for a molecule which has a center of symmetry, ill be Raman active. This is the contribution; this is one of the most pioneering contributions by the Indian physicists, Sir CV Raman, for which he eventually even taught to win the noble prize, in physics.

This is the benzene symmetric mode; let us see a molecular motion in which there is a large dipole moment for benzene.

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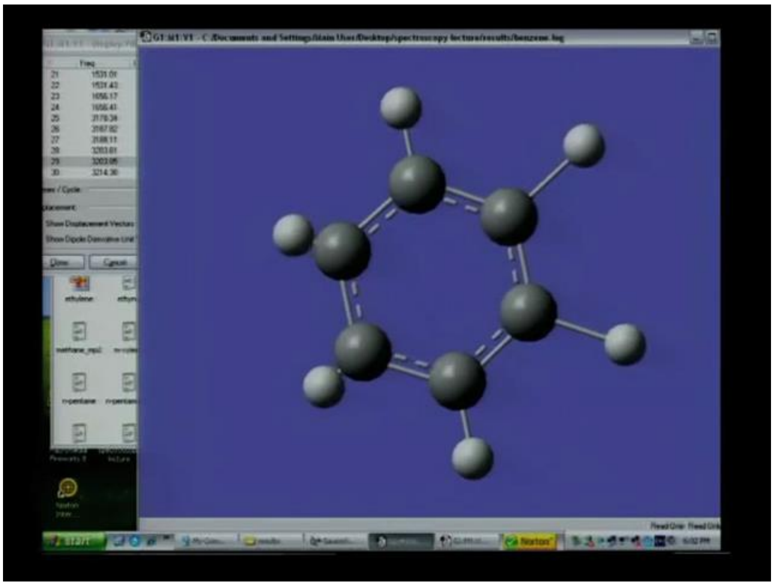

Here is one example, this is a high energy stretching mode, and you see that the dipole moments add, because when this increases this decreases, which means the dipole moments vectors, and, and the vectors add, therefore, this has to, this has a large dipole moment, and this is infrared active. This is a stretching mode bond stretching takes much more energy than bending about the bond, than tartion of the ring and so on, therefore, you see there is a pattern in describing the molecular motion of the polyatomic molecules, tartional motion has small energies, bending modes have slightly higher energies, and the stretching modes symmetric and anti symmetric stretching, which involve the bond stretching, have higher vibrational frequencies, this is for benzene.

Let me give the last example of a very complicated molecule, to tell you that this can go to any extent. As a last example for today, let us look at t and t, Trinitro Telvin, explosive.

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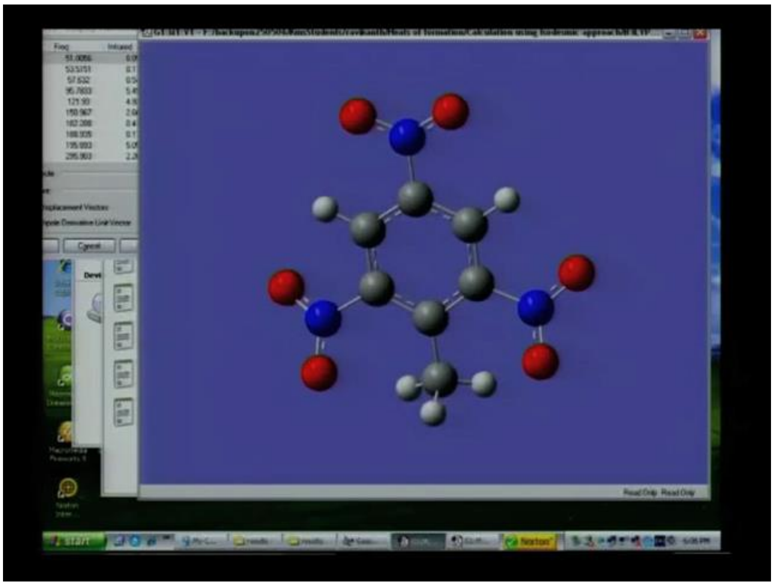

Hopefully the molecule does not explode on the screen, let us see what it does, when it vibrates, the explosion happens when the vibrations goes uncontrolled, and what we have here is control very small amplitude oscillations for the molecule.

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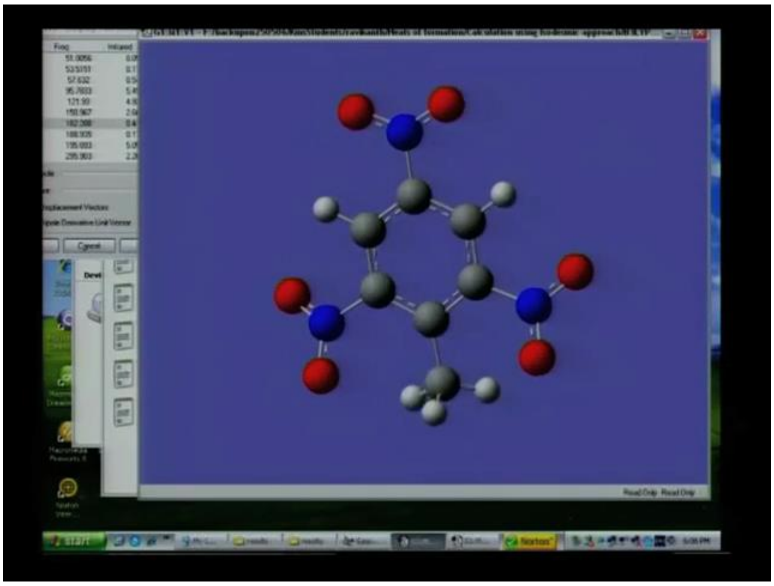

Let us look at a few small amplitude motions, and then examine likewise the, amplitude vibrations for other higher oscillations, higher energy vibrational motion. What do you see here is a very low energy vibrational motion, and it looks like most of the atoms do not move, but they do, in the normal mode approximation, every atoms moves from it is equilibrium position by a small amount, but it is inversely to it is masses, therefore, the Telvin group, this is the c h 3 group, 2, 4, 6, Trinitro Telvin that is what you have here, the nitrogen's are the blue atoms, the oxygen are the red atoms, the carbons are the gray atoms, and the hydrogen's are the white, small ones.

So, what you have here is a t and t molecule, which in which you have a tartional motion of the methyl group, relative to rest of the ring, and to compensate for the, the effect of this, the rest of the rings moves by a very, very small amount. You can see this in various angles, to see that there is in fact a very small motional change in the rest of the molecule. Let us look at the very large amplitude motion. In fact, let us look at the high frequency motion, highest frequency.

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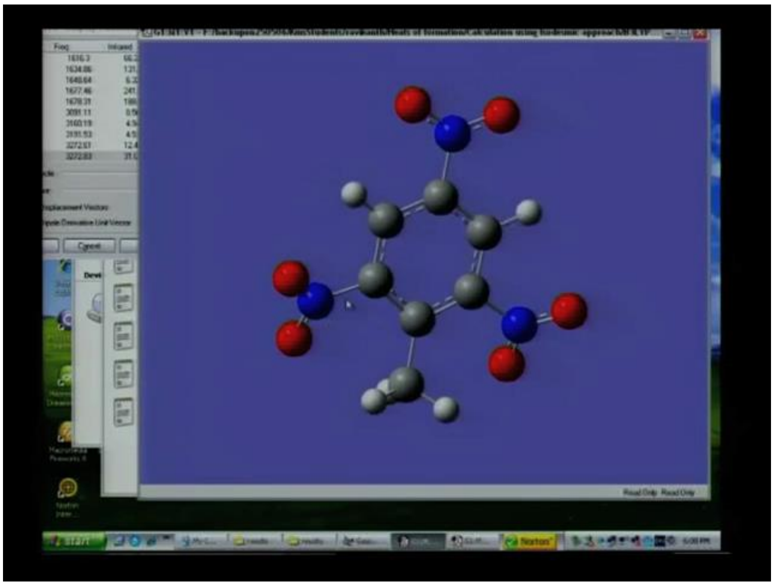

Let us look at what it does, that is not very interesting, only 2 atoms seem to be moving away from each other, for this motion, but again as you see that the rest of them are nearly stationery, because the amplitudes of the vibration, relative to that stretching of the 2 hydrogens is going to be very small. It is a stretching motion therefore, it has a high frequency motion, and here is the stretching of the methyl group, here is a stretching again of the methyl group symmetrically.

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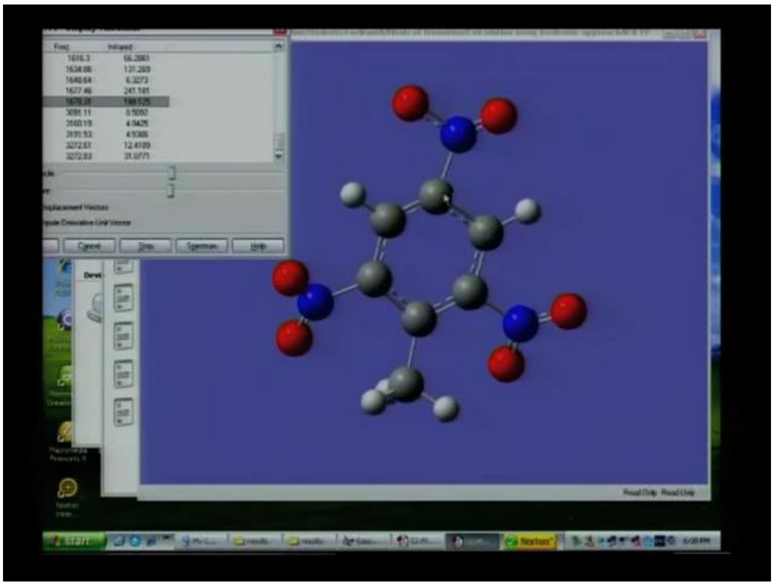

Here this is now, the tarsh, the, let us look at, other is a stretching all over the places, this is nitro group for example, is stretched; this carbon carbon group is stretched.

See that, this is a very complicated motion, how many degrees of freedom does this molecule have? I leave it you as an exercise, and will tell you that the answer is 57, find out why. Here is an another stretching motion, let us go up and look at that, yes, here is the, what you see here is again the stretching of the n o group, and so on. Now the current day computational chemistry programs, can pictorially obtain the normal modes of vibrational of polyatomic molecules, including several 10s and 20s 30s of atoms and even more. With a little bit of approximate theories, we can obtain the normal modes of vibrations of many, many atom polyatomic molecules, these are collective motions.

I will not be in a, I not had the time to describe the local motion, but we will continue this in the next lecture, with a description of the local motion and vibrational frequencies and so on, how we do this in the laboratory, but let us summarize todays lecture by saying, that the normal modes of vibrations of polyatomic molecules, are the exact analogs of the normal vibrational or the harmonic vibrations of a diatomic molecule, and what we did today, is a qualitative description of the vibrational motion, with a little bit of, about the origin of how they come, come, come into effect. There are 3 n minus 6, or 3 n minus 5, degrees of freedom, depending on the molecular type, and it is possible for us to view under small amplitude motion, all these vibrational motions, very, very accurately. We will continue this in the next lecture, to study the local modes of vibration, until then.

Thank you very much.