PROFESSOR ROBERT FIELD: So last time we talked about intermolecular interactions. Intermolecular. It's complicated enough talking about individual molecules, what molecules can do, but we could also talk about interactions between molecules, and we can use perturbation theory, and what we discover is something universal about all pairs of molecules. Molecules which don't have any reason to interact with each other, like being charged or even having dipole moments, and we discover that all molecules are attracted to each other.

And we know the force law, we know how everything scales, and we also know that we can look at molecules, and say this molecule is going to be a good molecule for intermolecular interactions because either it has a lot of low-lying transitions, or they have very strong transitions. And so you can compare different atoms or different molecules. And one of the important messages is that really big molecules are really sticky. They want to attract each other because they have a lot of vibrations, and each vibrational node can act as a dipole in this dipole-dipole interaction, whether it's induced dipole-induced dipole or whatever.

So it's one of these things where something from one half of your brain is able to explain something from the other half, and that's really wonderful, and we're always aiming for that. Now, today we're talking about photochemistry. And this is an enormous topic. And I would say that there are vastly more physical chemists and biophysical chemists working on photochemistry than on spectroscopy. So what happens when a molecule gets excited by a photon? Does it just fluoresce or does it do interesting stuff?

And there's a lot of really beautiful semi-empirical theory that enables you to estimate the rates of everything that a molecule can do, and the uses for what these things do. But in order to put this in perspective, I have to do a little bit of review of the different kinds of spectroscopy-- rotation, rotation-vibration, rotation-vibration-electronic in order to get the energy scales and to describe the actors in this problem of photochemistry.

There's two sets of notes, what I'm going to be working from, which is because I'm a small molecule person, bottom-up, and I'm trying to take what I know and I've taught you about

small molecules, and extend it to regions of incredible complexity, but using most of the same concepts. And Troy's notes, which are top-down, and he's basically interested in photochemistry, and condensed phases, and big molecules. And I'm afraid to go to condensed phases and big molecules, but the two shall meet, and many of the topics will be understandable with both approaches.

OK, so let's just set the framework. We have three kinds of spectra, and the typical energy associated with that is one wave number. And we have rotation-vibration, and the typical energy scale is 1,000 wave numbers. And then there is the rotation-vibration-electronic, and that's, going to say 20,000 wave numbers and higher. Now, this is peanuts compared to the strength of molecular bonds and interactions between molecules, but this is big news because now the photon that excites the molecule is sort of acting like a reagent.

This energy, it goes up as far as you want. These energies are comparable to the energies of chemical bonds, and the electronically excited molecules can do chemistry that the rotational or vibrationally excited molecules can't do. That's why it's so interesting, and that's why it's so complicated. OK, now, what can an excited molecule do? Well, maybe I should ask you. Yes?

AUDIENCE: Rearrange.

PROFESSOR ROBERT FIELD: OK, so we can call it isomerization. Anything else?

AUDIENCE: Fragmentation.

PROFESSOR ROBERT FIELD: I'm sorry?

AUDIENCE: Fragmentation.

PROFESSOR ROBERT FIELD: Yes.

AUDIENCE: It can relax.

PROFESSOR ROBERT FIELD: By?

AUDIENCE: Emitting a photon.

PROFESSOR ROBERT FIELD: Yes, fluorescence. That's what we do. There's lots of things that can happen and the kinds of things that can happen depends on what kind of exaltation we've produced, but the big photons are going to produce really complicated stuff. Now, one framework we can talk about is what is the rate of-- I can't imagine what I wrote there. So this is the total rate, and it can be composed of the radiative decay and the non-radiative decay.

Now, there's a size scale here. Oh, I know what I wrote here. That's measured. So if you had a system and you measured the exponential decay of the population in that system, that's composed of the radiative part and everything else, and the radiative part corresponds to lifetimes no shorter than 10 nanoseconds. There is absolutely no way that molecules or atoms can fluoresce at a rate much faster than one over 10 to the minus eight seconds, and then there's other stuff.

And so when the other stuff, the non-radiative decay is fast compared to the fastest the molecule could decay by emitting a photon, then we're getting into something complicated and interesting. When the molecule just radiates a photon, and this stuff is very small, well, that's nice, but it doesn't tell us very much except what is the radiative lifetime of the particular excited state. So there's various kinds of de-excitation, and there's collisional, and there's-- well, we can call it collision-free.

Now, remember, if there's no collision, energy is conserved. We have a Hamiltonian. The expectation of the Hamiltonian for an isolated system is not time dependent. So we have energy conservation, yet in the absence of-- collisions are what change the energy. We remove energy from the system. We can have an incredibly complicated range of processes which are collision-free, and these collision-free processes have the signature of the molecule all over it. They are telling you something about what the molecule thinks it can do and does, whereas the collisional stuff is purely statistical.

So the collisional processes, we can say-- we can estimate how fast they are. And first of all, there is this number that many physical chemists carry in their head, especially if we work in the gas phase. A collisional rate is on the order of 10 megahertz per torr. Now, I'm an old guy. I do two torr instead of bar or millibar, but a torr and a millibar are about the same thing. And at atmospheric pressure, that corresponds to 10 gigahertz per atmosphere, and so that means 10 to the minus 10 seconds.

So the collisional rates can be competing with radiative rates at atmospheric pressure. Or in

condensed phase, they really can compete. But this number, 10 megahertz per torr, is a good number to carry around for estimating the frequency of collisions. Now, there are different kinds of collisions. And one collision with this sort of rate is all it takes to relax rotation, and about 1,000 solutions are required to relax vibration.

And now, it's very hard to estimate what it takes to relax electronic excitation because the electronic excitation is so big, there's so many different things that can happen. And so you could say, well, if nothing really chemical happened, it would take about a million collisions to relax electronic, but there are so many other things. I don't want to put a number here because this is really the interesting and complicated stuff. OK.

In particular, suppose you have an electronically excited molecule, and it collides with an unexcited molecule, and you end up doing A plus BCD or all sorts of things. That's chemistry, right? But this wouldn't happen if this star wasn't there. And there's a tremendous complexity to chemistry. That's why we have-- it's a BSD subject. It's a major area of science, and so we're engaging with chemistry when we start talking about electronically excited atoms, and vibration and rotation excitation is largely irrelevant to chemistry. it's small potatoes. You can see chemical effects by rotation and vibrational excitation, but that's for the purists like me.

OK, now collision-free effects are initially surprising. We can have several, and we've got some of those from the initial discussion, but I'm going to just list them again. We can have the molecule breaks, and that could be dissociation or ionization. This is something that all molecules do if you excite them enough. They either fall apart into smaller molecules or ionize.

There's nothing surprising there. But then there's the unexpected processes, or at least they used to be unexpected. When I was a graduate student, there was still a lot of confusion about what happens in the absence of collisions. And there are several names for them. IVR-- intramolecular vibrational redistribution. This process, which you understand from perturbation theory-- I talked about this early in the semester.

This put closed to the idea of vibration or mode-specific chemistry by putting an excitation into a molecule-- a high vibrational excitation into a particular molecule, activate a bond to chemistry. IVR is always faster than chemistry. Or faster than collisions until you get to the condensed phase. IVR, that's one. There was so much confusion about IVR in the old days that people didn't even know what it meant. It just meant I don't understand what's going on. But it is intramolecular vibrational redistribution.

Then there's another process called internal conversion, and another process called intersystem crossing. So IVR is something that happens in one electronic state, internal conversion involves relaxation into high vibrational levels of a lower electronic state of the same spin, and intersystem crossing is a relaxation into a high vibrational levels of another electronic state with a different spin. These are really two sides of the same coin, except that they depend on different molecular properties, and one can make generalizations that are different for IC and ISC.

So for a small molecule, we've looked at this before, but-- we can excite directly to an excited state, and that's direct association that comes like this, and there's all sorts of really neat things you can do, where you can calculate the Franck-Condon factors or the vibrational intensities for the different energies, here, by knowing that you have-- you can calculate the wave function for the continuum, and you know you have a big lobe here, and as it gets faster and faster, the lobes get smaller, and smaller, and closer, and closer together. And there's a thing called the reflection principle that describes the rate of excitation to a repulsive state. And by looking at the spectrum, you can learn the slope and position of this state.

OK, there's also suppose you have a level here of this excited state. Well, that excited state has access to this crossing point, and so that can free-disassociate. So there's direct and free-dissociation. I like this stuff too because if I know the rate of free-disassociation, and what happens with free disassociation is you have a spectrum where you measure several vibrational levels in this state, and the vibrational lifetimes of these states are more or less the same, and all of a sudden the lifetime decreases. Or all of a sudden the spectrum goes from being sharp to broad.

Or the fluorescence decreases. The intensity decreases because the quantum yield or the fluorescence quantum yield is one over tau radiated over one over tau radiated plus one over tau non-radiated. And the pre-disassociation rates can be much faster than the radiative rates. So this fluorescence quantum yield goes down. But the neat thing is that you generally know what the radiative component of the decay is, and so by measuring what the actual fluorescence quantum yield or the decrease in intensity, you learn something about the non-radiative decay.

OK, I've also taught you we can also ionize. And we can have direct ionization, and it looks sort of like this, or we can have what's called auto-ionization where somehow, the molecule is

able to convert rotation and vibration of the core, and transfer it into the electronic excitation, and the electron is free. So before you're actually accessing directly, an ionization continue, you can have this other process. These are things that I've studied for my whole career, and I know about it, and I love to talk about them, and we're not going to talk about them.

OK, I also told you about quantum beats. So suppose we have a bright state and a dark state. In other words, we have two states, one of which has an allowed transition with the ground state, and one has a forbidden transition with the ground state. But these are zero order states, and they can interact to make mixed states because there's some term in the Hamiltonian connects the bright state to the dark state.

So what you do with a short excitation pulse is you make some coherent superposition of these bright and dark states, which at t equals zero is the bright state, and you get quantum beats, and quantum beats can look like this. They start out phased up, and they go down like that, and so we have modulation of the fluorescence. Now, it doesn't have to be 100% modulation. It could be something really small, but it's always going to be phased up if we're looking at the bright state. So we understand quantum beats.

Now, suppose instead of having one bright state and one dark state, light, dark, we have a whole bunch of dark states. Well, in that case, if you make this coherent superposition, you'll get many quantum beats, but they'll all have different frequencies, and the quantum beats will dephase, and it will look just like the fluorescence decays to zero faster than it's supposed to be able to. The ceiling on decay rate of one over 10 to the minus eight or 10 to the eight per second, that can be violated by mixing of the bright state into the dark state.

So the ability of the molecule to fluoresce goes away fast, but the excitation doesn't decay. What you've done is you've mixed a bright state, a decaying zero order state, with states that don't decay, and the average lifetime is very long, but the experiment says the lifetime is really short. Because what's happening is not that the population is decaying, but the ability to decay has been spread among many eigenstates, and so none of them are very good at it.

OK, so now you're starting to get the idea of how we can have fast decay without collisions. And all of these three processes, which I've hidden, IVR, internal conversion, intersystem crossing, are based on relaxation of one kind of state into many dark states. So nothing is happening without collisions. Energy is conserved without collisions, but the signal goes away, and it's tempting to say that either something magic has happened and the molecule has

decayed, or you really haven't gone to low enough pressure, and there really are collisions.

This was a very bitter battle in the mid 1960s. There was one faculty member who taught the quantum mechanics course, very much like the one I've been teaching for years, but he believed that there was no such thing as radiationless transitions. It's always that the fluorescence was quenched, but he's wrong. In the absence of collision, what decays? What decays is the ability to fluoresce or the ability to do other things like absorb another photon to some other excited state.

You've produced the molecule not just in one eigenstate, but in a bunch of eigenstates, and this bunch of eigenstates, since the initial preparation, is the bright state that's in that bunch, and there's a couple among them. What happens is it's time dependent, and the evolution of this coherent superposition state is the key. Let's talk a little bit about IVR some more.

When we have 3n minus six vibrational modes, there can be a very large number of dark states. States that couldn't be excited by whatever method you use to excite them, whether it be an ultraviolet photon, or a microwave-- anything. You have a bright state and a whole bunch of states that you are not supposed to be able to excite, an anharmonic interactions among them. And we know some things.

So if we have a cubic interaction, where we have one normal mode. So this would be a term in the Hamiltonian. And again, I lectured on this before at a time when it was probably impossible to understand the significance of this, but you used perturbation theory to say OK, what's happening when you have an anharmonic coupling term that couples one mode to another? And we know how do all that sort of stuff. And the selection rules for that are delta vi equals plus and minus one, delta vj equals plus and minus two and zero.

We also know when we go from the real coordinate to the dimensionless coordinate, we factor something out. And for each power of Q, that thing that we factor out is a factor of 100 smaller. We have cubic terms that we have quartic terms, and the quartic terms are a factor of roughly 100 smaller, but there's more of them. And so there is an order sorting thing, which we can call delta capital V, which is the sum from i equals one to 3n minus six of the absolute value of delta vi.

So if the total change in number of vibrational quanta is three, well, we have a cubic term. If it's four, it's quartic term, and the quartic term has a coefficient, a factor of 100, roughly, smaller than the cubic one, but there's more possibilities. And so suppose we are going to talk about

benzene. Well, it has 30 nodes. And so we could imagine delta v on the order o 30. Well, it's 10 to the 60 smaller than the delta v of three, except that there's a lot more possibilities.

So we have to think about how big is the coupling matrix element, and how many states are being coupled? And so there's a thing that's really relevant called the vibrational density of states. So at a particular excitation energy, you want to be able to know how many vibrational states there are because that, more or less, tells you OK, we're going to have some kind of statistical coupling. And if we know the density of states and the average matrix element, we could do a Fermi golden rule of calculation, and we can predict what's going to happen.

Now, there are ways of calculating the density of states, which are rigorous and beautiful, but there's also a very simple minded way of doing it, which I'm going to present here. So the vibrational density of states. This is one of the most primitive, crude estimates of density of states, and I'll explain how it works, but I'll explain it by going even cruder. And I also want to make sure that I have it--

OK, this frequency is in wave numbers, and this is in wave numbers. So we just changed both quantities. This is OK, and this will give me the number of states per wave number. OK, so let me do an example for benzene. We have 30 modes, and here's a big assumption, which is completely wrong, but it leads to an underestimate. Let us say that all of the modes have the same frequency-- 1000 wave numbers. That's a typical number for a vibrational frequency, but benzene has a lot of modes that have much lower frequencies, and only a few that have higher frequency, and so this is going to be a gross underestimate.

And now let's say we have the vibrational energy divided by Hc, and that that is 10,000 wave number. So we have 10,000 wave numbers of vibrational excitation in benzene, and we have all the modes having the same frequency. So we need 10 quanta to make 10,000, and there's 30 choices. So we have 30 to the 10. So each quanta we pick, we have 30 choices. And we have to do 10 of them, and so it's 30 to the 10, but now we have 10 factorial. We have to divide that by that because the order of the 10 choices has to be corrected.

OK, and so this number is 1.6 times 10 to the eighth. That's a big number. I'm used to talking about states one at a time, and it's very rare that I have two states within one wave number, and here we have 10 of the eight. So let's go down in energy a little bit. Let's say instead of 10,000, let's go to 3,000. And when we do the same calculation for 3,000, we get 4,500 states instead of 100 million states.

So two messages. One is the number of states is really large, and it goes up really, really fast. And this takes us into a region of quantum mechanics that we hadn't thought about before because I'm doing bottom-up, and there is no place in what I do for a million states or even 100 states. OK. Now, let's talk about a typical energy level diagram. This is the ground state, This is the excited triplet state, which is almost always the first excited state, and then here is the first excited sigma state.

And so for small polyphonic molecules, we have a very low density of states here, a somewhat higher density of vibrationally excited levels of the triplet here, and a very high density of states from the ground state. So you normally look at relatively low vibrational levels, and there's nothing much happening here, and maybe there's some perturbations by a triplet state. So we get local glitches in the energy levels and spectroscopic properties, and the density of high vibrational level in a ground state is so high that they might as well not be there.

But now when we talk about these collisional processes of bigger molecules, we want to use Fermi's golden rule, and you've seen Fermi's golden rule. It tells you the rate of various processes. And so a rate, we can call gamma. Two pi over h bar times the vibrational density of states times H bright, dark squared. So that's the Fermi's golden rule rewritten in terms to describe radiationless processes. It's directly related to the first way we saw it. And so we have the vibrational density of states, which as you go up in excitation energy, increases really rapidly.

You have the average of the matrix elements between the coupled states, squared. This is going to go down because remember when I talked about vibrational matrix elements, each additional number in the change in total vibrational quanta causes this to go down by roughly a factor of 100. We have a big increase here, and a big decrease here, but this guy wins. You can show that. So now, we can draw sort of a manifold of states.

So what's happening is the density of triplet states is much higher than the density of singlet states. And so if you were just interested in IVR, well, you'd look at that. But this is a much faster process, and this is enormously faster because the energy gap between s1 and t1 is much smaller than in the energy gap between s1 and s0. And so the s1-s0 interaction is called internal conversion, and that's usually way bigger than the s1-t1 intersystem crossing, but not always.

The intersystem crossing is due to spin orbit interactions. Spin orbit interactions are

predictable for each atom. Extending what you got in five-eleven-one and five-eleven-two, you can predict what the spin orbit interaction is, and it's related to the amplitude of the wave function at the nucleus. But anyway, what happens is that carbon has a spin orbit coupling constant of 10 wave numbers, and oxygen has one of about 150 wave numbers.

And since we're talking about squared matrix elements, oxygen is 225 times more effective than carbon. And so if we have a couple of oxygen atoms in the molecule-- or nitrogen atoms-- the spin orbit interactions are much bigger, and they can win over internal conversion sometimes. Depends on what the energy gap is. And now, molecules which have strong electronic transitions have chroma force. It's not the whole molecule. It's something about a part of the molecule.

And if you have a strong transition at relatively low energy, there is always oxygen or nitrogen. And so the thing that you're exciting is going to have a fast intersystem crossing rate because it involves oxygen and nitrogen. But if you have just a pure hydrocarbon, intersystem crossing is probably not so important, but internal conversion is going to win.

And for most hydrocarbons, you can have a nice, strong absorption spectrum, but very little fluorescence, and that's mostly because of internal conversion. But the crucial thing is the energy gap s1-t1, or s1-s0 controlling the relative importance of ISC versus IC. Now, you could also have several different excited states like s1 and s2, and they could be talking to each other through a small gap or to the ground state by an even larger gap. There's all sorts of stuff. Yes?

AUDIENCE: The internal conversion process, you're going from the first singlet excited state to the lowest level singlet ground state. Where does the energy get redistributed to?

PROFESSOR ROBERT FIELD: It gets excited into a vibrational excited level of the ground state, but the energy hasn't gone anywhere. It's just now these guys are not fluorescing, and if there are collisions, the collisions can cause removal of energy from the molecule. And since the vibrational energy gaps are really small, collisions start to be very effective in cooling. But if you have a laser, and the laser involves somehow exciting the s1 state, and the s1 state likes to fluoresce to high vibrational levels of the ground state because of Franck-Condon, so it has gain, but there is often a t1 to t2 excitation, which is in the region of the gain of the laser, and it quenches it.

And so diolasers, which are a fantastic way of generating tunable radiation, are always worried about quenching by triplets, and you have to do something clever to quench the triplets to

remove that. So there's all sorts of stuff about competing processes that you can use it as insights. OK, we don't have much more time, and the most important topic, I'm not going to talk about at all. So we can have isomerization, and isomerization takes many forms. I've spent the last 30 years looking at isomerization in a really simple polyatomic called acetylene.

And in the ground state, you can isomerize from high vibrational levels of the ground state to another isomer called [? venility, ?] and this is a really interesting problem. And in the excited state, we have two conformers. The trans-bent conformer and the cis-bent conformer, and they're separated by a barrier, and we can understand both of those processes. But the important thing is if the molecule isomerizes, its chemistry changes, and so it will act differently.

Now, there's all sorts of kinds of isomerizations. This is a 1,2 hydrogen shift, but there's also intramolecular proton transfer. There's torsions where a structure-- one isomer or conformer is locked in by a lot of hydrogen bonding, and the bigger the molecule, the larger number of isomerization structures you have to consider, and there's a lot of insight there. So isomerization is a very crucial thing in the behavior of large molecules.

The topic that I don't really have time for is FRED-- fluorescence resonance energy transfer. Let's just draw a little picture of a molecule doing all sorts of neat things, and another confirmation of that molecule, and we have donor and acceptor. So at the opposite ends of this thing, clever chemists can put things that-- and so this is a molecule which has an electronically excited state. This fluoresces in the loop.

We excited, say, in the UV, and it fluoresces to the red of the excitation because that would happen. In condensed phases, you remove some energy, and you fluoresce from v equals zero. And we have an acceptor which absorbs in the blue, and fluoresces in the red. And the donor-acceptor energy transfer is related to one over r to the six. Doesn't that look familiar? It's a dipole-dipole interaction, or an induced dipole-induced dipole interaction. It goes as one over r to the six, and so we might get a lot of red fluorescence from this molecule exciting in the UV, and much less red fluorescence or none because we've increased the distance.

And this works in the range of I think one to 10 nanometers. Yeah. So it's a fantastic ruler. How much red shifted fluorescence do you get from donor to acceptor energy transfer? And it's a measure of the distance. And so you have a protein and a denatured protein. This distance changes, and one can use the way in which the red fluorescence appears as a

measure of the structure.

So this is not like small molecule spectroscopy where you calculate moments of inertia and vibrational frequency. This is really crude. This has nothing to do with quantum mechanics, except it is, and it's just a simple measurement of how far two things are apart. And there are all sorts of ways of using this, including time resolved waves, where you actually look at the rate at which the one kind of fluorescence goes away, and the other kind of fluorescence comes in, and many other things.

OK, so that's it for me on photochemistry, and you should read Troy's notes because they are much more germane to what you might encounter in real life. But the bottom-up approach, I think, is useful too, especially in the importance of how the matrix elements and the density of states scale using simple ideas. So I'll see you on Monday and blow you away on Monday.