ROBERT FIELD: This is the first of two lectures on spectroscopy and dynamics. Now, I'm a spectroscopist, and so this is the core of what I really love. And there are a lot of questions about, well, what are we trying to do?

And you heard two lectures from Professor Van Voorhis, and he talked about ab initio calculations-- electronic structure calculations-- where you can get really close to the exact answer. And it's really a powerful tool. And it gets you the truth. But it gets you so much truth that you don't know what to do with it.

And the same thing is true for spectroscopy. You get a spectrum. It contains a huge amount of information. And you can take lots and lots of spectra. But what are we trying to do?

When I was a graduate student, we were doing a unique super high resolution spectroscopy. And so we thought what we were generating was excellent tests for quantitative theory. And if, in those days, I went to a lecture by a theorist, they were saying, we're generating stuff to check against experiment.

And it's a circle, and that's not what we're trying to do. The theory and the experiment are just the beginning. And you can start from either extreme. What we want is, how does it all work? What is going on?

Can we build a picture, which is intuitive and checkable and predictive, so that we can say, oh, yeah. If we want to know something, we can get to it this way. And the purpose of this lecture is to not provide a textbook view of spectra, but to give you a sense of how you can get to stuff that challenge your intuition.

What we want to do as scientists is to be surprised. We want to do a good experiment or do a good calculation. And we want to find that the result is not what we expected. And we can figure out why it's not what we expected. And that's never conveyed in any textbooks.

Now, this lecture is based on my little book of lecture notes. And I have a number of copies of it. And if people have a strong wish to have a copy, you can have one. I can give it to you. And a lot of this lecture is based on the first chapter of this book. But many of the topics are developed throughout the book.

OK. So this is a two lecture sequence, and the first half will cover this stuff on this board. And it's in the notes, so you don't have to copy all this stuff. I just want you to see where we're going.

So I've already talked a little bit about experiment versus theory. They complement each other. We can use theory to devise an experiment, which is path breaking. Or we can use an experiment to challenge the theorist to calculate a new kind of thing.

And I hope that some of these things, those ideas, present themselves in this lecture. And it's really important that if there's something that you don't understand or don't capture the importance of, you should ask me a question. I really want to talk about what it's all for.

OK. So I'm going to talk about spectra, and it will be what kinds-- rotation, vibration, electronic, and other ramifications. And going from atom to diatomic to polyatomic to condensed phase. Each step along this path leads to new complexities and new insights.

Then I'll talk about, OK, we got a spectrum. What do we expect to be in the spectrum? Well, one of the things that's important is the transition selection rules or transition rules. Selection rules correspond to an operator-- eigenvalues of an operator-- that commutes with the exact Hamiltonian. And those correspond to symmetries.

And there are propensity rules like, OK, which transitions are going to be strong and which are going to be weak? And a beautiful example of propensity rules are based on the Franck-Condon principle. And the Franck-Condon principle is one of the first keys you use to unlock what's in a spectrum, or what a molecule is doing. Because it's the first level of complexity that is presented to you in the spectrum. What are the vibrational bands, and how do we assign them, and what are they telling us?

There is a very different kind of information in an absorption spectrum, because it's always from the lowest electronic state, lowest vibrational level. And so there's a simplicity, because of a kind of state selection. And in emission, it's a very different ballgame. Because in the gas phase, the emission is from many different levels. In the condensed phase, it's not. Why?

OK. And then we get to dynamics. And the main thing I want to do in these two lectures is to whet your appetite for dynamics. And there are many kinds of dynamics ranging from a simple two level quantum beat to intramolecular vibrational redistribution.

Which you can understand by perturbation theory to the strange behavior of electronically excited states losing their ability to fluoresce not because the molecule breaks, but because the bright state-- that's an important concept-- the bright state is something. It's not an eigenstate. It's a special state that we understand well.

It's one of the things that we build perturbation theory around. The bright state mixes into an enormous number of dark states. And the molecule forgets that it knows how to fluoresce because the different components, different eigenstates dephase. And that is a beautiful theory.

And when I was a graduate student, this theory of radiationless transitions-- Bixon-Jortner theory-- was just created and many people didn't believe it. They thought molecules, big molecules, they're really easy to be quenched by collision and the loss of the ability to fluoresce or the absence of fluorescence was somehow collision related as opposed to a physical process.

So there's lots of good stuff. And some of the good stuff is Ahmed Zewail's Nobel Prize where he claims-- and that's why he got the Nobel Prize, because people believed that claim. Now, I'm not saying it's wrong.

But part of getting famous is to have a package, which you can sell. And he sold the daylights out of it. And he calls it clocking real dynamics in real time. And it's basically wave packets. But they're wave packets doing neat stuff.

And for example, one way a molecule can lose the ability to fluoresce is because the molecule breaks. And what is the mechanism by which a molecule breaks? Does the bond just simply break or is there some motion that precedes that?

And what Zewail did was to show what are the motions that lead the molecule into the region of state space where the bond breaks. And, of course, if you want to manipulate molecules, you either want to get to those regions or avoid them. And so there's all sorts of insight there.

OK. Now this is what I believe. That if you understand small molecules, you will see examples of everything you need to know to deal with almost any dynamical process in chemistry. Now, this is certainly an exaggeration, but this has been my motto for years. And so I really stress the small molecules.

And it's not that small molecules are really hard. They're really beautiful, and they do enough so that you can anticipate what you need to deal with bigger molecules. So let's begin.

OK. So what is a molecule? As chemists, we would never think of a molecule as a bag of nuclei and electrons. We wouldn't think of it as a bag of atoms either. We believe in chemical bonds. This is an important thing. It's not a conserved quantity.

Bonds can break. But we believe that bonds tell an important story. And so almost all of our pictures for complicated phenomena are based on the-- I hesitate to use the word sanctity-- but the importance of bonds.

OK. We start-- I'm going to erase this, because I've made my point, and it's embarrassing to keep emphasizing my secret motto. But it is true. OK. We have the Born-Oppenheimer approximation. And this is very important, because we can't solve a three body problem.

We can solve a two body problem. But we have molecules, which are consisting of nuclei and electrons. And this Born-Oppenheimer approximation enables us to separate the nuclear part of the problem from the electronic part of the problem. Because these two things move at very different velocities. And so it's a profound simplification.

We get potential energy curves or potential energy surfaces. And that is the repository of essentially everything we want to know. If we know the potential surface, we can begin to do almost anything. And certainly for a big molecule, it's not just a simple curve like this. If you have N atoms, there's 3N minus 6 vibrational modes.

And well, that sounds terrible. But even for this, you have essentially an infinite number of vibrational levels and an infinite number of rotational levels. And so if you have a polyatomic molecule, you have 3N minus 6 infinities of infinities. So you're not wanting to get everything.

You want to generate enough information to be able to calculate anything you want. And sometimes, you make approximations and you're not sure that those approximations are good. And you want them to break. You want to discover something new.

So the Born-Oppenheimer approximation, we go from clamped nuclei calculation where the-- since the nuclei moves slow compared to the electrons, well, let's not let them move at all. And then we build a perturbation theory picture where we let them move. And we can deal with that because we understand vibrations and rotations.

OK. So we have a potential energy surface. And there are things that we can anticipate about a potential energy surface. And LCAO-MO theory enables you to say a lot of important things about the potential energy surface. So it provides a qualitative framework.

And so from molecular orbital theory-- and this is not what Professor Van Voorhis talked about. This is the baby stuff. And we don't expect to get the exact answer. But we do expect to be able to explain trends. Trends within a molecule and between related molecules.

So this provides a framework for expectations. And there are things that we get like bond order. And we talk about orbitals that are bonding, non-bonding, and antibonding. And this comes directly out of the simple ideas.

Recall when we had atom with a hydrogen, the hydrogen doesn't make pi bonds. And so they're pi orbitals for the atom A, which have nothing to interact with. And they're usually non-bonding. So we have these sorts of things.

We have spN hybridization. And this is just telling you if a molecule wants to make the maximum number of bonds, you do something. And if it's sp cubed, you have four tetrahedrally arranged bonds. And if it's sp cubed, sp squared is planar with 120 degrees. These things tell you something about geometric expectations.

Now, molecules don't follow the rules exactly, but they come pretty close. And so if you have some reason to believe that a particular hybridization is appropriate, then you have certain expectations for the geometry and how that's going to present itself in the spectrum.

So bond order's related to internuclear distance and vibrational frequencies. Sp hybridization has to do with geometry, and all of these things are really important. So we have a potential surface. And let's say this is a boldface thing, implying that there are 3N minus 6 different displacement coordinates.

This potential encodes the normal modes. What's a normal mode? Well, it's a classical mechanical concept. And it basically corresponds to situations where all of the atoms move at the same frequency in each normal mode. And these normal modes each has an expected frequency and expected geometry.

Because if it's a polyatomic molecule, you have not just two things moving. They'll always be moving at the same frequency. But you have three or four or 100. And OK. So you learn about the shape of the potential and the force constants and so on.

Now, we have the rotational structure. Now, molecules are not rigid rotors. But it's useful to think about molecules as rigid rotors to develop a basis set for describing rotation. And perturbation theory enables us to describe the energy levels of a non-rigid vibrating rotor. And it's straightforward.

It may be ugly, but it tells you how you take information from the spectrum and learn about, say, the internuclear distance dependence of molecular constants like a spin orbit constant. Or some hyperfine constant. Or just the rotational constant. And it's a simple thing.

And I'm toying with the idea of using this sort of problem on the exam. And I'm not sure whether I did on the second exam. But if I did, you'll have a chance to redeem yourself.

OK. OK. Then in the gas phase, nothing much happens. You can have collisions, but the time between collisions can be controlled by what the pressure you use. And so you can sort of think about the gas phase as something where the molecules are isolated.

And another way of saying that is the expectation value of the Hamiltonian in any state is time independent. The Hamiltonian is energy. Energy is conserved. And unless there are collisions, energy will be conserved. And so.

But in the condensed phase, you have lot of collisions. They're very fast. And so one big difference between the gas phase and the condensed phase is energy is not conserved. And it's not conserved at different rates for different kinds of motions. And you want to understand that.

OK. So now let's talk about the kinds of spectra. We have rotational spectra. And that usually is in the micro region of the spectrum. And it requires that the electric dipole moment be not equal to zero. I'll talk about this some more in a minute.

We have vibration. And vibrational spectrum is in the infrared. And the requirement for vibration is that the dipole moment-- which is a vector quantity if you don't have a diatomic molecule-- changes with displacements, each of the normal modes. And so we have a molecule like CO2.

CO2 does not have a dipole moment at equilibrium. It's a linear molecule, symmetric. But it can do this and that is a change in dipole moment. It can do this and that produces a new dipole moment. Or produces a dipole moment. And it can do this, which does not.

So you have different modes, which are infrared active and infrared inactive. And it's related to this dipole moment. Now notice, I put a vector sign on it. It corresponds to motion, directions in the body frame where the dipole moment changes.

When you do this, the dipole moment is perpendicular to the axis. When you do this, it's along the axis. And so there is stuff-- really a lot of stuff-- just looking at what vibrational modes are active.

And then there's electronic. And that's mostly in the visible and UV. But the electronic spectrum could be in the X-ray region even. But mostly, molecules break when they get outside of the ordinary UV region. And so there's not much there.

OK. What's needed. Well, what's needed is the electronic transition moment. Let's call this e1, e2. Going from two different electronic states, there is an electric dipole transition moment, which is not equal to zero. So H2, which has no vibrational spectrum and no rotational spectrum has an electronic spectrum. Everything has an electronic spectrum.

OK. Now, a diatomic molecule. Here is sort of a template for everything a diatomic molecule can do. Now, they're cleverer than this. But this is sort of in preparation for dealing with greater complexity. And then we can have up here.

OK. So this is the electronic ground state. And normally, if you have a diatomic molecule, you can predict what is the electronic ground state and how is it going to look-- how is its potential curve going to look relative to the excited states. That's something you should be able to do using LCAO-MO theory.

OK. So this is the ground state. This is the repulsive state. And usually, the ground state correlates with ground state of the atoms. And so here we have a repulsive state, which also correlates with the ground state of the atom. So this is an excited state, and that correlates with an excited state of the atoms.

And this is AB plus an electron. So that's one way the molecule breaks. And this dotted curve represents Rydberg states They're Rydberg states converging to every rotation vibration level of this excited state. And it can be complicated. But it's beautiful, because I know the magic decoder for how do you deal with Rydberg states.

Because there's a lot of them, but they're closely related to each other. And we can exploit that relationship in guiding an experiment. And so here, now we have a curve crossing between a repulsive state and a bound state. And that leads to what we call predissociation.

So the vibrational level of this state-- which would normally be bound above the curve crossing-- are not bound. And that's encoded in the spectrum too. And so for more complicated molecules, they're going to be these curve crossings or surface crossings. And we want to know how do we deal with them, and what is a diatomic-like way of dealing with them.

And the important thing is at that internuclear distance where the curves cross, then you could be at a level-- starting at a level on this state-- the bound state. And it will have the same momentum at the crossing radius as the repulsive state. And that's where it goes. That's where it leaks out.

I mean, we're normally used to thinking about processes-- non-radiative processes, all kinds of processes-- as an integral overall space. But because the momenta are the same on the two curves at this radius, they can go freely from one to the other. The molecules can go freely from one to the other. We get a tremendous simplification.

And this is something that is always ignored in textbooks and is a profound insight. Because you know exactly where things happen and why they happen. And so you can arrange the information to describe what's going on at this point. And this is where semi-classical theory is really valuable.

Because not only do you know that you have stationary phase at this point. But you know what the spatial oscillation frequency is. Because the spatial oscillation frequency is H-- or the wavelength-- is h over p. And you know what the momentum is at this point. And so you know where the nodes are. How far the nodes are apart and what the amplitude is here.

And so it tells you exactly what you want to know in order to describe this non-radiative process. And my belief is that almost all of the complex things that molecules do happen at a predictable region in coordinated space. And you can get the information you need to understand them, because all of a sudden, the molecule is behaving in a kind of classical way. And we're entitled to think locally rather than globally.

OK. I'm going very slowly. We may get through most of what I planned to talk about today. I have 11 pages of notes, and this is-- I'm on page three. So maybe we'll take off. OK. So how do you do spectra?

Well, in the old days, you had some light source like a candle, and you had a lens, and you had an absorption cell. And there would be some sort of a spectrometer here. Could be a grading. It could be a prism. It could be anything.

But it's something that says, OK, I looked at the selected wavelengths at which the gas in this cell removed light from the continuum. And then you have a detector, which in the old days was a photographic plate. But it could be a photo multiplier, and you're looking at the spectrum by scanning the grading or something like that.

And so what you would get is some kind of a record where you have dark regions corresponding to where there has been no absorption and, well, actually it would be the other way around. There'd be bright regions, because there'd be no exposure of the emulsion on the plate and dark regions where there-- yes-- where the light hits.

OK. So but we're much cleverer than this. And we can do all sorts of wonderful things. And again, I've been around for a long time and lasers were just beginning to be used when I was a graduate student. And I was one of the first small molecules spectroscopists to use lasers. But not as a graduate student.

I wanted them, but we had such-- lasers were so terrible in the region between 1965 and 1971 when I was a graduate student. And so lasers were things to be admired, but hardly to be used. But one of the crucial things was dye lasers. Because these guys are monochromatic, and they can be tuned and tuned continuously over a wide region of the spectrum.

And so that's way better than a candle or a light bulb. Because it's monochromatic, and you're asking one question at a time as you tune the laser. Now, lasers enable you to do many kinds of experiments. You can simply tune the laser through a series of transitions, and you get fluorescence every time the laser tunes through a transition.

And if one laser is good, two lasers are better. And so you can do all sorts of things like suppose this spectrum is really complicated. And you want to be able to simplify it. And so you can do a double resonance experiment where you tune this laser to one line and then you tune this laser through a series of transition.

That spectrum is going to be simple, and it's going to be telling you who this was. And there's just no end of tricks. And often, instead of detecting the fluorescence, you tune the laser.

Let's do this. And so starting here is some kind of a continuum, ionization continuum. And so you have this photon being used twice. One here and one to take it above the ionization limit. And so you have an excitation, which you do want to know how strong it is. And so you might monitor the fluorescence.

But you don't know who this is, and you find out by tuning this. But you would detect the excitation here by subsequent ionization. It's easy to collect ions. Every ion you produce, you can detect.

Every photon you produce, you can't detect. Because you have a solid angle consideration and photo multipliers are not perfect. And so ionization detection is way more sensitive. So you can do that kind of thing.

You can also do-- this is a kind of sequential excitation. You could imagine doing an experiment where you have an energy level here, and you have a laser, which is not on resonance. That's a coherent process. It uses the oscilltor strength at this level to get to here. And that's related to many other kinds of current experiments. And that's neat.

Now, we're recording spectra, and we need to know what the rules are. And so there are certain transitions that are allowed and certain transitions that are forbidden. Now, I talked about the transition requirements for rotation, vibration, and electronic. But let's just talk about the electronic spectrum, because the other two are simple.

The transition operator is equal to the sum over electrons of e times r sub i. It's a one electron operator. And that means if we have wave functions which are Slater determinates of spin orbitals like 2s alpha. This one electron operator can only have a non-zero matrix element if the two states differ by one spin orbital.

That's a big simplification. And so one can actually use this to selectively access different kinds of states by designing an experiment. But the important thing is that for electronic transitions, we have the selection rule delta so is equal to 1. Not 2. Not 0.

And now, the operator doesn't have any spin involved with it. And so that means delta s equals

0. You did not change, you did not go from a singlet state to a triplet state. And the only way you can get from a singlet state to a triplet state is if the triplet state is perturbed by a singlet state.

So this picture I drew where I had a repulsive state crossing through a bound state, it might have been that one of those was a triplet. And as a result, and the other is a singlet, and you have spin orbit interactions, and you get extra states, extra lines appearing. But you get this wonderful selection rule.

There is also for the electric dipole that we have plus to minus parity. Now what's parity? I don't like talking about parity, because the useful definition leads to complexity. But basically, parity corresponds to the symmetry, the inversion symmetry in the laboratory frame.

Now, you say, well, a molecule doesn't have any inversion symmetry. But space is isotopic. And so you can go from a left handed to a right handed coordinate system. And that's what happens when you invert space. And so you can classify levels according to whether they're odd or even with respect to space inversion.

This is close to the truth. This is close to all you need to know unless you're actually going to do stuff with the parity operator. But it's a useful way of saying, OK, I put parity labels on things. I learned how to do that, and that's enough.

Now, you follow selection rules where good quantum numbers are conserved. Or they change in a way that you predict based on the way you did the experiment. A good quantum number, I remind you, is the eigenvalue of an operator that commutes with the exact Hamiltonian.

There are very few rigorously good quantum numbers. But if a molecule has any symmetry, group theory tells you a bunch of things that commute with the Hamiltonian, and it gives you symmetry labels. And that's very important in inorganic chemistry where you have either molecules with symmetry or molecules with atoms with ligands in a symmetric arrangement. And since the transition is on the center atom usually that you can classify them using group theory as allowed or forbidden.

So if we have an electronic transition, the easiest thing to observe is vibrational bands. If you have a relatively low resolution spectrum, you're going to see vibrational bands. You have to work harder to see the rotational transitions in each vibrational band, but you get an enormous amount of qualitative information just looking at the vibrational bands.

Because the vibrational bands encode the difference between the ground state potential and the excited state potential. Now, this is a universal notation. Ground state is always double prime. Upper state is always single prime. Very strange, but that's the way it is.

And so if these potentials are different, the vibrational bands encode the difference. And this comes from the Franck-Condon principle, which says nuclei move slowly, electrons move fast. The transition is an instantaneous process, as far as the nuclei are concerned. And so there's no change in nuclear coordinates, and there is no change in nuclear momentum.

This is what's in all the textbooks, and nobody ever talks about this, because we don't really normally know or think about momentum. But we do know what it is. We do know what the operator is. And we know that kinetic energy is related to the momentum squared over 2 times the mass.

So what is this? This means transitions are vertical. In other words, if we have a pair of electronic states, we draw these vertical lines. Not slanting lines. This means momentum is conserved. And this, here at this vertical point, we have this much momentum. And, well, there's the same amount here.

Now usually, this just means-- the delta p is equal to 0-- means that of all the strong transitions, turning point to turning point transitions are the strongest. Because at a turning point, the vibrational amplitude is large. But there's more to it than that, because there are secondary maxima in the vibrational transition intensities.

These correspond to stationary phase between the initial state and the final state. And so in addition to the strongest transitions, you get other transitions that you can explain by this delta p equals 0.

Now, you don't know anything when you start. You know something maybe about the ground state. And this could be a polyatomic molecule if we're just looking at one mode. And suppose we have an excited state where the vibrational frequency is the same. In other words, there is no change in bonding character.

And so what you end up getting is just the zero to zero transition in absorption. Or if you have many vibrational levels up here, you see v to v, delta v equals 0. Now, you could have a bound state, and it's usually true that the excited state is less bound. And so you would have-- the Franck-Condon active region corresponds to turning point to turning point in the lower state.

So I shouldn't draw this. Let's draw a vertical transition. Well, I missed. Let me just start again. So we have an excited state, and we have a ground state. Ground state is bound. And this is v equal 0. And so we go from here to there.

So if the excited state is less bound, it's a larger inner nucleus and smaller vibrational frequency. We have many vibrational levels accessed by the Franck-Condon principle. And if we have, in the other sense, we have an excited state, which is more bound than the ground state then the Franck-Condon region is narrower. Because this wall is nearly vertical.

You have more transitions when it's displaced this way. And this branch of the potential is nearly much flatter, and you have fewer transitions here. So the vibrational pattern tells you qualitatively from the get go whether you're going to a more bound or a less bound state. That's very useful information.

Now, you want to go further. You want to say, oh, well, I'm observing a bunch of vibrational levels in the excited state. What are their quantum numbers? Are we seeing the v equals zero level? How do we know what vibrational level we're observing? Or levels?

And we can calculate Franck-Condon factors. But you can do many things. So I mean, if you have a situation like this, you might not get to the lowest vibrational level. But if you have a situation like this, you probably will get to the lowest vibrational level.

So one way to get vibrational numbering is seeing the vibrational pattern terminate. That's a good sign it's v equals 0. If it terminates abruptly, it's v equal 0. But if it terminates slowly, you're not sure. But there are other really wonderful things about this.

And you can do isotope separation. Isotope shifts. Since the vibrational frequency is the square root of k over mu, we can change and reduce mass. That changes which vibrational bands you observe, and it changes it in a quantitative way, and so you can often use that to tell.

Another thing you can do is to now. If you have an excited state, the vibrational wave function is going to look like this. And there's a node here, and a node here, and node here, node here, node here. And so if we're looking at the vibrational progression observed from such a level, the intensities will have minima corresponding to how many nodes there are in the excited state. And the number of nodes is the vibrational quantum number.

So there are lots of ways of doing it. And then there is something else. If you observe at moderately low resolution a vibrational band in an electronic spectrum, it will have the peculiar shape like that or like that. This is called a band head.

And it corresponds to the fact that because the rotational constants in the upper and lower state are different, one of the branches-- you have delta J equals plus or minus 1, 0. And the delta J plus 1 is called the R branch and minus 1 is called the P branch. And delta J of 0 is called the Q branch.

Now, these two guys are such that depending on the sign of the difference in B values, you get ahead on the high frequency side or ahead on the low frequency side. Well, actually, it's the other way around. But it tells you then the rotational constant, which is also a signal of how bound the state is.

The rotational constant-- the shading of these band heads-- confirms your vibrational assignment. And typically, if you have a smaller vibrational frequency, you'll also have a smaller rotational constant. It's not always true. And it's always interesting when it doesn't happen.

And so the vibrational bands have this asymmetric shape unless the rotational constant upstairs and downstairs is the same. And then you have a branch going this way and a branch going this way. And a gap in the middle that might be filled with some Q branch lines.

And the Q branch lines tell you, oh, yeah, that was a transition where the lambda, the projection of L on the internuclear axis changed. And if it doesn't have this Q branch, it'll tell you this delta lambda equals 0. All sorts of stuff. And if you have no sign of band heads, but just this double hump structure, it tells you that the rotational constant is about the same as in the ground state. And it tells you also that the vibrational frequency is expected to be about the same.

I better stop. So as soon as you go to polyatomic molecules. Instead of having just one vibration, you have 3n minus 6. And so 3n minus 6 downstairs, 3n minus 6 upstairs, that looks bad. But only some of the vibrational modes correspond to a distortion from-- a difference in geometry between the ground state and the excited state.

And so most of the vibrational modes correspond to identical frequencies. And what we call that is Franck-Condon dark. Because the only transitions that are allowed are delta v equals 0 for that mode. And so only the modes that correspond to a change in structure appear as long progressions.

And so there are only a few, and so the spectrum of a polyatomic molecule is not too much different from a diatomic molecule, because of the small number of Franck-Condon active modes. But you look closer and you see big differences.

OK. So well, we'll talk more about this on Friday. And we might go to three lectures on this, because this is really-- you know the whole point of this course is to be able to understand how molecules talk to us.