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ROBERT FIELD: My spies tell me that there was a good mood after the exam. And it was an exam that was created to show the power of intuition and how you build intuition based on stuff that seems kind of ordinary. And all of a sudden you have the power to exercise chemical insight in ways which are more than just textbook ways of solving differential equations, memorizing pictures, and so on. So this is my purpose, and at the end of the course I'm going to try to really stretch your imagination.

That's the probable schedule. And so I'm taking more time with the lecture on electronic spectroscopy and dynamics because this is really the core of what I do and what I care about. And so I don't know what I'm going to say in this lecture. I want to spend some time talking about Zewail's Nobel Prize work, and certainly that will be partly on Monday.

Then, intermolecular interactions is basically why isn't everything in the gas phase? You know everything isn't in the gas phase, and this is the first step towards not being in the gas phase, kind of important. And then probably photochemistry, which is a little bit more of electronic spectroscopy but in a different framework. Delta functions is a way of dealing with complicated potentials without perturbation theory. And it's really neat and it's very abstract, and it's called the discrete variable representation, and it's a very powerful way of approaching complicated problems without having to do a lot of algebra because the computer does all of it, but it does it in a funny way. And I've been putting off this lecture on time-dependent Hamiltonians for a long time, and I hope that the last lecture will be an honest approach to time-dependent Hamiltonians.

So this is kind of a motto for me. Small is a template for large. If you really understand everything a diatomic molecule can do, you're prepared to understand most of what big molecules do. And so this is sort of a bottom-up approach.

And what I presented last time was sort of a template for everything a diatomic molecule can do. You have a ground state, and that dissociates the ground-state atoms. You have a repulsive state. Now it's not always just two states, but for H_2^+ or for H_2 we sort of expect this

sort of structure. And then there are excited states which are usually less bound than the ground states. So they have smaller rotational constants, larger internuclear distance. And if they don't, there's a good reason for it which you're supposed to be able to produce.

Now the repulsive states often cross through a bound state, and this results in what we call predissociation. In other words, it happens before it was intended to. And it also is an example for all sorts of interesting effects associated with this curve crossing. And we'll talk more about that.

And so predissociation and autoionization, these are dynamical effects that occur as you approach some special limit. Now this is you're above the dissociation limit, so it could happen. But as far as this data is concerned, you're not, and so it happens earlier.

Now here you have ionization. And below the ionization there's a whole infinite manifold of Rydberg states which look almost identical to the potential energy curve for the ion. And there's all sorts of stuff that you can understand about the electron-ion interaction by studying Rydberg states. And that's been, for the last 20 years, roughly half of my research.

Now encoded in Rydberg states is autoionization. If you have a vibrational level of a Rydberg state which lies above the ionization limit, well, then it can ionize, and that's interesting too. So this is a very quick summary of what I talked about before, and I want to add to that.

So in order for a transition to occur, you either need a permanent dipole moment, a dipole moment derivative with respect to the displacement coordinate, or an electronic transition. So this is the rule. This is what you need for a pure rotation transition which is looked at in the microwave. This is what you need for a vibrational transition. The dipole moment has to depend on displacement from equilibrium for one of the coordinates. If it's a diatomic, there's only one. If it's a polyatomic, there's $3n - 6$. And so these two things are very important.

And then the electronic transition moment, you can always have transitions where you promote an electron from the ground state to an excited state. But since the operator is a one-electron operator, the strong transitions are a very small subset of all the possible ones.

And one of the important things for dealing with electronic transitions is the Franck-Condon principle. The Franck-Condon principle is basically a restatement of the Born-Oppenheimer approximation that the electrons move fast, nuclei move slowly. And as a result, $\Delta R = 0$, $\Delta P = 0$. Now I'm using capital letters just to mean all of the coordinates. And this is

what we call a vertical transition.

And $\Delta P = 0$ is stationary phase. Now I like stationary phase. You have integrals of oscillating functions, and you're integrating usually over all space. But the integral accumulates to its final value in a very small region of space, and that region of space corresponds to where the momenta on the upper and lower states, or whatever you're looking at, where the momentum are the same.

And this enables you to use classical insights because instead of having quantum mechanics where you're thinking about wave functions and thinking like I've got an integral to do and I can't say anything simple about it, but if you know that the integral accumulates in a particular geometry, then you can even estimate it. You know what determines how big that integral is. And this is almost always neglected in talking about the Franck-Condon principle, but it's a very important part, especially for me, because I want to find out simple things, and the simple things are always in simple places in state space or in coordinate space.

And then there's the Franck-Condon factor. The Franck-Condon factor is something you calculate. If you know the potential or you have a reasonable estimate of the shape of a potential, you can calculate all the vibrational wave functions in that potential. Not a big deal. I haven't taught you how to do it. I will talk about it in 573, but that's next year, and that's a different life for most of you. But you can calculate the vibrational wave functions. And the Franck-Condon factor is the square of the overlap between the vibrational wave function for the initial state and the final state.

So principle, factor, big difference. We want ideas. Franck-Condon factors are numerical. We want to know what's behind the Franck-Condon factors, and the Franck-Condon principle and stationary phase is what's behind it. And so you're now charged with being able to understand everything that happens in electronic transitions guided by this very important principle, which is really relegated only to calculating Franck-Condon factors, which is just something you do as opposed to something you think about. So that was kind of a summary of what we did last time.

So we can have an electronic band system. So that's a transition between two electronic states, and these electronic states have vibrational levels, and the vibrational levels have rotation levels. And so it depends on how deep you want to go into understanding electronic transitions but what are the questions we want to answer? When we record a spectrum, we

record a spectrum not just to publish a paper or to fulfill an assignment but to ask questions, and so what do we want to know? And there's how questions and why questions. How is a particular excited state different from the ground state?

This means excited state. This means ground state. Spectroscopists use that notation. People who don't know anything about spectroscopy use whatever notation they feel like, and that's really stupid. But anyway, that's a different sort of thing.

And so how are states different? Well, they have different equilibrium geometries. They have different vibrational frequencies. They have different energies. It's a transition between states pretty far apart in energy. There's permanent dipole moment. There's transition dipole moments. There's radiative lifetimes. There's all sorts of things that are distinct from one electronic state to another.

And so this is how they're different, but then why? This is much more interesting, but you do this in order to start asking why. And so you already have qualitative electronic structure stuff like LCAO, MO. Now you could calculate things really accurately, but you wouldn't be using your brain, and this is MIT for God's sake. You do want to use your brain to explain why one state is different from another, and there's all sorts of qualitative theories that are your guide or your framework for doing this. And LCAO-MO, Huckel theory, these are the kinds of things that you can use.

And we also have ideas about orbitals, bonding. So we have orbitals that are bonding, nonbonding, antibonding, and we know this by drawing a molecular orbital diagram. And we know the properties of what happens when you have bonding and antibonding orbitals.

We have hybridization. So a tremendous amount is gained by asking for a carbon atom, and for many other atoms, what is the spⁿ hybridization? We make a special set of orbitals which focus on the structure around each atom. And again, you can be guided by what you know from the spectrum or what you know from simple rules to saying, OK, if we have this hybridization, there is a certain geometry around that atom. Or if we have that geometry or if it's constrained to have that geometry, it will have this hybridization. And we haven't talked about this very much, but it's a very important part of understanding chemistry.

And then we have these things where we-- so we look at families of molecules where you have the same number of electrons. And that was on the exam, and it's really beautiful how you can say, OK, even though we have the same number of electrons, if we change the difference in

ionization energy between the two atoms, terrible things happen or wonderful, beautiful things happen. It depends on what you like. And homologous is just the same number of valence electrons but from different rows of the periodic table, and you had that on the exam too. These are the tricks we use.

And then there's dynamics. And some people might say we study structure so that we can understand dynamics. I'm not quite there yet, but dynamics is interesting because it's harder than structure. You have a static structure. The spectrum is telling you what that is. But it's also telling you, if you look at it the right way, what the molecule can do when it gets excited.

And I frequently start my talks with two slides, one called molecules at play where the molecules are in the ground state, and they're not doing anything interesting, and then molecules at work where molecules are highly excited and doing what they're supposed to do. And our job is really not to understand play. Let them do what they want, but we'd like to understand when they're working and how do we work with them? So dynamics is really that kind of a question.

There's all sorts of kinds of dynamics. There's dissociation. There's ionization. There's Born-Oppenheimer breakdown. And you probably notice these letters, and that's what I do. I'm known for being a specialist in Born-Oppenheimer breakdown.

It appears in many different ways. And so there's predissociation. There's autoionization. There's avoided crossings. And there's adiabatic versus diabatic.

So these two things are really different sides of the same coin. Suppose you have two potential curves that cross. Well, this is what we think about as chemists where a potential curve corresponds to following the energy without really significantly changing the electronic structure. And so these crossing curves are what we call diabatic. But if you're a quantum chemistry, what you would do is you would calculate the adiabatic curves, and they would look like that. They don't cross. And so we have two ways of looking at the interaction between two electronic states, the adiabatic one and the diabatic one, and we use whichever one is simpler for the particular case.

And at some point later in this lecture I hope to talk about a thing called Landau-Zener. And it basically is suppose you're driving at night on a very curvy road. And you're mostly awake, but you're driving too fast. And so if you have a situation like this where there's a sharp curve, and maybe if you're lucky there is another sharp curve on another road somewhere over here.

You're going too fast. You're going to go off the road, and maybe you'll end up on this other road or you'll end up hitting a tree.

So if you're going fast, you're going to jump off the curve. That's diabatic. And that's the point of view we take as chemists. And if you're going really slowly, you'll stay on the road. You won't even remember this intersection because you didn't die at it. And that's adiabatic. And depending on the gap and the curvature for a particular situation, the molecule knows how to either do this or do that. And it's not fatal for the molecule, but if the molecule is going through a curve-crossing region fast, it's going to jump the gap.

And that's one of the things that Zewail looked at. If you can start a system at energy high above the energy where the curves cross, you're going through really fast. If you excite it really close to the energy of the curve crossing, you're going through slowly. And so by changing the conditions, you can understand what's going to happen. This is really powerful for insight.

What I'm trying to convey is that there are very simple pictures to describe really complicated-looking things. And sometimes the data on these complicated things are very hard to either obtain or to interpret because it looks-- well, often it looks-- what would people say? It looks statistical.

Now statistical is really a cop out. It says, I don't understand what's going on here, and so I'll approach it as if there isn't any law. And we just count the density of states, and we'd use simple formulas. And the shameful thing is that that usually works, but it only works so far. It doesn't lead to insight. It just leads to a representation, and our job is to understand, not just to represent.

So back to this question of electronic transitions and the Franck-Condon principle. So if we have a transition between two potential curves that have the same geometry, we get a $\Delta v = 0$ propensity rule. It has good and bad sides. One is the spectrum gets to be really simple because you only see transitions between the same vibrational quantum upstairs and downstairs. And this is true for polyatomic and diatomics as well. You get a simple spectrum and you say, oh crap, I can go home early.

But you don't know anything about other vibrational levels, and if you're starting in the zero vibrational level of the ground state, well, you only know about the zero vibrational level of the

excited state if the potential curves are the same, and there's all sorts of stuff you don't know.

And if you're doing emission, well, maybe in an emission spectrum you excite more vibrational levels. But what's going to happen is if they're all have the same-- if the potential curves are the same, well, then all the vibrational transitions are going to be on top of each other in emission, and you might as well not have bothered. It's just a horrible situation.

So $\Delta v = 0$ depends on what your point of view is. If you want to understand things, this is bad. And then you can have transitions between states which have different shapes or displaced, and the Franck-Condon calculation tells you how this works. But here you have $\Delta v = \text{many}$.

But now for a polyatomic molecule where you have n atoms, you have $3n - 6$ normal modes. And some of them are going to be like this, and some of them are going to be like this. And that's good and bad because what it's saying is, yeah, you could have had a really complicated spectrum because there's so many vibrational-- I mean, for example, benzene has 30 vibrational levels, 30 vibrational modes-- not 1 but 30, and some of them have relatively low frequency. And benzene for most of you is a simple molecule. For me, it's really just beyond complex.

And what happens when you have a lot of vibrational levels is the vibrational density states gets very high, very fast, so high that it's hopeless to be able to resolve the individual eigenstates. When that happens, frequency domain spectroscopy stops being so useful because a lot of the key details are hidden.

So if it's not frequency domain, it wants to be time domain, and you can ask really good questions using time-domain techniques, which is what I'm going to talk about when I spend some time with Mr. Zewail.

So you're going to have certain normal modes which are what we call Franck-Condon dark because they don't contribute to the spectrum. You only see $\Delta v = 0$ for modes. And the ones that lead to a change in geometry or a change in bond structure, those are the ones you see. Those are the Franck-Condon bright ones, and they're also much more interesting because why did the geometry change? What part of the molecule was responsible for the geometry change? This is what chemists want to ask. So that's the framework.

Now, I've spent the last 30 years of my life looking at the acetylene molecule. Acetylene, for

me, it's as big as I want to get, but for most of you that's really, really small.

And acetylene has ground state which we can denote by a zero here, s_0 , lowest singlet. If we had a different number of electrons we might say-- if we had an odd number of electrons, the lowest state would be D_0 or T_0 if it had a triplet ground state like oxygen. The notation is simple.

But we also use-- spectroscopists use notation where we use a Roman capital letter with a tilde over it for polyatomic molecules and not for diatomics, and the electronic state, the ground state is this. And have to be careful because the notation that organic chemists would use for acetylene is just this. And my point is I want to talk about where the hydrogens are.

And so this is kind of a cheat because it sounds like I put a hydrogen on a butene because you have carbon here, these bonds. OK, you know the [INAUDIBLE].

And then there's an excited state which we could call S_1 . And the excited state looks like this. It's trans bent. This has a triple bond. This has a double bond.

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: What?

AUDIENCE: There's also [INAUDIBLE].

ROBERT FIELD: Yes, there's a-- you know about this paper here. But the lowest equilibrium geometry for the excited state is trans bent. You can have this structure too, and we have looked at the isomerization between these two, and how did we do that? How did we characterize the transition state for the isomerization? This is 20, 30 person years of work getting to the transition state, and it led to a paper in *Science*, my first in 40 years of trying.

And so this is a molecule I really like because there are four modes which are Franck-Condon dark and two that are Franck-Condon bright. And we can do all sorts of really neat things.

So in the ground state at high vibrational excitation, what do we expect? Well, one thing is nothing special. Well, the molecule could just go on doing nothing interesting, having four modes which are Franck-Condon dark and two modes that are Franck-Condon bright. It will remain boring.

And another would be just increasing complexity because there can be anharmonic

interactions between different normal modes. And so when that starts to happen people start to say, let me out of here. It gets complicated, and everything gets destroyed, and the spectrum just becomes uninterpretable, which is wrong.

And then there is chaos which is another way-- or quantum chaos-- which is another way of waving your hands and saying it's statistical. And we know my opinion about that because bonds are really sacred in chemistry and if there are bonds, there isn't bag of atoms behavior. And then there's other possibility, isomerization.

So this guy at high exaltation can go to that vinylidene. And I spent a hundred person years chasing after this. So there is a very shallow vinylidene well, and how is this kind of isomerization encoded in the spectrum? So in order to have a chance of understanding about vinylidene or things that happen in the ground state at very high excitation, I invented a fairly important method for looking at high vibrational levels. It's called stimulated emission pumping, and it looks like this.

So we have two-- now this initially was demonstrated on a diatomic molecule, but its true importance is for something like acetylene. So what happens is you can excite to this distorted molecule from the ground state, and some vibrational levels are accessible because you have a little bit of room between two turning points. So you can excite a few vibrational levels by vertical transitions.

But the important thing is that each vibrational level has an inner turning point, which is how you access it, and an outer turning point, which enables you to do-- so this is called the pump, and this is called the dump. Now I'm not sure whether I came up with pump and dump before it was talked about on Wall Street, but it was a very apt name for stimulated emission pumping.

And so what we can do then is to access very high vibrational levels in the electronic ground state by pump and dump. And the way we detect it is we get fluorescence from this level. And when we hit the dump transition, the fluorescences decrease in intensity. And we can do a very significant map of what's going on at high excitation in the ground state.

And when I invented SEP, I believed in quantum chaos. So I expected as we went up higher and higher we would see breaking of all the usual patterns. And I even wrote a paper saying we had seen quantum chaos when we excited to very high vibrational levels. And the reasoning for that is complicated, but the reasoning was correct except it didn't apply to chaos.

It just applied to the spectrum getting complicated, really complicated.

So what I really wanted to be able to do was to be able to somehow sample this transition state. And that experiment in its initial form was doomed to fail because this transition state involves a local bend. In other words, acetylene has normal modes, suspend, trans bend, CH symmetric stretch, CH antisymmetric stretch, and CC stretch. And this coordinate is mostly just that, a large-amplitude local band.

And so when I started this, I didn't know that local bands would magically emerge from the spectrum, but they do and we saw them, and that led to a lot of good stuff. I should mention that I got tenure at MIT because of stimulated emission pumping. That was a long time ago.

So we had not seen the isomerization in the ground state because we couldn't get high enough because Franck-Condon factors prevented us from getting high enough. And the spectrum also gets complicated, and there's all sorts of reasons why it didn't work. But as far as the cis-trans isomerization in the excited state, we killed that, and we killed that because we saw new patterns emerge, and that was more robust than normal modes. And then we saw those new patterns break, and the breaking is due to isomerization. And we worked out the theory, and that's what the *Science* paper was all about.

So now, gas phase versus condensed phase. People who work in the gas phase don't talk to people who work in the condensed phase and vice versa because the spectra are profoundly different. So we have a ground state and we have some excited state. And whether it's a diatomic molecule or a polyatomic molecule, it doesn't matter that much. So what we have in the absorption spectrum is vertical transitions to a few vibrational levels, depending on the difference in geometry. And in the condensed phase, instead of staying in the vibrational level we populated, there is rapid transfer of energy from the molecule into its surroundings, and you end up in v equals 0 of the excited state. And then the spectrum is to a few vibrational levels of the ground state.

And so you get something that looks like this. This is the sort of classic diagram for absorption versus emission spectra of a polyatomic molecule. So this is emission. This is absorption. And frequency is on the right.

So what happens is in the absorption spectrum you observe transitions to higher vibrational levels-- to several vibrational levels, v prime equals 0 and higher. And so those are to the blue

of the band origin. And in emission, you get emission only from v equals 0 in the excited state, and that's to the red of the origin. And so you get this classic double-hump picture.

And there's all sorts of vibrational levels that are not resolved, and this is basically the kind of crappy spectrum you get when you look at a big molecule in the condensed phase. And so it's telling you frequency domain for this sort of thing is the wrong approach because there's nothing much here.

So this thing, the expectation value, the Hamiltonian for the molecule as opposed to the overall system is time dependent. We're used to the Hamiltonian being time independent. There can be dynamics because you excite a coherent superposition of states.

So for condensed-phase systems, the Hamiltonian or energy is not conserved in the molecule. But of course thermodynamics says if you have an isolated system it's conserved. That's irrelevant because we always want to look at something more interesting than a bulk sample.

Now I want to talk about dynamics that is more subtle than the naive stuff-- so subtle dynamics. Well, let's have no collisions. Well, we can do that in the gas phase if the pressure's low enough. No breaking of molecules. So if there is no predissociation or autoionization-- so we can restrict ourselves to a low enough energy that things don't break.

Now this is subtle. Molecules will fluoresce, and populations in excited states will decay. And as a rule, the fluorescence lifetime, if it's truly only fluorescence and not other dynamics, the lifetime is longer than 10 nanoseconds. So if we're looking at times shorter than 10 nanoseconds we can say there's no fluorescence. We're going to ignore that. That's OK because there still can be dynamics.

So simplest case, two-level quantum beats, and you know about quantum beats. You've already looked at them in various problems. And so you have a system where you have a ground state and you have two excited states, and one of them is bright and one of them is dark with respect to transitions from this state. But there is an interaction between them, and so they're mixed character and with a short pulse. You prepare a coherent superposition of two eigenstates. The intensity of the fluorescence oscillates, and it isolates at the frequency difference of these two levels.

And the modulation depth of the fluorescence tells you something about what is the coupling matrix element between these two states relative to the energy difference between them? So

there's a lot of information in there, and so this is something that can happen faster than the spontaneous fluorescence. One is observing it in the spontaneous fluorescence, but the whole point is you're looking at some dynamics that is encoded in eigenstates. And that's one of my mottos.

We know how to write all the theory for this. We have something that looks broad, but in reality it's a whole bunch of eigenstates. And the pattern of these eigenstates is telling you what the dynamics is.

Now normally we think of dynamics as the width of something. And this collection of eigenstates behaving in some coherent way has a width, but that's only the beginning. What was the thing that gave intensity to these eigenstates? What was the zero-order state, and what was the coupling matrix element between the bright state and the dark state, and what are the rules for these? And so if you can resolve these eigenstates, you learn about much more detailed picture of dynamics than just saying, well, dynamics is a width.

If you're below the energy where molecules can break, there is no width. But if you do a crappy experiment, you don't resolve stuff and it looks broad. Now, sometimes the molecule sets the standard for what's a real experiment by having its density of states so large you couldn't resolve it even if you had the best experiment in the world. But there's still the idea that inside this broad thing there is some interpretable dynamics. That's my goal.

Well, one kind of interpretable dynamics is, OK, so you have some excited state and some ground state, and there's a range of vibrational levels that you can excite. And if you have a short pulse, you make a coherent superposition of all of those vibrational levels. And then what you have is some wave packet which has got an energy, sort of the average of these. And the wave packet starts out at a turning point because you started out with essentially zero momentum. And the wave packet moves, and it goes back and forth and back and forth. And it's telling you what the vibrational frequency of that mode is.

And so you can then observe the fluorescence from this evolving wave packet, or you can monitor this evolving wave packet either by looking at fluorescence back to where you started. And so when it's over here, it can't fluoresce to where you started. When it's over here where it was born, it can. And so the fluorescence is going to be doing a kind of quantum beating.

You could also use some kind of pump-probe experiment where you say, I'm going to look at the wave packet when it's here because I have a transition to another electronic state. And so

the vertical excitation is at that energy, and so I wait for the wave packet to get to a point. And so you have a periodic motion. And you have dephasing because this wave packet is built out of vibrational levels which are not harmonic so that there is some dispersion of the vibrational frequencies around the average. As a result, that causes this thing to dephase. And its dephasing time could look like a width, but it's actually a particular mechanism.

And then there are other things that can happen, and I love this. So we've got a few minutes. So suppose we have two electronic states that are crossing, and you're starting out in this level. You made a wave packet.

So this is going back and forth, and every half oscillation it goes through this critical region. What's that region? What's special about that region? Come on.

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: I'm sorry?

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: Not if this is a bounce state. That's a good try. That is, in fact, if this were a repulsive state, then predissociation would occur when it cross through the region. This is the stationary phase region. This is where the momentum on the two potential curves is the same.

And so the molecule can make up its mind which potential curve it wants to leave on because there's no impulse that causes a change in its momentum, and it just makes a decision which one.

And so when that happens, if you're following the dynamics, you have a series of beats. And I'm just sketching them as a stick, but really, they have width. And then at some later time you start seeing a new family of oscillations because now you've got some amplitude on this other state, and it has a different frequency.

But the important thing-- and I should stop here-- is that the only time the molecule has to change its mind between one state and another is when it's crossing through this stationary phase region. So it's a complicated thing, but it's isolating a particular region where the curves cross. And where the curves cross, instead of having crossing curves, you could have something like this and something like that. Now we're back to Mr. Landau and Mr. Zener.

And so if there's a curve crossing, depending on how far above the curve crossing, it tells you how fast you're going through it. See, there's all sorts of wonderful stuff here, which is not the trivial dynamics that-- this is the only way you get broadening is the molecule breaks. And the fluorescence is usually so slow-- 10 nanoseconds is slow-- that you don't see any broadening because 10 nanoseconds corresponds to a pretty high resolution, and most people aren't looking at that kind of resolution.

And so we have quantum beats which then can show beautiful dynamics in a way that if you're prepared to build a model and to say, well, we could have this case and this case-- this is the chemists' case. We have quantum chemists' case-- you can interpret everything.

This is very much related to what Mr. Zewail does. And I will spend a significant amount of time on Monday talking about the Zewail experiments and how the whole point of his experiments are not just saying, OK, I excite the molecule and it breaks. It breaks in this much time. Well, that's a useful question, but what did it do before it broke? One particular bond breaks, but what about the motions of the other bonds?

Or maybe you're talking about breaking in a particular normal mode. Does the molecule arrange itself to be broken? Or once it's excited it goes downhill to the graveyard in a particular path, but there are wonderful things you can do by asking, what is the mechanism by which the molecule breaks? And by varying how you excite the molecule, you're looking at different aspects of that mechanism.

Now Zewail sold this really hard, and it worked. And so I'll leave that for Monday.