# Lecture #34:  ELECTRONIC SPECTROSCOPY AND PHOTOCHEMISTRY

The ability of light to induce electronic transitions is one of the most fascinating aspects of chemistry.  It is responsible for the colors of the various dyes and pigments we manufacture and forms the basis for photosynthesis, where photons are converted into chemical energy.  This all arises because electrons are the "glue" that holds molecules together, and it makes electronic spectroscopy perhaps the most natural form of spectroscopy for chemistry.

The selection rules for purely electronic spectroscopy are fairly easy to write down. The transition between *i* and *f* is forbidden if the transition dipole between the states is zero:

$$\vec{\mu}^{i \to f} = \int \ \Psi_{el}^{f*} \hat{\mu} \Psi_{el}^{i} d\tau_{el} = e \int \ \Psi_{el}^{f*} \hat{r} \Psi_{el}^{i} d\tau_{el}$$

where we have noted that the dipole moment operator takes on a simple form for electrons.  Unfortunately, the electronic wavefunctions of real molecules are so complicated that we typically cannot say anything about whether a given transition is allowed or not.  There are only two cases where we get selection rules.  The first case is if the molecule has some symmetry. For example, if the molecule has a mirror plane, we will be able to characterize the electronic eigenfunctions as being odd or even with respect to reflection.  Then we will find that transitions between two even (or two odd) functions will be forbidden because *r* is odd, (even)×(odd)×(even)=odd and the integral of an odd function gives zero. In general, we see that **allowed electronic transitions must involve a change in symmetry**. For large molecules, or even small molecules in asymmetric environments, it is rare that we have a perfect symmetry.  However, for an approximate symmetry we expect the functions to be nearly symmetric, so that transitions that don't involve a change in (approximate) parity will be only weakly allowed.

The second thing we note is that the dipole moment is a *one electron operator*.  That is to say, it counts up contributions one electron at a time. This stands in contrast to an operator like the Coulomb interaction, which counts up energy contribution between pairs of electrons repelling one another – the Coulomb repulsion is a **two electron operator** while the dipole is a **one electron operator**.  As a result, the brightest transitions (i.e. the ones with large transition dipoles) tend to be dominated by the motion of **one electron at a time.**          Thus, a $(\sigma^2\pi^2) \to (\sigma^2\pi\pi^*)$ transition would typically be allowed because we are just moving one electron (from π to π*). Meanwhile, a $(\sigma^2\pi^2) \to (\sigma^2\pi^{*2})$ transition would typically be forbidden because we have to move two electrons from π to π* to make it work.  In practice the one-electron selection rule is only approximate because real electronic states never differ by a purely one electron or two electron substitution.  As we saw in discussing electron correlation, the wavefunctions will be mixtures of many different substituted states.  However, in practice, the one electron transitions provide a good *propensity rule* – the brightest transitions will typically be dominated by one-electron excitation, while multi-electron excitations will tend to be dark.

The final class of forbidden transitions arises due to spin.  In particular, we note that we

can re-write the electronic wavefunction as a space part times a spin part, so that the transition dipole becomes

$$\vec{\mu}^{i\to f} = \int \Psi^{f*}(r)\Omega^{f*}(\sigma)\hat{\mu}\Psi^i(r)\Omega^i(\sigma)drd\sigma = \int \Omega^{f*}(\sigma)\Omega^i(\sigma)d\sigma \int \Psi^{f*}(r)\hat{\mu}\Psi^i(r)dr$$

where, in the second equality, we have noted that the transition dipole factorizes into (spin)x(space) integrals. The spin integral is just the overlap of the spin wavefunctions. If the two electronic states have different spin multiplicity (e.g. one is a singlet and the other is a triplet) then the spin integral will vanish. Thus we see that **allowed electronic transitions preserve spin**. This is consistent with the experimental observation that most bright absorption features correspond to spin preserving transitions. The one exception to this rule occurs when you have a heavy atom (i.e. high Z) in your molecule. In this case the effects of relativity become important and the factorization into (space)x(spin) is not precisely correct. As a result, in these cases spin-changing transitions can become weakly – or even strongly for large enough Z – allowed.

The rules above for electronic transitions are of only limited use in interpreting spectra, because one is very rarely concerned with purely electronic transitions. To get the qualitatively correct picture, we must realize that, just as vibrational transitions were always coupled to rotations, so **electronic transitions are always accompanied by vibrational transitions**.
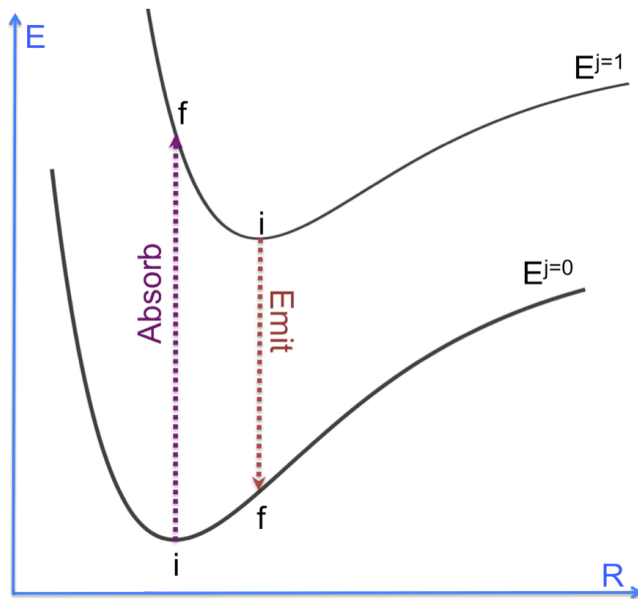


**Figure 1**. Classical picture of absorption and emission processes.

First, let us review the Born-Oppenheimer picture of potential energy surfaces. In the BO approximation, we clamp the atomic positions at some value, **R**, and solve for the instantaneous electronic eigenstates in the field produced by the nuclei

$$\hat{H}_{el}(\mathbf{R})\Psi^i_{el}(\mathbf{R}) = E^j_{el}(\mathbf{R})\Psi^j_{el}(\mathbf{R}).$$

The energy, $E^j_{ed}(R)$, is the potential energy surface for the j$^{th}$ electronic state. As mentioned previously, most of chemistry happens in the ground (j=0) electronic state. However, for electronic spectroscopy we will necessarily be interested in transitions between different electronic states

and so i will be non-zero in general. The resulting PES's for the ground and first excited states of a diatomic molecule might look like the black curves in Figure 1. We note that because the electronic wavefunctions are eigenfunctions of the same Hamiltonian, they are orthonormal

$$\int \Psi^{j*}_{el}(\mathbf{R})\Psi^k_{el}(\mathbf{R})d\tau_{el} = \delta_{jk}$$

which will prove useful in a moment.

Now, consider an electronic transition (absorption) from j=0 to j=1 and take a purely classi-

cal picture of the nuclei.  There are clearly many energies that this could occur at, because the energies of the two states depend on **R**. First we note that the energy scale for electronic transitions is typically  several eV.  Meanwhile, the energy scale for thermal motion is governed by $k_B T$ 0.025 eV at room temperature.  Thus, at typical temperatures, it is  reasonable to pretend the molecule is just at the very bottom of the well and we label this point as "initial".  The final state is usually fixed by the **Condon approximation**.  Here, we note that the nuclei are much heavier than  the electrons, and so when we zap the molecule with photons, the electrons will respond much more quickly than the nuclei.  Thus, to a good approximation, we can assume that **the nuclei don't move during an electronic transition**.  The physical basis of the Condon approximation is  similar to the Born-Oppenheimer approximation and governs the way  chemists think about electronic spectroscopy.  In the picture in Figure 1, the Condon approximation corresponds to considering only transitions that do not change **R** – that is to say, the Condon approximation singles out transitions  that are vertical lines as being most important.  Thus, the final state for absorption will have the same value of **R** as the ground state.

If we perform the same analysis for emission spectra, the initial state  becomes j=1 and the final state j=0.  At room temperature, the molecule will spend most of its time around the minimum of j=1, which changes the initial state, and the Condon approximation dictates that the most important  emission transitions will be those that proceed directly downward from the  excited state minimum.  Both absorption and emission transitions are depicted in Figure 1.  The important thing to realize is that, even though the  Condon approximation dictates that electronic transitions don't move the  nuclei, yet still we probe nuclear motion with the electronic spectrum because the absorption and emission correspond to different portions of the PES.  The difference between absorption and emission wavelengths is known  as the **Stokes shift** and it is a qualitative measure of "how different" the ground and excited potential surfaces are.  If they are very similar, the Stokes shift will be small, while large confromational changes in the excited  state will lead to a large Stokes shift.  In particular, we note that the Stokes shift is always a redshift – the emitted photon always has lower  energy than the absorbed photon.

In order to extract more information from the electronic spectrum, it is  necessary to account for the fact that the nuclei are quantum mechanical, as well. How do we obtain the nuclear wavefunction?  BO provides a presciption for the nuclei as well.  Specifically, we envision the nuclei as moving on the PES defined by the electrons, so that they will have wavefunctions like those pictured in Figure 2.  Mathematically, we think of the nuclear wavefunctions as solving the Schrödinger equation

$$\left( \frac{\hat{\mathbf{P}}^2}{2M} + E_{el}^j(\mathbf{R}) \right) \Phi_n^j(\mathbf{R}) = E_n^j \Phi_n^j(\mathbf{R})$$

where we note that the vibrational eigenstates change both as we increase  the vibrational quantum number

*(n)* and as we change the electronic state (i). The figure clearly illustrates this fact: there is a different "ladder" of vibrational energies built on each electronic surface. The vibrational states on the ground electronic state have systematically shorter bond lengths than those on the first excited state. So both the energies and the wavefunctions are different. The vibrational states on a given electronic state are orthogonal (because they arise from the same PES)

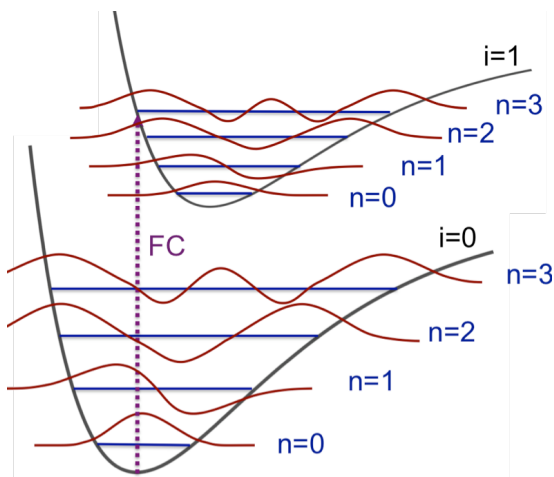$$\int \Phi_n^{j*}(\mathbf{R})\Phi_m^j(\mathbf{R})d\mathbf{R} = \delta_{mn}$$



**Figure 2**. Born-Oppenheimer picture of the vibrational levels on two electronic potential energy surfaces. The vertical line illustrates the Franck-Condon allowed transitions.

but the vibrational states on *different* electronic states need not be orthogonal (because they arise from different PESs)

$$\int \Phi_n^{j*}(\mathbf{R})\Phi_m^k(\mathbf{R})d\mathbf{R} \neq \delta_{mn}\ .$$

In this case the overlap has physical content: it tells us how similar the vibrational wavefunction on one surface is to a vibrational wavefunction on another surface. If the overlap is large they are very similar, if the overlap is small they are very different. In any case, the total wavefunction in the BO approximation is a product of the electronic and nuclear parts:

Getting down to the nitty-gritty, we write the transition dipole for $(j,n) \rightarrow (k,m)$ in the BO approximation as

$$\vec{\mu}^{fi} = \int \Theta_n^{j*}(\mathbf{R})\hat{\vec{\mu}}\Theta_m^k(\mathbf{R})d\tau = \int \Psi_{el}^{j*}(\mathbf{R})\Phi_n^{j*}(\mathbf{R})\hat{\vec{\mu}}\Psi_{el}^k(\mathbf{R})\Phi_m^k(\mathbf{R})d\tau_{el}d\mathbf{R}$$

$$= \int \Phi_n^{j*}(\mathbf{R})\Phi_m^k(\mathbf{R})\int \Psi_{el}^{j*}(\mathbf{R})\hat{\vec{\mu}}\Psi_{el}^k(\mathbf{R})d\tau_{el}d\mathbf{R}$$

$$= \int \Phi_n^{j*}(\mathbf{R})\vec{\mu}^{k\leftarrow j}(\mathbf{R})\Phi_m^k(\mathbf{R})d\mathbf{R} \qquad \left[\vec{\mu}^{k\leftarrow j}(\mathbf{R}) = \int \Psi_{el}^{j*}(\mathbf{R})\hat{\vec{\mu}}\Psi_{el}^k(\mathbf{R})d\tau_{el}d\mathbf{R}\right]$$

On the second line, we have tried (rather unsuccessfully) to factorize the integral into an electronic part times a nuclear part. Our factorization was thwarted by the fact that, within the BO approximation, the electronic wavefunctions also depend on the nuclear configuration. At this point, we invoke the quantum equivalent of the Condon approximation and assume that the electronic part of the transition dipole does not depend on the nuclear conformation:

$$\vec{\mu}_{el}^{k\leftarrow j}(\mathbf{R}) \xrightarrow{\text{Condon Approximation}} \vec{\mu}_{el}^{k\leftarrow j}$$

The physical justification for this approximation is not as clear as it was in the classical case, but it is mathematically clear that it achieves the same end: the nuclear motion and the electronic motion separate (into a product) as one would expect if the electrons move and the nuclei don't. In any case, within the Condon approximation,

$$\vec{\mu}^{fi} \approx \vec{\mu}_{el}^{k\leftarrow j} \int \Phi_n^{j*}(\mathbf{R})\Phi_m^k(\mathbf{R})d\mathbf{R}$$

Thus, we see that the intensity of a particular vibronic (vibration+electronic=vibronic) transition is governed by two factors. The first is the electronic transition dipole, which has the selection and propensity rules discussed above. The intensity of the transition is modulated by the Franck-Condon factor:

$$\left| \int \Phi_n^{j*}(\mathbf{R})\Phi_m^k(\mathbf{R})d(\mathbf{R}) \right|^2$$

This FC factor is just the square of the overlap between the initial and final vibrational wavefunctions. Thus if the two wavefunctions are similar, then the transition will be very intense, while if the wavefunctions are very different (e.g. one has a much larger average bond length than the other) then the transition will be weak or absent.

FC factors dictate that a fairly narrow range of final vibrational states is actually allowed. Semiclassically, only those energy levels that have a turning point that lies between the turning points of the initial state will have significant amplitude. As we have seen , the overlap with any other state, will involve lots of "wiggles" (in the classically allowed region) or an exponential tail (in the classically forbidden region). In either case, the FC factor will be small and the transition will be weak. The region of space between the turning points of the initial state is typically called the Franck-Condon "window", because it is only states in this region that can be seen in an absorption experiment. To see states outside of this window requires cleverness.

Let us work out the impact that the FC principle has on absorption spectra. Consider the PESs shown in Figure 3 and let us examine the expected absorption spectrum starting from ground electronic and vibrational state (Note: nearly all of the molecules will be in this state at room temperature). It is clear from the picture that the n=0 vibrational state on the ground electronic surface has the best overlap (i.e. the best FC factor) with the n=3 vibrational state on the excited surface. So we predict that the $(i = 0, n = 0) \rightarrow (i = 1, n = 3)$ transition will be most intense. The intensity will gradually decrease for vibrational states on the excited surface with n > 3 or
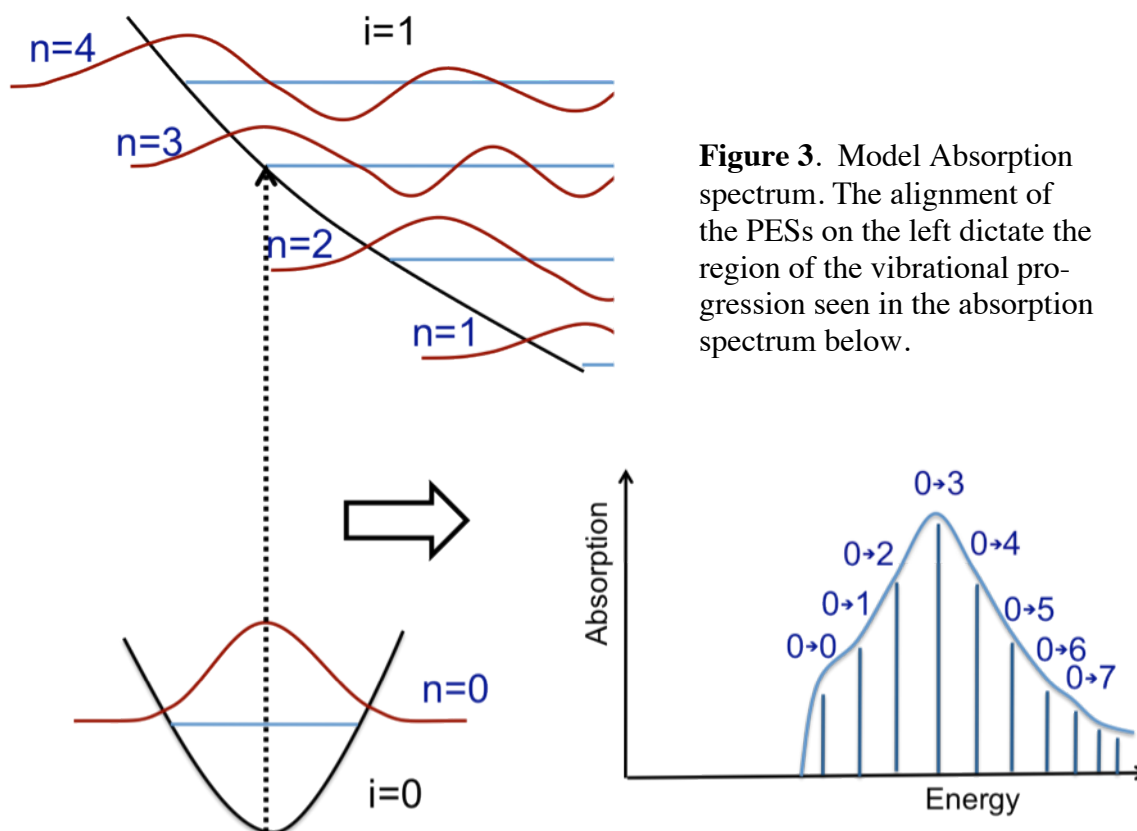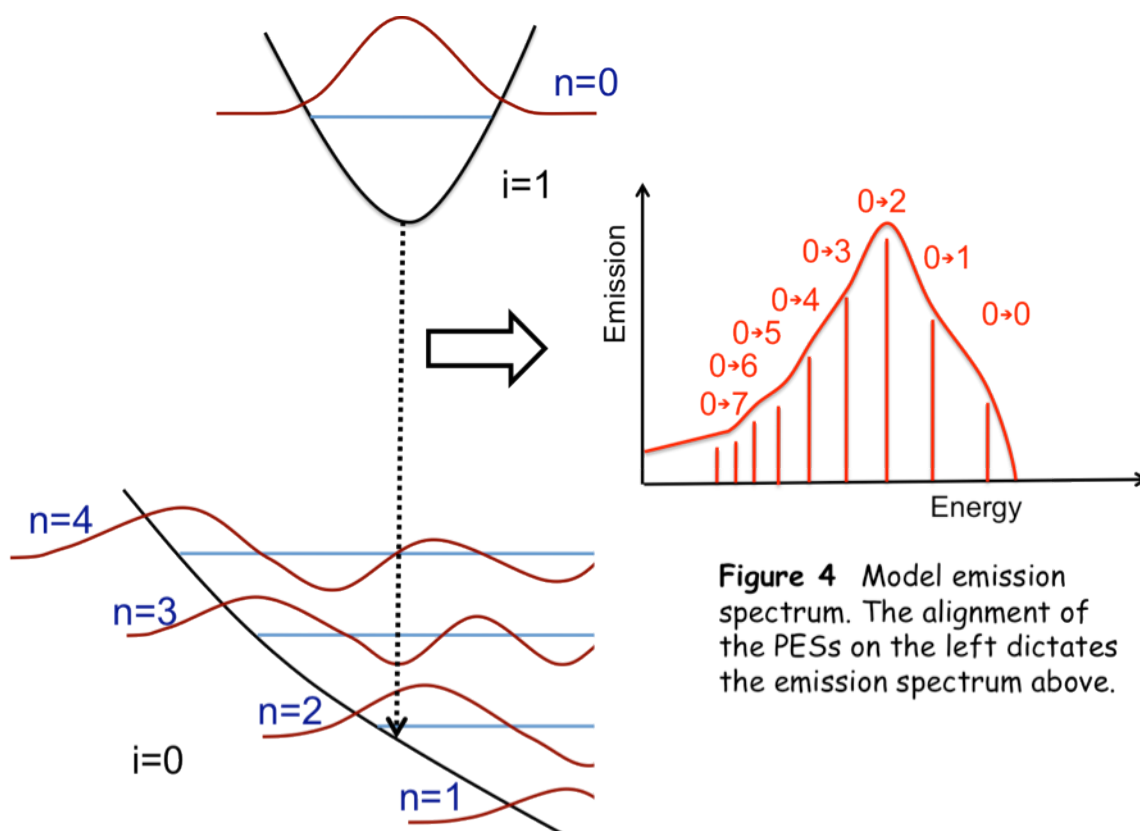
**Figure 3**. Model Absorption spectrum. The alignment of the PESs on the left dictate the region of the vibrational progression seen in the absorption spectrum below.

n < 3. Hence, we expect to see an absorption spectrum something like the right hand pane of Figure 3. Thus, we see a *vibrational progression* in the electronic absorption. The spacings between the lines will reflect the vibrational energy spacings on the *excited* PES. For a harmonic excited PES, the spacing between adjacent peaks will be $\hbar\omega$]. Meanwhile, the length of the progression (i.e. the number of important peaks) will approximately reflect on the difference between the equilibrium separations of the two oscillators. If the ground and excited states have very different equilibrium positions for a given bond (which might happen if the excited state had more anti-bonding character than the ground state) then n=0 on the ground surface will have its largest overlap with some very large n state on the excited surface, and the progression will be very long. Meanwhile, if the two surfaces are nearly the same, n=0 on the ground surface will have its largest overlap with n=0 on the excited surface and we will see almost no vibrational progression. Note that a smooth curve has been drawn over the peaks to illustrate what the spectrum might look like in the presence of broadening. In the presence of broadening, we simply see a diffuse absorption band, with a sharp edge on the low-energy side and a long tail on the high-energy side. All of the features predicted above are seen in the absorption spectra of real molecules.

**Figure 4** Model emission spectrum. The alignment of the PESs on the left dictates the emission spectrum above.

The FC principle also has a crucial impact on the structure of emission spectra. Here, we are considering $(i=1) \rightarrow (i=0)$ transitions. In a typical fluorescent molecule at room temperature, most of the molecules will be in the lowest ($n=0$) vibrational state on the excited PES. Thus, we will be looking at $(i=1,n=0) \rightarrow (i=0,n=?)$ transitions. In this case, the typical PESs will look like those in Figure 4. It is clear from the picture that the $n=0$ vibrational state on the excited surface will have the best FC overlap with the $n=2$ state on the ground surface. The transitions above or below this will have worse overlap, and lower intensity, as evidenced in the stick spectrum in Figure 4. However, in this case the lower $n$ values will correspond to the larger transition energies, so that the band will have a sharp edge on the high energy side and a long tail to low energies. In this case, the line spacings correspond to the vibrational levels on the ground potential energy surface. Thus, whereas for a nearly harmonic system, one expects only one intense line in the vibrational spectrum, for the same system one expects to see a vibrational progression in the electronic emission spectrum. In this way the electronic spectra can actually be a more powerful tool for studying vibrations than vibrational spectroscopy!

Clearly, there should be some relationship between the 0→1 absorption and 1→0 emission spectra. To align the spectra, we note that the (i=1,n=0)→(i=0,n=0) and (i=0,n=0)→(i=1,n=0) transitions will occur at the **same**
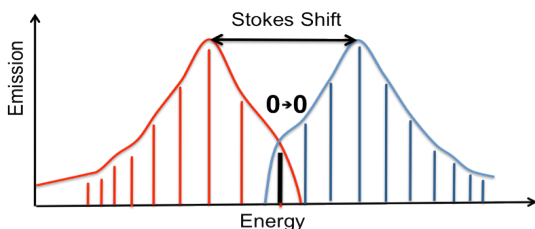


Figure 5. Alignment of Emission and Absorption Spectra

**frequency** because the energy difference is the same. Thus, we can align the two spectra as shown in Figure 5. There is thus a shift between the absorption maximum and emission maximum.

This is the *Stokes shift* we predicted earlier based on classical arguments. We should note that in the situation where both surfaces are Harmonic, the envelope functions of absorption and emission are exact mirror images of one another, so that any differences between absorption and the mirror image of emission reflect anharmonicity in (at least) one of the PESs.

## Time Dependent Picture and Photochemistry

One can derive an entirely equivalent (and in some ways more transparent) version of the FC principle in terms of time evolution, as illustrated in Figure 1. If we start out in the ground electronic and ground vibrational state, the FC approximation says that after an electronic excitation, we will end up on the electronic excited state *but the nuclear wavefunction will not have changed*. As is clear from the picture, the nuclear wavepacket is <u>not</u> an eigenstate on the excited PES. Hence, it will evolve in time. As it evolves, the wavepacket will initially lose potential energy by moving to the right, as illustrated by the curved arrow in

the picture. Of course, if we were fast enough, we would be able to <u>watch</u> the molecule relax after the excitation. That is to say, we would be able to zap the system with a pulse of light and then watch the chemical bond vibrate as the molecule dissipates some of the energy it just absorbed. To perform such experiments, we must first realize that molecules move on the femtosecond time scale. So in order to follow the relaxation, we need access to *very* short laser pulses (ca. 25 fs in duration). Anything longer than this and we run the risk that the dynamics will be finished before we can turn off the laser pulse.
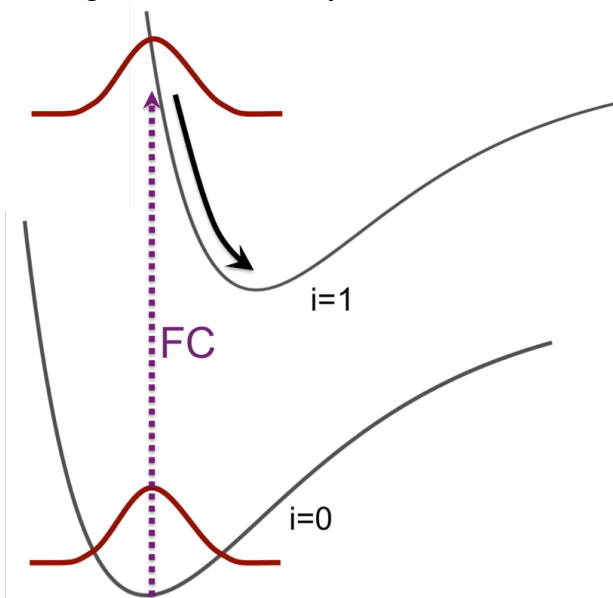


Figure 1 Dynamic picture of the FC principle. Excitation promotes the nuclear wavepacket vertically up to the excited PES, where it evolves in time.

Assuming we have the requisite time resolution, we can envision an experiment where we initially excite the system and then monitor the emission spectrum as a function of time. Immediately after the absorption, the emission spectrum will resemble the absorption spectrum (because the molecule hasn't had time to move). Meanwhile, after a long time, the molecule will relax to the lowest vibrational level on the excited surface and we will recov-

er the equilibrium emission spectrum.  At intermediate times, we can watch the spectrum very quickly convert from one to the other, reflecting the dynamic relaxation of the mole- cule.  This is illustrated in Figure 2.  This type of spectrum is called dynamic Stokes shift spectroscopy (DSSS), because it gives a time-resolved picture of how the Stokes shift ap- pears.  Of course, DSSS will only work if the molecule is fluorescent.  For other molecules, one might want to monitor the transient absorption, or time-resolved photoemission or any of a number of other time resolved probes of the electronic structure.

The goal of all these techniques is to moni- tor the molecular motion that ensues after the molecule has been excited.  Where does the energy go?  How does the molecule re- spond?
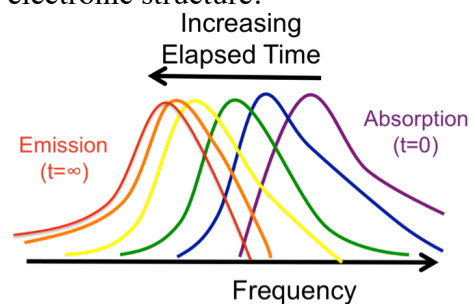


Figure 2 Dynamic Stokes Shift Spectroscopy

Generally, an electronic excitation dumps on the order of 1-4 eV into vibrations (because that is the ballpark range of interesting electronic excitations). Not coincidentally, this is also the ballpark range for the **strength of chemical bonds**.  Thus, the dynamics that ensue after we excite the system generally has enough energy to do chemistry.  The molecule can use the absorbed energy to react with another molecule, break a bond, rearrange …. In most cases, molecules are adept at absorbing visible photons and converting them into other forms of energy (chemical energy, thermal energy, electrical energy, work …) so that no photon emission occurs. In general, this type of dynamics is referred to as *nonradiative de- cay* which includes an array of different interesting photochemical processes.  Below, we discuss just a few possible channels for nonradiative decay after photoexcitation.

**Collisional Deactivation**

This is probably the most common pathway for nonradiatve relaxation. If you have a molecule, M, in a liquid or solid (or even a dense gas) then it can get rid of electronic en- ergy by colliding with another molecule and transferring its energy to that molecule. The most efficient means of doing this is:

$$M^* + X \rightarrow M + X^*$$
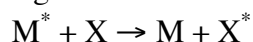
That is to say, the initially excited molecule transfers its energy to a solvent or impurity molecule X, allowing M to return to its electronic ground state and producing an excited X molecule.  Because of the rapid rate of collisions in liquids, fluorescence is only possi- ble in solution if it happens very quickly (e.g. faster than the collision rate) otherwise, the emission will be quenched. Of course, once X is excited, we have to deal with the ques- tion of how $X^*$ disposes of its excess energy, which usually occurs by one of the

mechanisms below.  The quantum yield of emission from a given molecule is governed by

$$Q = \frac{k_r}{k_r + k_{nr}}$$

where $k_r$ is the rate for radiative decay (i.e. emission) and $k_{nr}$ is the rate of non-radiative decay (i.e. all of the other mechanisms below).  Typically in going from molecule to mol-

ecule, radiative decay rates change by "only" a factor of 100 or so. For spin-allowed emission, $k_r$ is ~1 ns$^{-1}$. For spin forbidden transitions, $k_r$ is ~100 $\mu s^{-1}$. On the other hand it is not uncommon for non-radiative decay rates to change by a factor of a billion going from one molecule to the next. Hence, predicting whether or not a molecule is fluorescent is most often a game of figuring out whether there are any fast non-radiative decay pathways.

### Resonant Energy Transfer

Collisional energy transfer is quite boring both because it is non-specific (i.e. the character of the species 'X' is not really important) and because as long as X does not have a strong emission spectrum, it leads to quenching. A much more interesting process occurs if both species involved in the energy transfer (D and A) have emission spectra. Then, consider excitation energy transfer from D to A:

$$D^* + A \rightarrow D + A^*$$
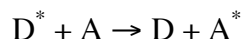
As we commonly do in chemistry, we can imagine decomposing this process into two half reactions:

$$D^* \rightarrow D \qquad \text{[Emission of Donor]}$$
$$A \rightarrow A^* \qquad \text{[Absorption of Acceptor]}$$

We should note that these half reactions *are not real*. Recall that in RedOx chemistry, we typically break the reaction down into a reductive half reaction and an oxidative half reaction. That is not to imply that the two reactions happen independently; merely that we can think about the raction as having two parts. In the same way here, we merely think of the process of energy transfer as being a combination of emission and absorption – no photons are actually being emitted or absorbed.

Now, we know that energy is conserved in this process. Thus, the energy loss for the Donor emission must match the energy gain for Acceptor absorption. There is thus a *resonance* condition that must be satisfied here in order for energy transfer to occur. As a result, this mode of energy transfer is usually called **F**luorescent **R**esonant **E**nergy **T**ransfer (FRET). It is possible to work out a rate expression for FRET – the required ingredients are Fermi's Golden Rule and some machinery for dealing with the satistics of quantized energy levels. We haven't discussed the requisite Statistical Mechanics in this course, and so we will merely state the result. If the donor and acceptor are separated by a distance $R_{DA}$ then the rate of FRET is governed by:

$$k_{\text{FRET}} \propto \frac{1}{R_{DA}^6} \int f_D(\omega) \varepsilon_A(\omega) \omega^2 d\omega \qquad \begin{cases} f_D(\omega) \equiv \text{Donor Fluorescence spectrum} \\ \varepsilon_A(\omega) \equiv \text{Acceptor Absorption spectrum} \end{cases}$$

The integral enforces the energy balance we already discovered – in order for the integral to be nonzero, there need to be some frequencies at which the donor can emit a photon and the acceptor can absorb that same photon. The integral in the FRET rate arises from the delta functions in Fermi's golden rule combined with some statistical arguments. The prefactor ($R_{DA}^{-6}$) arises from the transition moment $|V_{fi}|^2$ in Fermi's Golden Rule. The characteristic $R^{-6}$ behavior here comes from the same source as the $R^{-6}$ decay of the dispersion interaction – both can be interpreted as arising from the interaction of dipole moments separated by a distance $R$. This prescription for FRET rates is usually called Förster theory – so much so that sometimes FRET is used to abbreviate <u>F</u>örster <u>R</u>esonant <u>E</u>nergy <u>T</u>ransfer.

In any case, we note that FRET can only occur if two conditions are met: 1) If the molecules

are close enough together. If they are very far apart, the factor of $R^{-6}$ will make the FRET much smaller than the radiative rate and excited acceptor molecules will not live long enough to transfer energy. Thus, there is some critical distance, $R_0$, beyond which FRET will not take place. In practice, these critical distances are on the order of 1-10 nm. 2) FRET will only occur in the *downhill* direction. Note that we must have that the emission spectrum of the donor must match (or at least partially overlap) the absorption spectrum of the acceptor. This means that, typically, the absorption spectrum of the donor will occur at higher energy than absorption on the acceptor (because of the Stokes shift). Similarly, the donor emission will be at higher energy than the acceptor emission. Note that FRET can also occur if donor and acceptor have the same spectra, although it will only be efficient in this case if the Stokes shift is small. One never sees FRET in the uphill (red→blue) direction.

Whereas collisional deactivation is boring, FRET is intensely interesting for two reasons. First, it is an extremely useful measure of molecular distance. Suppose you label the ends of a protein (or other large molecule) with two dyes: one (R) that absorbs green and emits red and another (G) that absorbs blue and emits green. Then when the protein is "unfolded" the two dyes will be far apart and no FRET can occur. Thus, if you shine blue light on the system, you will see green light out (the light will be absorbed and emitted by G). However, if the protein folds, then R and G can come close to one another. In this situation FRET will be very efficient and if you shine blue light on the system, you will see red light out (the light will be absorbed by G, transfer to R and emit from R). Thus, this type of FRET experiment gives you a colorimetric method of measuring the distance between two residues: if the distance is less than a few nm, you'll see red. Otherwise blue. As the molecule fluctuates, you'll see color changes red→blue→red→blue… as the distance between the residues shifts. *This technique is particularly powerful because the lengthscale involved (1-10 nm) is much smaller than the diffraction limit (~200 nm) for the photons involved. For this reason FRET is often called a "molecular ruler".*

On the more qualitative side, FRET is important in Photosynthesis. In order to efficiently harvest photons, the plants have a light harvesting complex that roughly resembles a large radio antenna. There are many, many molecules that can absorb different wavelengths of light. However, they are carefully arranged so that the most "blue" of the molecules exist on the outside of the antenna, the more "green" ones are just inside those and the most "red" absorbers are in the center. Thus, no matter where the energy gets absorbed, it will always get transferred downhill via FRET and end up at the center of the antenna where a reaction can take place.

### Internal Conversion

The most common motif for uni-molecular nonradiative decay is called internal conversion. Consider the situation in Figure 3. After excitation, the wavepacket in the excited state will relax toward n=0. However, the n=0 state on the excited surface is actually very close in – both in energy and in space – to the n=10 state on the ground PES.
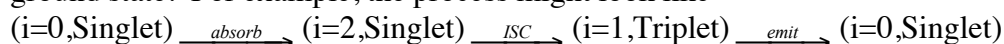
Figure 3 Interconversion from (i=1,n=0) to (i=0,n=10)
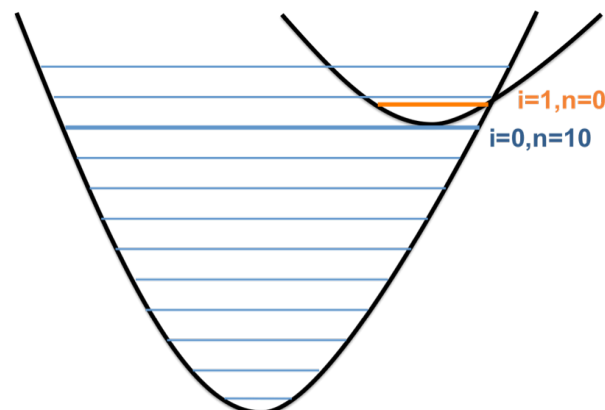
i=1,n=0
i=0,n=10

Thus it is possible for the molecule to make the (i=1,n=0)→(i=0,n=10) transition. The small amount of energy lost in this transition is easily transferred to rotations or other vibrations. This relaxation process is called internal conversion (IC). As is clear from the picture, in order to have both good wavefunction overlap and good energy matching, it helps if the two potential energy surfaces cross one another. Real surface crossings are rare – within the Born-Oppenheimer approximation surfaces tend to avoid one another rather than cross. However, in order to get fast internal conversion, it is typically enough for the surfaces to nearly cross, and such narrowly avoided crossings are the primary means of IC in photochemical reactions.

It is also important to recognize that a single IC may not get the molecule all the way to the ground PES. If we excite to the i=2 electronic state, the molecule could, for example, undergo IC to reach the i=1 state but then be unable to find an efficient pathway down to the ground state. In this situation, one would typically see fluorescence from the i=1 state after excitation of i=2. On the other hand, one also encounters scenarios where one reaches the ground state not by a single IC, but by several. Thus, starting in i=3, one might undergo one IC to get to i=2, another IC to get to i=1 and then a final IC to reach the ground state.

### Intersystem Crossing (ISC)

ISC is related to internal conversion in that both processes involve conversion of one electronic state into another, with some energy lost to vibrations in the process. The distinguishing feature of ISC is that the initial and final electronic states will have different spin multiplicities. Thus, a state that is initially a singlet might convert into a triplet or vice versa.

Such reactions are forbidden by our electronic selection rules, but they become important when we take into account relativistic effects (which relax our selection rules). Thus, for molecules with heavy atoms ISC can be a very important pathway for non-radiative decay. Of course, once the molecule undergoes ISC, it is somewhat stuck. It can't get back to the ground state easily because after ISC the excited state has a different multiplicity than the ground state. For example, the process might look like

$(i=0,\text{Singlet}) \xrightarrow{absorb} (i=2,\text{Singlet}) \xrightarrow{ISC} (i=1,\text{Triplet}) \xrightarrow{emit} (i=0,\text{Singlet})$

The last step is forbidden, so it will happen only very, very slowly. This process of de-
layed emission following absorption is known as **phosphorescence**. It
is typically not as effi-
cient or as bright as flu-
orescence, but it com-
monly occurs in mole-
cules that have a fast
route for ISC.

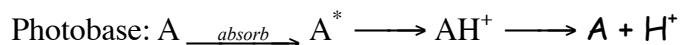Figure 4 *Photodissociation (left) and Predissociation (right)*
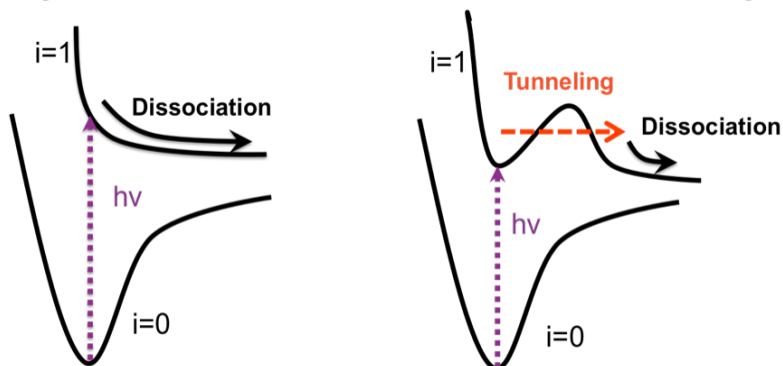


**Photochemical Reactions**
It is arguable whether the processes described above are really chemical changes – after all,
there are no bonds made or broken and no changes in state. The last nonradiative pathway
for a molecule is much more chemical in nature: the excited molecule can undergo a chem-
ical reaction to disspate – or even *store* – the absorbed energy. There are a number of clas-
ses of reaction that can be photocatalyzed in this way, including:

- **Dissociation**. This is perhaps the simplest scenario to envision. Take the first set
  of PESs in Figure 4.                Upon excitation from i=0 to i=1, the atoms
  will impulsively fly apart with no barrier to dissociation. Thus, upon absorption,
  the bond will break and one expects the atoms to come apart with significant ki-
  netic energy. Such reactions are somewhat hindered in liquids and solids, where
  caging effects hinder dissociation, but photodissociation can be quite powerful in
  the gas phase. An interesting twist on this phenomenon is illustrated by the se-
  cond set of curves in Figure.                Here, upon excitation, the molecule will
  spend some time bound in the i=1 state before eventually tunneling through the
  barrier to dissociate. As you might expect, this predissociative behavior has an in-
  tricate impact on the absorption spectrum of the molecule. For example, the life-
  time of the bound state can often be inferred from the widths of the associated vi-
  bronic peaks in the absorption spectrum.

- **Proton Transfer**. Because the electronic structure of the molecule changes
  in the excited state, it is very common for a photoexcited molecule to have a
  different pKa than the ground state. Thus, while

  the molecule might be a weak acid or base in the ground state, it might be a
  very strong acid or base in the excited state. In this situation the molecule
  can undergo nonradiative decay via proton transfer

$$\text{Photoacid: AH} \xrightarrow{\ absorb\ } \text{AH}^* \longrightarrow \text{A}^- + \text{H}^+ \longrightarrow \text{AH}$$

$$\text{Photobase: A} \xrightarrow{\ absorb\ } \text{A}^* \longrightarrow \text{AH}^+ \longrightarrow \text{A} + \text{H}^+$$

Of course, the efficiency of this process will be controlled by the pKa of the solvent and co-solutes. For this reason, photoacids and photobases are effective pH indicators: over a certain pH range they will be fluorescent, but outside that range fluorescence will be quenched by proton transfer.

**Ionization**. Just as an excited molecule can dissipate energy by proton shuttling, so it can release energy by electron transfer as well. For example, suppose a molecule were pumped with such a high energy photon that the molecule was above its ionization threshold (see Figure 5). Then it could dissipate energy by simply ejecting an electron

$$A \xrightarrow{\text{absorb}} A^* \longrightarrow A^+ + e^-$$

This is the principle behind the photoelectric effect.
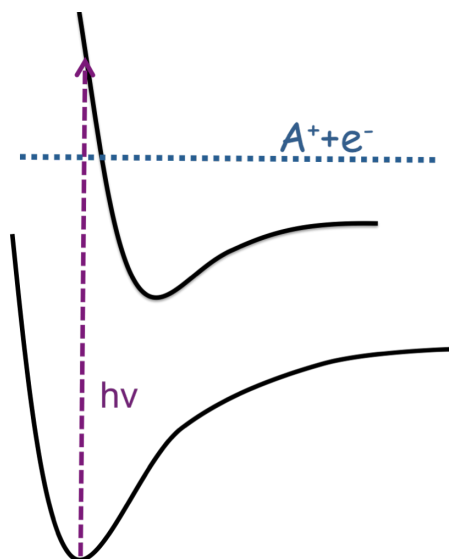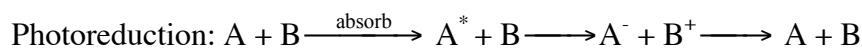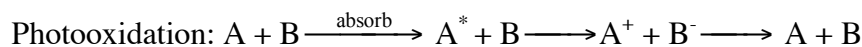


Figure 5 *Photoionization*

This type of process is much more prevalent in the condensed phase because the excited molecule can release an electron not just to vacuum, but also to other molecules

Photooxidation: $A + B \xrightarrow{\text{absorb}} A^* + B \longrightarrow A^+ + B^- \longrightarrow A + B$

Photoreduction: $A + B \xrightarrow{\text{absorb}} A^* + B \longrightarrow A^- + B^+ \longrightarrow A + B$

Here the collision partner, B, acts as a source or sink of electrons to quench the excitation on A. Here, the redox chemistry is made possible because $A^*$ has a different standard reduction potential than A. We note that, in principle, this process can return the fragments, A and B, to their neutral ground states, as shown in the last step. However, in practice the neutralization step can be **very slow**. Thus, the energetic ions $A^-$ and $B^+$ will typically live for a long time, and during that time they can engage in chemical reactions. It is this mechanism that photsynthesis uses to convert light energy into chemical energy. The light harvesting complex efficiently transduces photons into ions with high redox potentials and these ions are used to make chemical bonds.

**Isomerization.** Consider 1,2- dichloroe-
thene ($C_2H_2Cl_2$), which has *cis* and *trans*
isomers around its double bond. As a
function of the double bond twist, $\phi$, the
ground and first excited PESs look rough-
ly like the picture in Figure 6. Thus, upon
excitation both isomers will tend to relax
to the same 90° twisted geometry. This
twisted form in the excited state can then
relax to the ground state by internal con-
version through the nearby avoided cross-
ing. Once on the ground PES, the mole-
cule is actually at the barrier top, and will
decide to go left (towards *cis*) or right
(toward *trans*) with approximately equal
probability. Thus, excitation can accom-
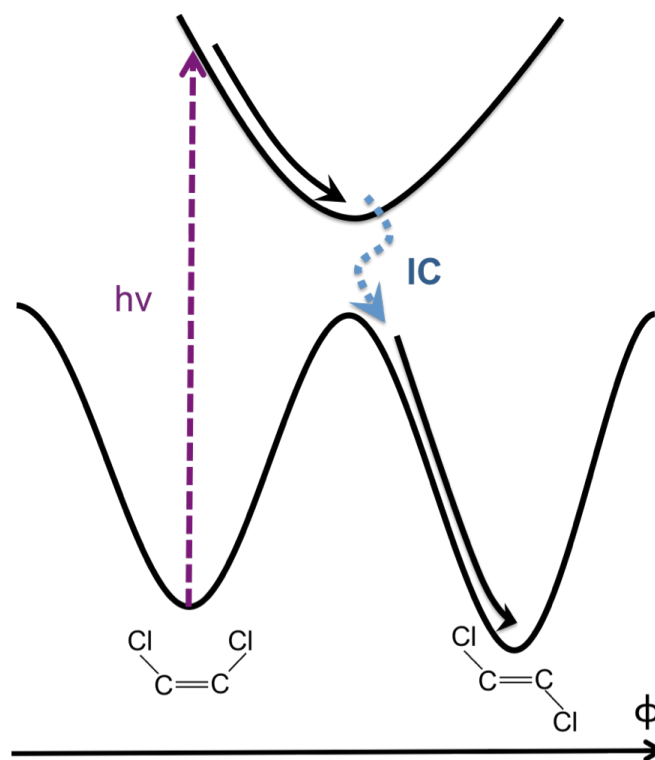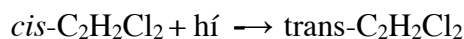plish the isomerization reaction.



Figure 6 cis-trans isomerization.

$$cis\text{-}C_2H_2Cl_2 + h\text{í} \longrightarrow trans\text{-}C_2H_2Cl_2$$

As stated, this reaction is not very efficient (only a 50% yield). However, by us-
ing multiple short pulses (e.g. one 300 nm pulse, followed by a 450 nm pulse 50
fs later, followed by a 325 nm pulse…) one can increase this yield to nearly
100%. The task of designing the best train of pulses for a given reaction is the
domain of *coherent control*. In this situation, one thinks of the photons as *reac-
tants* that can be used to direct chemistry.

Now, in a typical molecule, it is easy to tell when nonradiative decay is taking place –
one simply sees a decrease in the fluorescence. We can put a quantitative measure on
this by measuring the quantum yield, $\sqrt{}$, which is defined to be the ratio of the number of
photons emitted to the number absorbed. It is fairly difficult to measure this accurately,
because it requires precise measurements of the absorbed and emitted light intensity in-
tegrated over a range of wavelengths. However a $\sqrt{}$ that is significantly less than unity
indicates that nonradiative decay is important. The difficult question to answer is this:
Given that a molecule has a low quantum yield, *what is the dominant mechanism of non-
radiative decay*? The best tool to answer this question is ultrafast spectroscopy. In this
context, one can design different pulse sequences to isolate, say, IC from photooxidation.
One can also watch the molecule relax in real time in order to tease out the rates of the
various decay channels involved. Experiments of this kind can be very involved, but
provide the ultimate resolution for photochemical processes.

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