--fundamental frequency, here, nu.

Now, I should tell you that the model that we used to get these vibrational energies for a molecule is actually called a harmonic oscillator model.

It is a model. And it predicts that the spacings between these energies are all equal.

The reality is, that the spacings are not all equal. The reality is that this molecule is an anharmonic oscillator.

And that although way down here in the well, the spacings are just about equal, v equal zero, v equal one, v equal two, as you get further up in the well they do start to come together. And they actually converge to the dissociation limit. You don't have to know that, right now. You will see that in later courses, but I just wanted to make you aware of that, that the harmonic oscillator model works pretty well down here. But the harmonic oscillator potential function actually looks like that.

A real potential function looks like that.

This becomes anharmonic. So those spacings do get closer together. That is for the future.

Now, you can also put enough vibrational energy into the molecule to break a bond. When you get up to here, you can put enough vibrational energy.

And this hydrogen and the chlorine, as they oscillate out, they will just keep going, If you put enough energy.

You get up here, and when they stretch, they will just keep on their merry way.

They won't come back. There won't be a restoring force. So, by putting a lot of vibrational energy into the molecule, you can break your bond. And in fact, that is what happens when you break the bond.

You have a lot of vibrational energy in that bond, and the two atoms just keep flying apart.

That was our diatomic molecule. What I now want to just talk briefly about are polyatomic molecules because we said in a polyatomic molecule, such as water, we have several different vibrational modes.

And each of those vibrational modes actually has a different fundamental frequency. And each of those vibrational modes can be represented with this sort of interaction potential. Sometimes it is not as simple a coordinate system

because you have some bends so you have to plot this as a function of angles, which is not easy to draw. But each one of the vibrational modes in a polyatomic molecule can, in effect, be represented by some kind of energy of interaction, like we drew here for this diatomic molecule.

It is just a little bit more complicated because your coordinate system is a little more complicated.

Particularly when you start talking about bends.

But let's take a look here on the side walls.

What I am showing you is a vibrational spectrum of water.

And, again, this is some infrared radiation that is being directed at a sample of water molecules.

And we are measuring the intensity of that radiation at a photo detector as a function of the frequency of the radiation going through our sample. And when the molecule absorbs radiation at that frequency, that intensity at the detector goes down. What you see, here, is just a hypothetical spectrum for water.

You see that the molecule is absorbing some radiation, here, at 1,595 wave numbers. Well, that 1,595 corresponds to the fundamental frequency of vibration of this hydrogen bending mode. That is 1,595.

That is the frequency in wavenumbers with which that hydrogen-oxygen-hydrogen bond is bending or vibrating.

This is also the energy between the v equal zero and v equal one mode. This represents excitation from v equal zero to v equal one. And then, way up here, you see another transition at 3,652.

Well that, we know to be the symmetric stretch.

That is, both hydrogens moving in or out at the same time.

3,652 wave numbers is the fundamental frequency for that particular vibration. It also represents a transition from v equal zero to v equal one.

And then, finally, at 3,756, that is the anti-symmetric stretch, where one of the hydrogens is moving out and one of the hydrogens is moving in.

Anti-symmetric stretch. It also is the v equal zero to v equal one transition. And so, that is what you would measure on an infrared spectrum of water.

Actually, infrared plus Raman, but we will leave that out.

And what is interesting is that any molecule that has an OH stretch in it, or any molecule that has an OH group in it -- If you take an infrared spectrum of it, what you are going to see is that it has a transition somewhere in between 3,400 wave numbers and about 3,800 wave numbers.

If you had an unknown compound and you put it into your infrared spectrometer and saw a transition somewhere in between 3,400 and 3,800, immediately that is going to clue you in that you have an OH stretch.

Because now other molecules that are at all common are going to have a fundamental frequency in that range.

You can see how this infrared spectroscopy can be used as an analytical tool to figure out what molecule you have.

And, of course, the actual frequencies, then, are a fingerprint of the molecule.

But, just in general, if you did not know anything about the molecule and you saw a stretch in this range, you know you got an OH bond, there, that is undergoing a symmetric or an anti-symmetric stretch if you have two OH bonds. Likewise, say you had a carbon-hydrogen bond, what you would find is that all carbon-hydrogen bonds have fundamental frequencies from about 2,800 wave numbers to 3,100 wave numbers.

If you see a transition in that range, you know that you have a hydrogen bonded to a carbon. Because, again, there really isn't anything else that is common that has a vibrational frequency in that range.

When you get to a little lower frequencies, well, then it is a little more difficult because there are lots of different other modes that have vibrations, which are a little bit lower frequency.

But, again, the specific number will identify the molecule for you. One other thing is that just in general, bending modes have lower frequencies than stretch modes. That is a general statement that is true. Also, generally symmetric stretches have lower frequencies than anti-symmetric stretches.

That is true. And you will see more of this infrared spectroscopy used as an analytical tool, essentially, when you take some organic chemistry. Well, what I want to talk about now is the other internal degree of freedom in molecules.

That is molecular rotations. Well, molecular rotations are quantized, just like molecular vibrations are.

Let me take my HCl again and draw this intermolecular interaction potential. And let me put my v equal zero level down here. Then, just for ease of my diagram, I am going to put my v equal one level up here.

Rotational levels, they are quantized.

And the rotational quantum number is given the symbol J.

For example, if you have a molecule in the first rotational state, that first rotational state, then, will be right here. We will call that J equal one.

And then, if you have it in the second excited rotational state, that is going to be right there.

We will call it J equal two. And the third rotational state is going to be right there. We will call it J equal three.

And the fourth, J equals four.

Now, if you have a molecule in the ground rotational state, that ground rotational state, here, is J equal zero.

And it is sitting here right on top of the v equal zero level for the ground rotational state. The bottom line is, you can have a molecule in the ground vibrational state and the ground rotational state. If that is the case, this is how much energy it has. When you are in the ground rotational state, that is zero energy, as we are going to see in a moment.

You can have a molecule in the ground vibrational state in the first excited rotational state. If that is the case, that is the energy. You can have a molecule in the ground vibrational state and the second excited rotational state.

Then it has that energy. You can have a molecule in the ground vibrational state in the third excited rotational state.

It has that energy. But you can also have a molecule in the first excited vibrational state, right here, and in the J equal zero state.

Well, if that is the case, it has that energy.

You could also have a molecule in the first excited vibrational state and the first excited rotational state.

Well, then it has that energy. Or, a molecule in the first excited vibrational state and the second rotational state.

Well, then it has that energy. Each one of these vibrational states has, on top of it, a manifold of rotational states. The rotations and vibrations, for our purpose, are not coupled.

You can have so much in vibration, so much in rotation.

I want you to also notice, that the difference in energies between rotational states is much smaller than the difference in energies between vibrational states.

That is a general statement that is correct.

Now, we have a nice analytical expression, again, for the allowed rotational energies of molecules, and that analytical expression is the following.

E sub J is equal to h squared times J, J plus one over 8 pi squared times I.

I is the moment of inertia.

I will explain that in just a moment.

What does this say? It says that when J is equal to zero, the rotational energy, here, is equal to zero because it makes this all go away. So, the molecule has no rotational energy in J equal zero.

When J is equal to one, we put in J equal one, we calculate that, and it comes out to be h squared over 4pi squared times the moment of inertia.

This is J equal one.

For J equal two, the molecule has 3h squared over 4pi squared amount of rotational energy.

For J equal three, it has 3h squared over 2 pi squared times the moment of inertia.

The energies go up. Suppose I have a molecule in v equal zero, J equal zero, and it makes the transition, here, to J equal one, what is the energy difference between those states? Well, J equal one minus energy J equal zero. That is h squared over 4pi squared times I minus zero.

That is just h squared over 4pi squared I.

How do we make that transition? Well, to make this transition right here, we are going to need a photon, and that photon is going to have to have an energy exactly equal to this.

Our photon E equal h nu, that has got to be equal to h squared 4pi squared times I.

I can solve for the frequency of the photon that I need to make that transition. The frequency of that photon then is h over 4pi squared times I.

That is the frequency of the photon that I need. Now, in the case of HCl, we said that HCl has two rotational modes.

It has a mode rotation around this axis, and it also has a mode rotation around this axis, in the plane of the board.

These two rotations are degenerate.

If you put in a photon with this frequency, here, it will excite either this rotation or that rotation.

Now, let's look on the side wall here.

How do we do the experiment? Again, just like we do it in the infrared, except that the energy of the photon we now need is in the microwave range.

Microwave spectra measure rotational spectra of molecules.

And so, again we have a microwave radiation, monochromator, coming out, going through the sample, photo detector, look at the intensity of the photo detector as a function of the frequency.

At some frequency here, you see a dip in that intensity. Well, that is where the molecule absorbs. And, in the case of HCl here, the frequency of that absorption for J equal zero to J equal one, well, that frequency occurs at 6.3x10^11 hertz. That would be the frequency of the photon that you would need for absorption.

Yes? I'm sorry?

We got into the microwave range, here, because the spacings between the rotational states are much lower than the spacings between the vibrational states.

And I just actually wanted to make that point, here. We can calculate in terms of the energy, here, what this spacing is.

Let's do that.

If we want to know the change in energy from J equal zero to J equal one, that change in energy is just h times the frequency of the photon, that photon, there, that makes that transition happen. You can plug that in, there, so we have 6.6261x10^-34 joule seconds, times the frequency 6.3479x10^11 hertz.

When you do that, you should get 4.2062x10^-22 joules. Or, if I convert that to kilojoules per mole, it is 6.25330 kilojoules per mole. In general, the difference in the spacings here, the energy difference for vibration, we said is something between three to 40 kilojoules per mole. That is the difference between v equal zero and v equal one, generally, for a large range of molecules. The difference in the frequencies here for rotation, delta E, that is more like something on the order of 0.01 to about 1.0 kilojoules per mole. That is what is typical.

So, rotations are much more closely spaced in energy.

Yes? Well, in the case of the rotational spectra, there is a little bit more diversity in what units are used.

And the reason is this. They are more closely spaced.

And the whole wavenumber came into use in vibrational spectroscopy when the way people would analyze the spectra would be to take a photographic plate with the light coming in.

And you would see the lines separated in space.

And people would take a ruler in centimeters to measure the spacings between the lines. That is historically how the wavenumber unit came to be. The problem is that does not work so well in rotational spectroscopy, often, because the spacings are much closer together.

And so, depending exactly on what kind of diffraction grading used, the wavenumbers are not always used.

Sometimes they are the frequency.

We go back and forth. And, in your homework problems, I go back and forth, too.

You really have to deal with both kinds of units.

But now, one of the usefulnesses of this rotational spectroscopy in getting, say, this frequency for the transition, one of the usefulnesses, there, is to calculate the bond length of the molecule.

To determine the bond length of the molecule really very accurately. Because what we said over here is that the frequency for that transition is this.

The frequency of that transition is h over 4pi squared times I. And I is a moment of inertia.

The moment of inertia is the following.

Maybe you have had this 8.01. No, not yet?

Oh, you will. The moment of inertia is the reduced mass times the distance between the two masses.

In our case, for the HCl molecule, it is equilibrium bond length, r sub e squared.

The reduced mass is what I gave you before, m1 m2 over the sum of the two masses.

Again, it is a way to reduce a two-body problem to a one-body problem, where the one-body is this fictitious body of reduced mass. But it is exact.

There are no approximations. This is correct.

That is the moment of inertia of the molecule.

It is a property of the molecule, depending on the mass and the bond length. You can see that if I substitute that in there, h over 4pi squared times nu r sub e squared, and then I go and solve for r sub e, well, r sub e is (h over 4pi squared mu times nu) to the one-half.

In the case of HCl -- Actually, I think this is all in my slide, here. If I go and stick in the value for nu, the equilibrium bond length, here, is really 1.2748x10^-10 meters. We can really measure these frequencies with high precision and high accuracy.

All bond lengths, really, come from measurements, now, of rotational spectra. All bond lengths in the gas phase, wherever we can measure the rotational spectra of the molecule. That is one of the main uses for rotational spectroscopy. Questions?

If not, what I am going to do is leave the subject of internal motion. I want to talk for the rest of the hour, and a little bit on Friday about another topic, which is intermolecular attraction.

Interactions. Or, I am going to write it here as attractions. The bottom line is, I want to try to understand, on a microscopic scale, deviations from the inner gas law, PV equal nRT.

You know PV equal nRT, that if I made a plot of the volume versus the temperature and kept the pressure constant, say the pressure is at one atmosphere, and the number of moles in my gas is constant, well, you know that what I should see from that equation is a straight line.

But suppose I took a balloon filled with air and started to cool down that balloon--in that case, the atmospheric pressure is essentially constant--in that case, what would happen is that the volume would decrease. It would decrease in a linear manner with temperature; everything would be fine until at some low temperature, this volume would start to deviate from the straight line dependence, start to go down.

And then, all of a sudden, the volume would go very low because, of course, at roughly 77 degrees Kelvin, which is the boiling point of nitrogen, the liquid would condense. So, the volume gets very small.

I could also do that with helium.

If I took a helium balloon and cooled it down, the volume would decrease. But then, as I got pretty cold, the volume would start to decrease faster than predicted by the inert gas law. And right at 4 degrees Kelvin, the

boiling point of liquid helium, the volume would then just kind of plummet. And so you can understand what happens right here, but we also want to understand, why does the PV equal nRT start to deviate before we get to a boiling point of the liquid? The reason is because of these intermolecular attractions. For example, if I had in my gas this nitrogen molecule headed toward the wall of my container, and it has some initial straight trajectory, it is going to hit the wall, where it is going to exert this force, which will lead to my macroscopic pressure. But, if there is an oxygen molecule around, that nitrogen molecule could indeed be deflected by these attractive interactions, circle around it, and then finally hit the wall.

So the nitrogen would be delayed in hitting the wall.

If it is delayed, then my force is going to be not as great, because it is momentum change over the change in time between collisions, my pressure is going to be lower if, in fact, this nitrogen experiences some attractive interaction that delays it from hitting the wall. And, therefore, the pressure is lower, or vice versa.

In this case, if I kept the outside pressure constant, then the volume would go down.

Now, why is that the case? Why should nitrogen and oxygen actually attract each other? In order to talk about that, we have to think a little bit more carefully about what the electron distributions are around nitrogen molecules, oxygen molecules. We treated, in the sodium chloride, lithium chloride, those things as point charges.

We have to be a little more sophisticated now in thinking about what the electron distributions are in these kinds of molecules, nitrogen or oxygen.

And let me, for the ease of just drawing this, talk about the inert gas, here, argon.

As you may or may not know, on the average, the electron distribution around argon is spherical.

But, although quantum mechanics does not allow us to see this, this electron distribution does fluctuate.

And, at some momentary time, it could be that the electron distribution here is a little bit larger on one side of this argon. And then the argon nucleus here is a little bit deshielded, so we kind of have a charge shift here, positive here, minus.

When we do that, this is a dipole.

We have separated charge in space.

That is what a definition of a dipole is.

And then, of course, if there is another argon atom around, well, this dipole then is going to induce the charge

distribution around another argon, so that now, the positive end is going to attract or distort the electron distribution around argon in this way. And this will be the positive end. And so, we have an instantaneous dipole which has induced a dipole, an instantaneous dipole, in a neighboring argon atom.

Now we have these two dipoles together, and they are oriented in opposite directions. And that is an attractive interaction. The next result is an attraction. And, of course, we call that an induced dipole-induced dipole interaction. We also call that, sometimes, the London dispersion force.

This is not a permanent dipole. This is a momentary dipole.

This is an instantaneous dipole, which induces, then, an instantaneous dipole in the neighboring molecule or the atom. The result is, because you have these two dipoles now, align in opposite directions, a lowering of the energy.

There is a net attraction. That is a reason why, in this nitrogen and oxygen, there might be some attraction.

The nitrogen may, in fact, be deflected from its trajectory and hang around the oxygen a little longer before it hits the wall. Therefore, the pressure is lower than you would expect, or the volume is lower than you would expect, if you were keeping the pressure constant. And we can draw that interaction energy for two argons.

Here are two argons separated. Argon limit, we draw the energy of interaction, there is some net attraction. This is zero.

And that net attraction, here, as they come closer and closer together, is a whopping 0.996 kilojoules per mole. Not very large.

But there is a net attraction. You can also see that there is a value of r at which that attraction is the maximum.

And that is the equilibrium bond length of the molecule argon two. Can you form a molecule between inert gases? You sure can.

And sometimes we call this a van der Waal's dimer.

You can make these molecules. There is the bond length.

In the case of argon, that bond length is 3.8 angstroms. But the origin of that attraction is this induced dipole-induced dipole interaction. You can make two argon atoms stick to each other. But now, I do want to compare this energy of interaction right here between two argons with the energy of interaction between two hydrogen atoms that are covalently bonded. The energy of interaction between two hydrogen atoms that are covalently bonded,

what does that look like? Here are the two hydrogens separated, and the bond length, here, is 432 kilojoules per mole. Look at how much stronger the H two bond is in the case of a covalently bound molecule, 432 as compared to the 0.996 in the case of the argon.

Look at what the equilibrium distance is, here, in the case of H two. It is 0.74 angstroms, compared to 3.8 angstroms in the case of argon.

This is not a covalent bond, the induced dipole-induced dipole, but it is a bond. But now, you might say that was not really a fair comparison because hydrogen is much smaller than argon and, of course, the bond length in hydrogen is going to be much smaller than that in two argon atoms. Therefore, if the two hydrogens are much closer together, then the energy of interaction has got to be much stronger. Well, to show you that isn't really the appropriate way to think about it, look at this diagram, here, on the side board, where what I am plotting for you is the argon-argon interaction potential. Here it is.

It is this light kind of reddish line, argon-argon. Versus the chlorine-chlorine.

Here is chlorine-chlorine. Argon and chlorine are about the same mass. They are about the same size.

What do you see? Well, you still see that the argon-argon interaction is much weaker.

You can hardly see, in this drawing, the attractive part of the interaction potential on this scale. Chlorine-chlorine, on the other hand, look at that, minus 200 kilojoules per mole. And chlorine-chlorine is much closer in. The equilibrium bond length, what is it? 1.9, or something like that.

Whereas, we have 3.8 over here for argon-argon.

In that covalent bond between two chlorine atoms, that is a different interaction than this induced dipole-induced dipole where we have overlaps of electrons, the wave functions constructively, destructively interfering.

That is different than the induced dipole-induced dipole interaction. Now, it turns out that we actually do have a nice analytical form for the interaction potential due to these induced dipole-induced dipole interactions.

Let's take a look at that. They are sometimes called dispersion interactions. We leave off the name London.

We have a nice analytical form for these dispersion interactions. And the name of that analytical form is the Lennard-Jones potential.

Lennard-Jones was way ahead of his time, a gentleman in England in the late 1800s who decided when he got married that it was not really fair for his wife, whose last name was Lennard, to take his name. So, they both had

hyphenated last names, Lennard-Jones. That is Mr.

Lennard-Jones. And that potential function looks like this. We are going to call it capital U, LJ, Lennard-Jones.

It is going to be as a function of r.

R is the distance between, I am going to use argon as the example, the two argon atoms. That is going to be equal to 4 times epsilon, I will explain what epsilon is, times (sigma over r) to the 12 power, I will explain was sigma is in a moment, -- -- minus (sigma over r) to the 6 power.

That is my potential form. Now, when I plot it, it is going to look like every other interaction potential that we have drawn here because I cannot, on the board, draw things very accurately. This is argon plus argon, way out here. This is a function of r.

We are going to start out at zero, this is going to go down and then come back up. That is the general form, and this is the actual expression for that interaction.

What are these parameters, here?

Well, the epsilon is this well depth.

It is measured from the bottom of the well, although the argon atoms are never at the bottom of the well.

They have the zero point energy.

This epsilon, here, is this energy, from the bottom to the dissociated atom limit.

What is this sigma? Well, this sigma is related to the equilibrium bond length. In the Lennard-Jones potential, here, the equilibrium bond length is equal to 1.12 sigma.

That is a parameter. To get it, you would take the derivative of the potential function, set it equal to zero, calculate the value of r, and that would give you a zero in that derivative. That is a maximum or a minimum.

And it will turn out to be a minimum in this case.

That is what sigma is. What are these two components, right here? This component, this (sigma over r) to the 12.

What this describes are the repulsions in this interaction.

It is a good description of the core electron-core electron repulsion. Not the repulsion due to the outermost electrons in argon, but the repulsion due to the core electrons, the n equal one, the n equal two electrons. And it

describes the nuclear-nuclear repulsion. It is a (one over r) to the 12 dependence. If I plot that, it would look something like this.

It is repulsive everywhere. It is what we call a short-range interaction. And this is important.

What do we mean by short-range? Well, short-range means that it only has a value when r is small because it is a one over r raised to the 12 power.

If r is large, and you put a large number in the denominator and raise it to the 12 power, the result is nothing. The result is something close to zero. This first term is zero when r is very large. That is why we call it a short-range interaction. And you can see that this really starts taking on value when r is pretty small.

But then there is this part, the (sigma over r) to the 6 term. That is the attractive interactions. If I were to plot that, it would look like that. That is the induced dipole-induced dipole interaction.

We could actually write down the energy of interaction between these two induced dipoles and find out that this is a one over the r to the 6 power.

We are not going to do that, but we could do that.

These are always attractive. The sum of the two, of course, gives us the actual shape of that interaction potential. But this interaction, here, is longer range, or we call it longer range.

It is longer range because it is only one over r to the 6.

And so r does not have to be that small in order for this term to make the contribution.

As r has a larger power here in the denominator, that is shorter range interaction.

As it gets a smaller power in the denominator, that is a shorter range interaction.

The other thing that is interesting and important here is this value of sigma. And I said that r sub e was 1.12 times this sigma.

The value of sigma is actually the definition of what we call a van der Waal's radius. That is, in the case of argon here, the equilibrium bond length is 1.12 sigma.

And so, r sub e, 1.12 sigma.

For argon that parameter is 3.4 angstroms.

And so the bond length is 3.8 angstroms.

But the van der Waal's radius is given by this 1.12 sigma over in this case 1.9 here, is the radius that you use in these space filling models. On the side wall, that top model is a space filling model.

And somehow you have to decide, how large should those hydrogens be that are sticking out in space that are not bonded to anything? And the radii that are used are these van der Waal's radii, because that is the radius at which you have this attractive interaction due to the induced dipole-induced dipole. And that is how those sizes are determined.